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AVS Meeting Code of Conduct
It is the policy of the AVS that all participants, including attendees, vendors, staff, volunteers, and all other stakeholders at AVS meetings will conduct themselves in a professional manner that is welcoming to all participants and free from any form of discrimination, harassment, or retaliation. Participants will treat each other with respect and consideration to create a collegial, inclusive, and professional environment at AVS Meetings. Creating a supportive environment to enable scientific disclosure at AVS meetings is the responsibility of all participants. Participants will avoid any inappropriate actions or statements based on individual characteristics such as age, race, ethnicity, sexual orientation, gender identity, gender expression, marital status, nationality, political affiliation, ability status, educational background, or any other characteristic protected by law. Disruptive or harassing behavior of any kind will not be tolerated. Harassment includes but is not limited to inappropriate or intimidating behavior and language, unwelcome jokes or comments, unwanted touching or attention, offensive images, photography without permission, and stalking. Violations of this code of conduct policy should be reported to the AVS Managing Director or Events Manager. Sanctions may range from verbal warning, to ejection from the meeting without refund, to notifying appropriate authorities. Retaliation for complaints of inappropriate conduct will not be tolerated. If a participant observes inappropriate comments/actions personal intervention seems appropriate and safe, they should be considerate of all parties before intervening.
Welcome to the 19th International Conference on Atomic Layer Deposition (ALD 2019) featuring the 6th International Workshop on Atomic Layer Etching (ALE 2019). The Program Committees for both topics feel that members of the ALD and ALE communities benefit from close interaction to allow us to work collectively toward a future of atomic-scale processing. Therefore, conference registrants are invited to attend the joint tutorial session and the Welcome Reception on Sunday, the joint Plenary Session on Monday, and all parallel ALD and ALE oral sessions throughout the week. However, this year, the poster sessions will be held on separate days for better visibility; the ALE poster session will be on Sunday evening during the welcome reception, and the ALD poster sessions will be on Monday and Tuesday evenings. Given the large number of posters in ALD, we have made an effort to create subcategories of posters so attendees can quickly locate presentations related to their area of interest.

To accommodate the recent growth in the ALD and ALE community, in 2018 AVS fully assumed the conference leadership, taking on the financial management and all event management tasks of the ALD Conference and the ALE Workshop every year in both U.S. and international locations. This year the conference will take place from Sunday, July 21–24, 2019, at the Hyatt Regency in the beautiful city of Bellevue, Washington (East Seattle), which sits on the Puget Sound just across from Lake Washington. Close proximity to the Sea-Tac International Airport makes the location accessible to both the Asian and European attendees.

The Conference will begin with joint ALD/ALE Tutorials. For the ALD Tutorials, the Program Committee placed a focus on applications of ALD in various fields. The first tutorial by Stacey Bent (Stanford University, USA) will focus on “Area-Selective ALD for Semiconductor Manufacturing,” reflecting the importance of ALD in the semiconductor field and the need for new area-selective ALD processes. The next three Tutorials will be on energy-related applications of ALD with Andy Sun (Western University, Canada), Rong Chen (Huazhong University of Science and Technology, China), and Bart Macco (Eindhoven University of Technology, The Netherlands) presenting tutorials on applications of ALD in batteries, catalysis, and photovoltaics, respectively.

ALE Tutorials will cover two major areas of the technology. Thorsten Lill (Lam Research, USA) will discuss surface reaction control using a plasma-based approach through traditional dry etch processing parameters. The second tutorial, given by Steven George (University of Colorado at Boulder, USA) will cover the control and formation of volatile reaction products using thermal based ALE.

We are fortunate to have three distinguished plenary speakers. The Conference will open with the first Plenary Speaker, Erwin Kessels (Eindhoven University of Technology, The Netherlands) who is also the 2019 ALD Innovator Awardee “For Original Work and Leadership in ALD.” In his presentation, Prof. Kessels will address several recent and emerging trends in atomic scale processing and discuss how understanding of the underlying mechanisms has contributed to important innovations in the field, either in research or in industry. The ALD Innovator Award will be presented prior to Prof. Kessels’ lecture. In the next Plenary Lecture, Jeffrey Elam (Argonne National Laboratory, USA) will present an overview of how in situ measurements can reveal the fundamental mechanisms during ALD, and how these measurements can be combined with machine learning to accelerate ALD process development. Last, Eric Joseph (IBM, USA) will discuss the coming paradigm shift from Moore’s Law towards accelerator technologies for AI applications. Examples of this paradigm shift will be discussed and a vision for future challenges of atomic scale processes will be reviewed.

A total of 402 abstracts were accepted for this year’s Conference, 59 of which were for the ALE sessions. This total is almost the same as in 2017 and 2018 conferences, which also had over 400 submitted abstracts. Of these 402 abstracts, there are 27 invited speakers, 200 contributed orals, and 175 posters. ALE has shown significant growth in 2019, and will be running a session until Wednesday morning. The diversity and reach of ALD/ALE can be seen in the abstracts submitted from 27 different countries this year. Given the consistency in the submitted abstracts over the past few years, and the growth in certain areas such as ALE, we feel the future of atomic layer processing remains bright.
To accommodate the large number of abstracts and to allow more attendees to give oral presentations, we have scheduled four parallel sessions. Following ALD 2016–2018, the ALE Workshop will be held as the fourth parallel session starting Monday afternoon, but this year will extend into Wednesday morning reflecting the increase in the number of abstracts. Although we have done our best to organize the program into logical groupings of talks, we understand that these many sessions may lead to difficult choices in deciding which talks to attend. However, since all talks are recorded and will be available after the Conference, we believe this approach to be most effective.

Lastly, we would like to sincerely thank the AVS staff for their dedication and hard work in the organization of this Conference. We would also like to express gratitude to all our committee members, sponsors, and exhibitors who have contributed to make this year’s ALD/ALE Conference a success. We hope that the organization and structure of the Conference, as well as the special get-together opportunities provided by our industrial sponsors will allow you to meet new contacts and make new friends—enabling fruitful discussions and productive collaborations that will further brighten the future of ALD/ALE.

**ALD 2019 Program Chairs:**
Sumit Agarwal (Colorado School of Mines, USA)
Dennis Hausmann (Lam Research, USA)

**ALE 2019 Program Chairs:**
Craig Huffman (Micron Technology, USA)
Gottlieb Oehrlein (University of Maryland, USA)
General Information

Conference Location
Hyatt Regency Bellevue
900 Bellevue Way NE
Bellevue, WA 98004, USA

Tutorial Registration Hours
Sunday, July 21, 2019: 11:30 a.m.-1:00 p.m. Grand Ballroom Foyer

Conference Registration Hours
Sunday, July 21, 2019: 4:00 p.m.-8:00 p.m. Grand Ballroom Foyer
Monday, July 22, 2019: 7:00 a.m.-7:00 p.m. Grand Ballroom Foyer
Tuesday, July 23, 2019: 7:00 a.m.-7:00 p.m. Grand Ballroom Foyer
Wednesday, July 24, 2019: 7:00 a.m.-2:00 p.m. Grand Ballroom Foyer

Exhibit Hours
The exhibit will take place in the Hyatt Regency Bellevue Evergreen Ballroom and Foyer during coffee and lunch breaks as well as poster sessions. This year it will also be open during the Welcome Reception.

Sunday, July 21, 2019: 6:00 p.m.-8:00 p.m. Evergreen Ballroom and Foyer
Monday, July 22, 2019: 10:00 a.m.-7:30 p.m. Evergreen Ballroom and Foyer
Tuesday, July 23, 2019: 10:00 a.m.-7:30 p.m. Evergreen Ballroom and Foyer
Wednesday, July 24, 2019: 10:00 a.m.-1:30 p.m. Evergreen Ballroom and Foyer

Poster Sessions
Poster Sessions will be held in the Hyatt Regency Bellevue Evergreen Ballroom and Foyer throughout the week. Poster presenters are requested to be present at (or near) their poster during the times scheduled for poster viewing.

Poster Hours:
Sunday, July 21, 2019 (ALE ONLY): 6:00 p.m.-8:00 p.m. Evergreen Ballroom and Foyer
Monday, July 22, 2019: 5:45 p.m.-7:30 p.m. Evergreen Ballroom and Foyer
Tuesday, July 23, 2019: 5:30 p.m.-7:30 p.m. Evergreen Ballroom and Foyer

Poster Setup:
- Sunday Setup (ALE ONLY): After 5:45 p.m.
  Sunday posters will stay up until the end of lunch on Wednesday.
- Monday Setup: After 10:00 a.m.
  Monday posters will stay up until the end of lunch on Tuesday.
- Tuesday Setup: After 3:00 p.m.
  Tuesday posters will stay up until the end of lunch on Wednesday.

Poster Removal: Please note that we cannot take responsibility for any posters left on the boards after the session—any remaining posters will be discarded.

- Sunday (ALE ONLY) posters should be removed Wednesday by 1:20 p.m.
- Monday posters should be removed Tuesday by 1:20 p.m.
- Tuesday posters should be removed Wednesday by 1:20 p.m.

Welcome Reception
All registered attendees and exhibitors are invited to attend the Welcome Reception on Sunday, July 21, 2019, in the Evergreen Ballroom and Foyer from 6:00 p.m.-8:00 p.m.
Refreshment Breaks and Lunches
All refreshment breaks and strolling lunches will be held Monday-Wednesday in the Hyatt Regency Bellevue Evergreen Ballroom and Foyer *. Limited seating will be available. *While supplies last.

Internet Service
Free wireless is available in the Hyatt Regency Bellevue meeting rooms. The password is ALD2019.

Mobile App
Don't forget to download the ALD/ALE 2019 Mobile App from your devices App Store or at https://ald2019.avs.org/mobileapp/. Use the app and/or the online scheduler to view presentations, presenters, abstracts, sponsors, exhibitors, and to build your schedule. Login using your confirmation/ID number and last name.

Manuscript Submission

Conference Management
AVS
110 Yellowstone Dr., Suite 120
Chico CA 95973
Phone: 530-896-0477
Fax: 530-896-0487,
E-mail: events@avs.org
Website: www.ald-avs.org
Conference Locations

Exhibits and Posters
Lobby Level: Evergreen Ballroom and Foyer

Registration
Second Floor: Grand Ballroom Foyer

Technical Sessions
Second Floor: Grand Ballroom and Regency Ballroom
Committees

ALD 2019 Program Chairs
Program Chair: Sumit Agarwal (Colorado School of Mines, USA)
Program Co-Chair: Dennis Hausmann (Lam Research, USA)

ALD Program Committee
Parag Banerjee (Univ. of Central Florida, USA)
Sean Barry (Carlton Univ., Canada)
Stacey Bent (Stanford Univ., USA)
Iain Buchanan (Versum Materials, UK)
Robert Clark (TEL, USA)
Scott Clendenning (Intel, USA)
Rong Chen (Huazhong Univ. of Science and Technology, China)
John F. Conley, Jr. (Oregon State Univ., USA)
Arrelaine Dameron (Forge Nano, USA)
Neil Dasgupta (Univ. of Michigan, USA)
Charles Dezelah (ASM Microchemistry, USA)
Christophe Detavernier (Univ. of Ghent, Belgium)
Shi-Jin Ding (Fudan Univ., China)
Christian Dussarrat (Air Liquide, France)
Simon Elliott (Schrödinger, Ireland)
Ravi Kanjolia (EMD Performance Materials, USA)
Jiyoung Kim (Univ. of Texas at Dallas, USA)
Mato Knez (Nanogune, Spain)
Harm Knoops (Oxford Instruments, UK)
Se-Hun Kwon (Pusan National Univ., South Korea)
Adrien LaVoie (Lam Research, USA)
Han-Bo-Ram Lee (Incheon National Univ., South Korea)
Won-Jun Lee (Sejong Univ., South Korea)
Han-Jin Lim (Samsung Electronics, South Korea)
Mike McSwiney (Intel, USA)
Jin-Seong Park (Hanyang Univ., South Korea)
Paul Poodt (NTO/Holst Center, The Netherlands)
Matti Putkonen (VTT, Finland)
Somil Rathi (Eugenus, USA)
Mikko Ritala (Univ. of Helsinki, Finland)
Simon Rushworth (EpiValence, UK)
Seung Wook Ryu (SK Hynix, South Korea)
Uwe Schroeder (Namlab, Germany)
Nicholas Strandwitz (Lehigh Univ., USA)
Jonas Sundqvist (Fraunhofer IKTS, Germany)
Ganesh Sundaram (Veeco, USA)
Myung Mo Sung (Hanyang Univ., South Korea)
Christophe Vallee (LETI-LTM, France)
Charles Winter (Wayne State Univ., USA)
Angel Yanguas-Gil (Argonne National Lab, USA)

ALD Poster Chairs
Adrie Mackus (Eindhoven Univ. of Technology, The Netherlands)
Virginia Wheeler (U.S. Naval Research Lab, USA)

ALD Social Media Chairs
Riikka Puurunen (Aalto Univ., Finland)

ALD International Advisory Committee
Annelies Delabie (imec, Belgium)
Anjana Devi (Ruhr-Univ. Bochum, Germany)
Jeffrey Elam (Argonne National Lab, USA)
Steven George (Univ. of Colorado at Boulder, USA)
Roy Gordon (Harvard Univ., USA)
Cheol Seong Hwang (Seoul National Univ., South Korea)
Hyeongtag Jeon (Hanyang Univ., South Korea)
Erwin Kessels (Eindhoven Univ. of Technology, The Netherlands)
Hyungjun Kim (Yonsei Univ., South Korea)
Sang In Lee (Synos Foundation, USA)
Markku Leskelä (Univ. of Helsinki, Finland)
Gregory N. Parsons (North Carolina State Univ., USA)
Viljami Pore (ASM, Finland)

ALD Steering Committee:
Steven George (Univ. of Colorado at Boulder, USA)
Erwin Kessels (Eindhoven Univ. of Technology, The Netherlands)
Hyungjun Kim (Yonsei Univ., South Korea)
Gregory N. Parsons (North Carolina State Univ., USA)

ALE 2019 Program Chairs
Program Chair: Craig Huffman (Micron Technology, USA)
Program Co-Chair: Gottlieb Oehrlein (Univ. of Maryland, USA)

ALE Program Committee
Ankur Agarwal (KLA, USA)
David Boris (Naval Research Lab, USA)
Jean-Francois de Marneffe (imec, Belgium)
Bert Ellingboe (Dublin City Univ., Ireland)
Steve George (Univ. of Colorado at Boulder, USA)
Satoshi Hamaguchi (Osaka Univ., Japan)
Keren Kanarik (Lam Research, USA)
Harm Knoops (Oxford Instruments, The Netherlands)

ALE Steering Committee:
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Alok Ranjan (Tokyo Electron, USA)
Fred Roozeboom (Eindhoven Univ. of Technology, The Netherlands)
Dmitry Suyatin (Lund Univ., Sweden)
Tetsuya Tatsumi (Sony Corp., Japan)
Wei Tian (Applied Materials, USA)
Geun Young Yeom (Sungkyunkwan Univ., South Korea)
Ishii Yohei (Hitachi High Technologies USA)

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Eric Joseph (IBM, USA)
Keren Kanarik (Lam Research, USA)
Steven George (Univ. of Colorado at Boulder, USA)
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www.lesker.com/newweb/ped/atomic-layer-deposition-systems.cfm

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Exhibitors

Exhibit Hours
The exhibit will take place in the Hyatt Regency Bellevue Evergreen Ballroom and Foyer during coffee and lunch breaks as well as poster sessions. This year it will also be open during the Welcome Reception.

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Tuesday, July 23, 2019: 10:00 a.m.-7:30 p.m. Evergreen Ballroom and Foyer
Wednesday, July 24, 2019: 10:00 a.m.-1:30 p.m. Evergreen Ballroom and Foyer

Please visit the Mobile App for the Exhibit Floor Plan.

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Literature Display Tables

Evergreen Foyer

Hiden Analytical
Okyaytech
## Sponsor Product Guide

### ALD Precursors

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<tr>
<td>EMD Performance Materials</td>
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### ALD Systems

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<td>Jiangsu Leadmicro Nano-Equipment Tech. Ltd.</td>
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<td>Kurt J. Lesker Company</td>
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### ALD Components and Subsystems

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### ALE

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<td>Tokyo Electron Ltd.</td>
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### Other Products & Services

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11
# Tutorial Schedule

**Sunday, July 21, 2019, 1:00 p.m.-6:00 p.m.**

<table>
<thead>
<tr>
<th>Time</th>
<th>Session</th>
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<tr>
<td>1:00-1:05 p.m.</td>
<td><strong>Tutorial Welcome</strong></td>
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<tr>
<td>1:05-1:50 p.m.</td>
<td><strong>Area-selective ALD for Semiconductor Manufacturing</strong></td>
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<td></td>
<td>Stacey Bent (Stanford Univ., USA)</td>
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<tr>
<td>1:50-2:35 p.m.</td>
<td><strong>ALD for Battery Applications</strong></td>
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<td></td>
<td>Andy Sun (Western Univ., Canada)</td>
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<tr>
<td>2:35-3:20 p.m.</td>
<td><strong>ALD for Catalysis</strong></td>
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<td>Rong Chen (Huazhong Univ. of Science and Technology, China)</td>
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<tr>
<td>3:20-3:40 p.m.</td>
<td>Break</td>
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<tr>
<td>3:40-4:25 p.m.</td>
<td><strong>ALD for Photovoltaics</strong></td>
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<td></td>
<td>Bart Macco (Eindhoven Univ. of Technology, Netherlands)</td>
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<tr>
<td>4:25-5:10 p.m.</td>
<td><strong>Plasma Based ALE</strong></td>
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<td></td>
<td>Thorsten Lill, (Lam Research, USA)</td>
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<tr>
<td>5:10-5:55 p.m.</td>
<td><strong>Thermal Based ALE</strong></td>
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<tr>
<td></td>
<td>Steve George (Univ. of Colorado at Boulder, USA)</td>
</tr>
</tbody>
</table>
Plenary Lecture Schedule

ALD 2019 Innovation Awardee Lecture
“Atomic Scale Processing: From Understanding to Innovation”
Erwin Kessels (Eindhoven University of Technology, The Netherlands)
Monday, July 22, 2019, 8:45 a.m., Grand Ballroom H-K

The ALD 2019 Innovator Award is being presented “for pioneering work on unraveling atomistic-level mechanisms during plasma-assisted ALD and leadership in ALD.”

Biography: Erwin Kessels is a full professor at the Eindhoven University of Technology TU/e where he is also the scientific director of the NanoLab@TU/e clean room facilities. Erwin received his MSc and PhD degree (with highest honors) in Applied Physics from the TU/e in 1996 and 2000, respectively. His research interests cover the field of synthesis of ultrathin films and nanostructures using methods such as (plasma-enhanced) atomic layer deposition (ALD) and atomic layer etching (ALE). Within the field of ALD, he has contributed most prominently by his work on plasma-assisted ALD, his research related to ALD for photovoltaics, and ALD for nanopatterning (including area-selective ALD). Currently Erwin is focusing his research on atomic scale processing, a field which is believed to grow in importance quickly in the next decade for a wide variety of application domains. He was chair of the International Conference on Atomic Layer Deposition in 2008 (Bruges, Belgium) and he frequently (co-)organizes ALD-related workshops. He will serve as chair ALE workshop in 2020. Erwin is active within the American Vacuum Society and has been President of the Netherlands Vacuum Society. He is an associate editor of the Journal of Vacuum Science and Technology. He is also the founder of the blog AtomicLimits.com and of the ALD Academy.

ALD 2019 Plenary Lecture
“Elucidating the Mechanisms for Atomic Layer Growth through In Situ Studies”
Jeff Elam (Argonne National Lab, USA)
Monday, July 22, 2019, 9:30 a.m., Grand Ballroom H-K

ALE 2019 Plenary Lecture
“Mapping the Future Evolution of Atomic Scale Processing to Enable the World of Artificial Intelligence”
Eric Joseph (IBM, USA)
Monday, July 22, 2019, 11:00 a.m., Grand Ballroom H-K
# Technical Program Key

## Conference Topics

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>AA</td>
<td>ALD Applications</td>
</tr>
<tr>
<td>AF</td>
<td>ALD Fundamentals</td>
</tr>
<tr>
<td>ALE</td>
<td>Atomic Layer Etching</td>
</tr>
<tr>
<td>AM</td>
<td>ALD for Manufacturing</td>
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<tr>
<td>AS</td>
<td>Area Selective ALD</td>
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<tr>
<td>EM</td>
<td>Emerging Materials</td>
</tr>
<tr>
<td>NS</td>
<td>Nanostructure Synthesis and Fabrication</td>
</tr>
<tr>
<td>PS</td>
<td>Plenary Session</td>
</tr>
</tbody>
</table>

## Key to Session/Paper Numbers

Sessions sponsored by multiple topics are labeled with all acronyms (e.g. AC+EM+SS), then a number to indicate simultaneous sessions sponsored by the same topic(s) (e.g. SS1, SS2), then a dash followed by the first two characters of the day of the week: **Monday, Tuesday, Wednesday, Thursday, Friday,** then a single letter for **Morning, Afternoon, Evening, Poster,** and finally a number indicating the starting time slot for the paper.  
Example: SS1-MoM9 (Surface Science, Monday morning, 11:00 am).
## Technical Program Overview

<table>
<thead>
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<tbody>
<tr>
<td><strong>SuP</strong></td>
<td>ALE Poster Session 6:00 pm-8:00 pm</td>
<td>Welcome Reception &amp; Exhibits 6:00 pm-8:00 pm</td>
<td>ALD 2019 Opening Remarks &amp; ALD 2019 Innovation Award 8:30 am</td>
<td>PS1-MoM: ALD Plenary Session</td>
<td>ALE 2019 Opening Remarks 10:15 am</td>
<td>PS2-MoM: ALE Plenary Session</td>
</tr>
<tr>
<td><strong>MoM</strong></td>
<td>Exhibits 10:00 am-7:30 pm</td>
<td>Morning Break 10:15 am-10:45 am</td>
<td>ALE1-MoM: ALD for Biological &amp; Space Applications</td>
<td>AF2-MoA: ALD Precursors I</td>
<td>AF1-MoA: ALD Growth Mechanisms I</td>
<td>ALE1-MoA: Energy-enhanced ALD</td>
</tr>
<tr>
<td><strong>MoA</strong></td>
<td>Lunch 12:00 pm-1:30 pm</td>
<td>Afternoon Break 3:30 pm-4:00 pm</td>
<td>AA1-MoA: ALD for Biological &amp; Space Applications</td>
<td>AF3-MoA: Growth &amp; Characterization I</td>
<td>AF4-MoA: Growth Mechanisms II</td>
<td>ALE2-MoA: ALE of Compound Semiconductors</td>
</tr>
<tr>
<td><strong>MoP</strong></td>
<td>ALD/ALE Poster Session 5:45 pm-7:30 pm</td>
<td></td>
<td>AF1-TuM: In-Situ Characterization of ALD Processes</td>
<td>AA1-TuM: ALD for Catalysts, Electrocatalysts, &amp; Photocatalysts</td>
<td>AF2-TuM: ALD Precursors II</td>
<td>ALE1-TuM: ALE: Gas-phase and/or Thermal ALD</td>
</tr>
<tr>
<td><strong>TuM</strong></td>
<td>Exhibits 10:00 am-7:30 pm</td>
<td>Morning Break 10:00 am-10:30 am</td>
<td>AF3-TuM: Growth &amp; Characterization II</td>
<td>AA2-TuM: ALD for Batteries I</td>
<td>AS1-TuM: Area-Selective ALD Techniques</td>
<td>ALE2-TuM: Alternative Methods to ALD</td>
</tr>
<tr>
<td><strong>TuA</strong></td>
<td>Lunch 12:00 pm-1:30 pm</td>
<td>Afternoon Break 3:30 pm-4:00 pm</td>
<td>AA3-TuA: ALD for Memory Applications I</td>
<td>AA2-TuA: ALD for Batteries II</td>
<td>AS1-TuA: Area-Selective ALD by Area-Deactivation</td>
<td>ALE1-TuA: Modeling &amp; Instrumentation I</td>
</tr>
<tr>
<td><strong>TuP</strong></td>
<td>ALD/ALE Poster Session 5:30 pm-7:30 pm</td>
<td></td>
<td>AF-TuA: Plasma ALD: Growth &amp; Characterization</td>
<td>AA1-TuA: Emerging Applications I</td>
<td>AS2-TuA1: Area-Selective ALD: Combinations with Etching</td>
<td>ALE2-TuA: Modeling &amp; Instrumentation II</td>
</tr>
<tr>
<td><strong>WeM</strong></td>
<td>Exhibits 10:00 am-1:30 pm</td>
<td>Morning Break 10:00 am-10:30 am</td>
<td>Lunch 12:00 pm-1:30 pm</td>
<td>EM1-WeM: Spatial ALD, Fast ALD, and Large-Area ALD</td>
<td>AA1-WeM: ALD for Memory Applications II</td>
<td>ALE1-WeM: Integration &amp; Application of ALD</td>
</tr>
<tr>
<td><strong>WeA</strong></td>
<td>AA1-WeA: Emerging Applications II</td>
<td></td>
<td>EM2-WeM: Organic-Inorganic Hybrid Materials</td>
<td>EM3-WeM: Epitaxial Growth and III-V Materials</td>
<td>AA2-WeM: ALD for ULSI Applications II</td>
<td>ALE2-WeM: Materials Selective ALD</td>
</tr>
<tr>
<td></td>
<td>NS-WeA: 2D Nanomaterials by ALD (including Transition Metal Dichalcogenides)</td>
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<tr>
<td></td>
<td>AA2-WeA: ALD for ULSI Applications II</td>
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<tr>
<td></td>
<td>EM1-WeA: Ternary &amp; Quaternary Oxide Materials</td>
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</tbody>
</table>
Atomic Layer Etching
Evergreen Ballroom & Foyer - Session ALE-SuP
Atomic Layer Etching Poster Session
6:00pm

ALE-SuP1 Mechanistic Thermal Desorption Studies of Thermal Dry Etching Reactions for Cobalt and Iron Thin Films, Mahsa Konh, A. Teplyakov, University of Delaware


ALE-SuP3 Using Etching of the Atomic Layer to Remove Damaged Layers Obtained by Plasma-Chemical Etching with Subsequent Growth of GaAs Quantum Dots by the Method of Droplet Epitaxy, Victor Klimin, A. Rezvan, O. Ageev, Southern Federal University, Russia


ALE-SuP5 Study of the Chemical Fabrication Process of NSOM Probes and the Modification of its Surface for Sensing Applications, Muhammad Nazmul Hussain, J. Woehl, University of Wisconsin-Milwaukee


ALE-SuP8 Surface Reaction Analysis for Atomic-Layer Etching and Deposition by Means of Beam Experiments, Kazuhiro Karahashi, T. Ikai S. Hamaguchi, Osaka University, Japan

ALE-SuP9 Atomic Layer Etching of SiO2 and Si3N4 with Fluorocarbon, Hydrofluorocarbon and Fluoroether Compounds, H. Chae, Yongjae Kim, T. Cha, Y. Cho, Sungkyunkwan University (SKKU), Republic of Korea

ALE-SuP10 Cyclic Etching of Copper Thin Films using Two Sequential Steps, Eun Tack Lim, J.S. Choi, J.S. Ryu, M.H. Cha, C.W. Chung, Inha University, Republic of Korea

ALE-SuP11 Analysis of Mechanisms Involved in Cryogenic ALE, Thomas Tillocher, G. Antoun, P. Lefaucheux, R. Dussart, GREMI Université d’Orléans/CNRS, France; K. Yamazaki, K. Yatsuda, Tokyo Electron Limited, Japan; J. Faguet, K. Maekawa, TEL Technology Center, America, LLC

ALE-SuP12 Study on Dry Etching Characteristics of Germanium Oxide by Atomic Layer Deposition, Donghyuk Shin, J. Jeong, H. Song, H. Park, D.-H. Ko, Yonsei University, Republic of Korea


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<tr>
<th>Time</th>
<th>Event</th>
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<tbody>
<tr>
<td>8:30am</td>
<td>ALD 2019 Opening Remarks and ALD 2019 Innovation Award Presentation</td>
</tr>
<tr>
<td>8:45am</td>
<td>INVITED: PS1-MoM2 Atomic Scale Processing: From Understanding to Innovation, Erwin Kessels, Eindhoven University of Technology, Netherlands</td>
</tr>
<tr>
<td>9:00am</td>
<td>Invited talk continues.</td>
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<tr>
<td>9:15am</td>
<td>Invited talk continues.</td>
</tr>
<tr>
<td>9:30am</td>
<td>INVITED: PS1-MoM5 Elucidating the Mechanisms for Atomic Layer Growth through In Situ Studies, Jeffrey W. Elam, Argonne National Laboratory</td>
</tr>
<tr>
<td>9:45am</td>
<td>Invited talk continues.</td>
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<tr>
<td>10:00am</td>
<td>Invited talk continues.</td>
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<tr>
<td>10:15am</td>
<td>Break &amp; Exhibits</td>
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<tr>
<td>10:30am</td>
<td>Break &amp; Exhibits</td>
</tr>
<tr>
<td>10:45am</td>
<td>ALE 2019 Opening Remarks</td>
</tr>
<tr>
<td>11:00am</td>
<td>INVITED: PS2-MoM11 Mapping the Future Evolution of Atomic Scale Processing to enable the World of Artificial Intelligence, Eric A. Joseph, IBM T.J. Watson Research Center</td>
</tr>
<tr>
<td>11:15am</td>
<td>Invited talk continues.</td>
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<tr>
<td>11:30am</td>
<td>Invited talk continues.</td>
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<tr>
<td>11:45am</td>
<td>ALD/ALE 2019 Sponsor Preview</td>
</tr>
<tr>
<td>12:00pm</td>
<td>Lunch &amp; Exhibits</td>
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### Monday Afternoon, July 22, 2019

<table>
<thead>
<tr>
<th>Time</th>
<th>Session</th>
<th>Title</th>
<th>Speaker(s)</th>
</tr>
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<tbody>
<tr>
<td>1:30pm</td>
<td>AA1-MoA1</td>
<td>Atomic Layer Deposition on Pharmaceutical Particles for Inhaled Drug Delivery, <strong>Domiano La Zara</strong>, Delft University of Technology, Netherlands; D. Zhang, M.J. Quayle, G. Petersson, S. Folestad, AstraZeneca, Sweden; J.R. van Ommen, Delft University of Technology, Netherlands</td>
<td>J.J. Berry, Technology (KRICT), Republic of Korea, N.J. Jeon, Y.K. Lee, C.G. Kim, T.-M. Chung, J. Seo</td>
</tr>
<tr>
<td>1:45pm</td>
<td>AA1-MoA2</td>
<td>The Use of Atomic Layer Deposition to Increase the Availability of Medical Radio-Isotopes, <strong>Ruud van Ommen</strong>, J. Moret, B. Wolterbeek, E. Pidko, A. Denkova, Delft University of Technology, Netherlands</td>
<td>J.H. Park, J.-W. Son, Korea Institute of Science and Technology (KIST), Republic of Korea</td>
</tr>
<tr>
<td>2:00pm</td>
<td>AA1-MoA3</td>
<td>Atomic Layer Deposition for Biosensing Applications, <strong>Matthewie Weber</strong>, S. Balme, P. Miele, M. Bechehany, Institut Européens des Membranes, France</td>
<td>R. Prasanna, Stanford University; S. Nanayakkara, S. Christensen, K. Zhu, National Renewable Energy Laboratory; M. McGehee, University of Colorado Boulder; D. Moore, J.J. Berry, National Renewable Energy Laboratory</td>
</tr>
<tr>
<td>2:15pm</td>
<td>AA1-MoA4</td>
<td>Multi-layer Stacked ALD Coating for Hermetic Encapsulation of Implantable Biomedical Microdevices, <strong>John Hennessy</strong>, Jet Propulsion Laboratory</td>
<td>Juhana Kostama, Picosun Oy, Finland; A. Nurmikko, Brown University; Tom Blomberg, Picosun Oy/ASM, Finland</td>
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<tr>
<td>2:30pm</td>
<td>AA1-MoA5</td>
<td>Modification of Spaceflight Radiator Coating Pigments by Atomic Layer Deposition for Thermal Applications, <strong>Vivek Dwivedi</strong>, NASA Goddard Space Flight Center, R. Adomaitis, H. Solami, A. Uy, University of Maryland; M. Hasegawa, NASA Goddard Space Flight Center</td>
<td>E. Graugnard, Boise State University; Elton Graugnard, Boise State University</td>
</tr>
<tr>
<td>2:45pm</td>
<td>AA1-MoA6</td>
<td>Novel Atomic Layer Deposition Process/Hardware for Superconducting Films for NASA Applications, <strong>Frank Greer</strong>, D. Cunnane, Jet Propulsion Laboratory</td>
<td>M. Modreanu, S. O’Brien, M. Pemble, I. Povey, Picosun Oy, Finland; A. Nurmikko, Brown University; Tom Blomberg, Picosun Oy/ASM, Finland</td>
</tr>
<tr>
<td>3:00pm</td>
<td>AA1-MoA7</td>
<td>Fluoride-based ALD Materials System for Optical Space Applications, <strong>John Hennessy</strong>, Jet Propulsion Laboratory, California Institute of Technology</td>
<td>Juhana Kostama, Picosun Oy, Finland; A. Nurmikko, Brown University; Tom Blomberg, Picosun Oy/ASM, Finland</td>
</tr>
<tr>
<td>3:15pm</td>
<td>AA1-MoA8</td>
<td>Atomic Layer Deposition of Aluminum Fluoride for use in Astronomical Optical Devices, <strong>Alan Uy</strong>, H. Solami, A. Vadalapal, C. Grab, R. Adomaitis, University of Maryland; V. Dwivedi, NASA Goddard Space Flight Center</td>
<td>Juhana Kostama, Picosun Oy, Finland; A. Nurmikko, Brown University; Tom Blomberg, Picosun Oy/ASM, Finland</td>
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<tr>
<td>3:30pm</td>
<td>Break</td>
<td><strong>Break &amp; Exhibits</strong></td>
<td><strong>Break &amp; Exhibits</strong></td>
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<tr>
<td>3:45pm</td>
<td>Break</td>
<td><strong>Break &amp; Exhibits</strong></td>
<td><strong>Break &amp; Exhibits</strong></td>
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<tr>
<td>4:00pm</td>
<td>AA2-MoA1</td>
<td>Nucleation Layer for Atomic Layer Deposition Enabling High Efficiency and Flexible Monolithic All-Peroxskite Tandem Solar Cells, <strong>R. Prasanna</strong>, Stanford University; S. Nanayakkara, S. Christensen, K. Zhu, National Renewable Energy Laboratory; M. McGehee, University of Colorado Boulder; D. Moore, J.J. Berry, National Renewable Energy Laboratory</td>
<td>Juhana Kostama, Picosun Oy, Finland; A. Nurmikko, Brown University; Tom Blomberg, Picosun Oy/ASM, Finland</td>
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<tr>
<td>4:15pm</td>
<td>AA2-MoA2</td>
<td>Perovskite Solar Cells Fabricated using Atomic Layer Deposited Doped ZnO as a Transparent Electrode, <strong>Louise Ryan</strong>, M. McCarthy, S. Monaghan, M. Modreanu, S. O’Brien, M. Pemble, I. Povey, Tandayl National Institute, Ireland</td>
<td>Juhana Kostama, Picosun Oy, Finland; A. Nurmikko, Brown University; Tom Blomberg, Picosun Oy/ASM, Finland</td>
</tr>
<tr>
<td>4:30pm</td>
<td>AA2-MoA3</td>
<td>Metal Oxide Barrier and Buffer Layers by Atomic Layer Deposition and Pulsed-Chemical Vapor Deposition for Semi-Transparent Perovskite Solar Cells, <strong>Helen Hejin Park</strong>, T. Eom, R.E. Agbenyeke, S.M. Yeo, G.J. Kim, S.S. Shin, F.-Y. Yang, N.J. Jeon, Y.K. Lee, C.G. Kim, T.-M. Chung, J. Sea, Korea Research Institute of Chemical Technology (KRICT), Republic of Korea</td>
<td>Juhana Kostama, Picosun Oy, Finland; A. Nurmikko, Brown University; Tom Blomberg, Picosun Oy/ASM, Finland</td>
</tr>
<tr>
<td>4:45pm</td>
<td>AA2-MoA4</td>
<td>Particle Atomic Layer Deposition of Tungsten Nitride Environmental Barrier Coatings from Bis(t-butylimido)bis(dimethylamino) tungsten(VI) and Ammonia, <strong>Sarah Bull</strong>, A. Weimer, University of Colorado - Boulder</td>
<td>Juhana Kostama, Picosun Oy, Finland; A. Nurmikko, Brown University; Tom Blomberg, Picosun Oy/ASM, Finland</td>
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<tr>
<td>5:00pm</td>
<td>AA2-MoA5</td>
<td>Atomic Layer Deposition on Mg(BH4)2: A Route to Improved Automotive H2storage, <strong>Noemi Leick</strong>, National Renewable Energy Laboratory; K. Gross, H&lt;sub&gt;2&lt;/sub&gt; Technology Consulting LLL; T. Gennett, S. Christensen, National Renewable Energy Laboratory</td>
<td>Juhana Kostama, Picosun Oy, Finland; A. Nurmikko, Brown University; Tom Blomberg, Picosun Oy/ASM, Finland</td>
</tr>
<tr>
<td>5:15pm</td>
<td>AA2-MoA6</td>
<td>Plasmonic Mediated Hydrogen Desorption from Metal Hydrides, <strong>Katherine Hurst</strong>, A. Gaulding, M. Martinez, N. Leick, S. Christensen, T. Gennett, National Renewable Energy Laboratory</td>
<td>Juhana Kostama, Picosun Oy, Finland; A. Nurmikko, Brown University; Tom Blomberg, Picosun Oy/ASM, Finland</td>
</tr>
<tr>
<td>5:30pm</td>
<td>AA2-MoA7</td>
<td>Surface Modification of Solid Oxide Fuel Cell Cathodes by Atomic Layer Deposition, <strong>Dong Hwan Kim</strong>, M.I. Choi, J. Koo, Korea University, Republic of Korea; J.H. Park, J.-W. Son, Korea Institute of Science and Technology (KIST), Republic of Korea; J.H. Shim, Korea University, Republic of Korea</td>
<td>Juhana Kostama, Picosun Oy, Finland; A. Nurmikko, Brown University; Tom Blomberg, Picosun Oy/ASM, Finland</td>
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<tr>
<td>5:45pm</td>
<td>Poster</td>
<td><strong>Poster Session</strong></td>
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### Monday Afternoon, July 22, 2019

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<tr>
<th>Time</th>
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<th>Location</th>
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<tbody>
<tr>
<td>1:30pm</td>
<td>INVITED</td>
<td>AF2-MoA1 The Materials Supplier Challenge: Flawless Execution from Precursor Design to High Volume Manufacturing, Madhukar B. Rao, Versum Materials</td>
<td>T. Nabatame, M. Ritala, M. Leskelä, Microsysteme (IPMS), Germany</td>
<td>Grand Ballroom E-G</td>
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<tr>
<td>1:45pm</td>
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<td>Invited talk continues.</td>
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<tr>
<td>2:00pm</td>
<td>AF2-MoA3</td>
<td>Precursor and Co-Reagent Selection: A Figure of Merit, Séan Barry, M. Griffiths, Carleton University, Canada</td>
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<tr>
<td>2:15pm</td>
<td>AF2-MoA4</td>
<td>Designing Thermal Atomic Layer Deposition Processes for Gold Metal using New Organogold Precursors and Co-reagents, Matthew Griffiths, G. Bačić, A. Vargo, S. Barry, Carleton University, Canada</td>
<td></td>
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<tr>
<td>2:30pm</td>
<td>AF2-MoA5</td>
<td>A New Carbene Based Silver Precursor Applied in APP-ALD Yielding Conductive and Transparent Ag Films: A Promising Precursor Class for Ag Metal ALD, Nils Boysen, Ruhr University Bochum, Germany; T. Hasselmann, D. Theirich, T. Riedl, University of Wuppertal, Germany; A. Devi, Ruhr University Bochum, Germany</td>
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<tr>
<td>2:45pm</td>
<td>AF2-MoA6</td>
<td>Transition Metal β-ketoiminates: A Promising Precursor Class for Atomic Layer Deposition of Binary and Ternary Oxide Thin Films, Dennis Zwizinski, A. Devi, Ruhr University Bochum, Germany</td>
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<tr>
<td>3:00pm</td>
<td>AF2-MoA7</td>
<td>A New and Promising ALD Process for Molybdenum Oxide Thin Films: From Process Development to Hydrogen Gas Sensing Applications, Jan-Lucas Wree, Ruhr University Bochum, Germany; M. Mattinen, University of Helsinki, Finland; E. Ciftiyürek, K.D. Schierbaum, Heinrich Heine University Düsseldorf, Germany; M. Ritala, M. Leskelä, University of Helsinki, Finland; A. Devi, Ruhr University Bochum, Germany</td>
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<tr>
<td>3:15pm</td>
<td>AF2-MoA8</td>
<td>Atomic Layer Deposition of Gallium Oxide Thin Films using Pentamethylcyclopentadienyl Gallium and Combinations of H₂O and O₂ Plasma, Fumikazu Mizutani, Toyohashi University of Technology, Japan; M. Inoue, T. Nabetame, National Institute for Materials Science, Japan</td>
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<tr>
<td>3:30pm</td>
<td>Break &amp; Exhibits</td>
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<td>3:45pm</td>
<td>Break &amp; Exhibits</td>
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<tr>
<td>4:00pm</td>
<td>AF3-MoA11</td>
<td>Understanding Elemental Steps of ALD on Oxidation Catalysts, Kristian Kneumeyer, M. Piernavieja Hermida, R. Naumann d’Alnoncourt, Technische Universität Berlin, Germany; A. Trunschke, R. Schlögl, Fritz Haber Institute of the Max Planck Society, Germany; M. Driess, Technische Universität Berlin, Germany; F. Rosowski, BASF SE, Germany</td>
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<tr>
<td>4:15pm</td>
<td>AF3-MoA12</td>
<td>Advanced Lateral High Aspect Ratio Test Structures for Conformality Characterization by Optical Microscopy, Dilli Ylivaara, P. Hyytinen, VTT Technical Research Centre of Finland Ltd, Finland; K. Arts, Eindhoven University of Technology, Netherlands; F. Gao, VTT Technical Research Centre of Finland Ltd, Finland; W.M.M. Kessels, Eindhoven University of Technology, Netherlands; R. Puurunen, Aalto University, Finland; M. Utirainen, VTT Technical Research Centre of Finland Ltd, Finland</td>
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<td>4:30pm</td>
<td>AF3-MoA13</td>
<td>Dopant Concentration Analysis of ALD Thin Films in 3D Structures by ToF-SIMS, A.M. Kia, Wenke Weinreich, Fraunhofer-Institut fur Photonische Mikrosysteme (IPMS), Germany; M. Utirainen, VTT Technical Research Centre of Finland Ltd, Finland; R. Puurunen, Aalto University, Finland; N. Haufe, Fraunhofer-Institut fur Photonische Mikrosysteme (IPMS), Germany</td>
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<td>4:45pm</td>
<td>AF3-MoA14</td>
<td>Metallic Ruthenium Coating on SiO₂ Powder by Atomic Layer Deposition using H₂O Reactant., Chi Thang Nguyen, Incheon National University, Republic of Korea</td>
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<td>5:00pm</td>
<td>AF3-MoA15</td>
<td>Low Energy Ion Scattering Study of Pt@Al₂O₃ Nanoparticle Coarsening, Philipp Bruner, IONTOF GmbH, Germany; E. Solano, ALBA Synchrotron Light Source, Spain; C. Detavernier, J. Dendooven, Ghent University, Belgium</td>
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<td>5:30pm</td>
<td>AF3-MoA17</td>
<td>The Tailoring of the Single Metal Atom-Oxide Interface, Bin Zhang, Y. Qin, Institute of Coal Chemistry, Chinese Academy of Sciences, China</td>
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<td>5:45pm</td>
<td>Poster Session</td>
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<td>1:30pm</td>
<td>AF1-MoA1</td>
<td>Hybrid Computational Fluid Dynamics / Machine Learning Approaches to Reactor Scale Simulations and Optimization of ALD, ALEt, and LPCVD Processes, Angel Yanguas-Gil, S. Letourneau, A. Lancaster, J.W. Elam, Argonne National Laboratory</td>
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<td>1:45pm</td>
<td>AF1-MoA2</td>
<td>Scalable Kinetic Monte-Carlo Model for Parasitic Reactions in Silicon Nitride Growth using 3DMAS Precursor, Gem Shoute, T. Muneshwar, Synthergy Inc., Canada; D. Barlage, K. Cadieu, University of Alberta, Canada</td>
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<td><strong>Moderators:</strong> Simon Elliot, Schrödinger, Inc. Angel Yanguas-Gil, Argonne National Laboratory</td>
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<td>2:00pm</td>
<td>INVITED: AF1-MoA3</td>
<td>Diffusion and Aggregation in Island-Growth and Area-Selective Deposition, Fabio Grillo, ETH Zurich, Switzerland</td>
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<td>2:15pm</td>
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<td>Invited talk continues.</td>
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<td>2:30pm</td>
<td>AF1-MoA5</td>
<td>Surface Kinetics in ALD and ALE: Computing the Cooperative Effect by Automated Enumeration of Reaction Pathways with Spectator Adsorbates, Thomas Mustard, Schrödinger, Inc.; S. Elliot, Schrödinger, Inc.; T. Hughes, A. Bochevarov, L. Jacobson, S. Kwok, Schrödinger, Inc.; T. Morisoto, Schrödinger K.K., Japan; J. Gavartin, Schrödinger, Inc., UK; S. Pandiyan, Schrödinger, Inc., India; M. Halls, Schrödinger, Inc.</td>
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<td>2:45pm</td>
<td>AF1-MoA6</td>
<td>An Immiscible Fluids Approach for Correctly Predicting Agglomerate Dynamics during Particle Atomic Layer Deposition (Particle ALD), Julia Hartig, A. Weimer, University of Colorado - Boulder</td>
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<td>3:00pm</td>
<td>INVITED: AF1-MoA7</td>
<td>The Time-Resolved Interface between ALD and CVD, Henrik Pedersen, Linköping University, Sweden</td>
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<td>Break &amp; Exhibits</td>
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<td>Break &amp; Exhibits</td>
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<td>4:00pm</td>
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<td><strong>Moderators:</strong> Viljami Pore, ASM Mikko Ritala, University of Helsinki</td>
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<td>4:15pm</td>
<td>INVITED: AF4-MoA12</td>
<td>Monolithic Integration of Single Crystal Perovskites on Semiconductors with ALD, John Ekerdt, University of Texas at Austin</td>
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<td>4:30pm</td>
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<td>Invited talk continues.</td>
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<td>4:45pm</td>
<td>AF4-MoA14</td>
<td>Surface Enhanced Raman Spectroscopy Studies of Aluminum ALD Precursors for Al₂O₃ Growth, Michael Foody, Illinois Institute of Technology</td>
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<td>5:00pm</td>
<td>AF4-MoA15</td>
<td>Atomic Layer Deposition of Aluminum, Hafnium and Zirconium Oxyfluoride Films with Tunable Stoichiometry, Neha Mahuli, J. Wollas, S.M. George, University of Colorado - Boulder</td>
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<td>5:15pm</td>
<td>AF4-MoA16</td>
<td>Fundamental Study on the SiO₂ Growth Mechanism of Electronegativity Difference of Metal-O in the High-k Underlayers by PE-ALD Method, Erika Maeda, Shibaura Institute of Technology, Japan; T. Nobatame, National Institute for Materials Science, Japan; M. Hirose, Shibaura Institute of Technology, Japan; M. Inoue, A. Ohi, N. Ikeda, National Institute for Materials Science, Japan; M. Takahashi, K. Ito, Osaka University, Japan; H. Kiyono, Shibaura Institute of Technology, Japan</td>
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<td>5:30pm</td>
<td>AF4-MoA17</td>
<td>Low Temperature Aluminium Nitride Deposition: Comparing Hydrazine and Ammonia, Aswin L.N. Kondusamy, S.M. Hwang, A.T. Lucero, Z. Qin, X. Meng, The University of Texas at Dallas; D. Alvarez, J. Spiegelman, RASIRC; J. Kim, The University of Texas at Dallas</td>
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<td>5:45pm</td>
<td>Poster Session</td>
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| 1:30pm | INVITED: ALE1-MoA1 | Atomic Layer Etching – Advancing Its Application with a New Regime, Samantha Tan, W. Yang, K.J. Kanarik, Y. Pan, R. Gottscho, Lam Research Corp. | Atomic Layer Etching  
Session ALE1-MoA | Energy-enhanced ALE  
Moderators:  
Keren J. Kanarik, Lam Research Corp.  
Harm Knoops, Oxford Instruments Plasma Technology |
| 1:45pm | Invited talk continues. | | |
| 2:00pm | ALE1-MoA3 | Control of the Interface Layer in ALE Process by Alternating O2 Plasma with Fluorocarbon Deposition for High Selectivity Etching, Takayoshi Tsutsumi, A. Kobayashi, Nagoya University, Japan; N. Kobayashi, ASM Japan K.K., Japan; M. Hori, Nagoya University, Japan | | |
| 2:15pm | ALE1-MoA4 | Self-limiting Atomic Layer Etching of SiO2 using Low Temperature Cyclic Air/CHF3 Plasma, Stefano Dallorto, Lawrence Berkeley National Laboratory; A. Goodyear, M. Cooke, Oxford Instruments Plasma Technology, UK; S. Dhuey, Lawrence Berkeley National Laboratory; J. Szomoln, Lawrence Livermore National Laboratory; I. Rangelow, Ilmenau University of Technology, Germany; S. Cabrini, Lawrence Berkeley National Laboratory | | |
| 2:30pm | ALE1-MoA5 | Evolution of Photore sist Layer Structure and Surface Morphology in a Fluorocarbon-Plasma-Based Atomic Layer Etching Process, Adam Pranda, K-Y. Lin, S. Gutierrez Razo, J. Fourkas, G.S. Oehrlein, University of Maryland | | |
| 3:00pm | ALE1-MoA7 | Atomic Layer Etching of Silicon Nitride with Ultrahigh Etching Selectivity over Silicon and Oxide Materials by Utilizing Novel Etch Gas Molecule, Xiangyu Guo, American Air Liquide; N. Stafford, Air Liquide; V. Pallem, American Air Liquide | | |
| 3:30pm | Break & Exhibits | | | |
| 4:00pm | INVITED: ALE2-MoA11 | Developments of Atomic Layer Etch Processes and their Applications in Fabricating III-V Compound Semiconductor Devices, Xu Li, Y.-C. Fu, S.-J. Cho, D. Hemakumara, K. Floros, D. Moran, I. Thayne, University of Glasgow, UK | Atomic Layer Etching  
Session ALE2-MoA | |
| 4:15pm | Invited talk continues. | | | |
| 4:30pm | ALE2-MoA13 | GaN and GasOx Thermal Atomic Layer Etching Using Sequential Surface Reactions, N. Johnson, Y. Lee, Steven M. George, University of Colorado - Boulder | ALE of Compound Semiconductors  
Moderators:  
David Boris, U.S. Naval Research Laboratory  
Ishii Yohei, Hitachi High Technologies |
| 4:45pm | ALE2-MoA14 | Selective GaN Etching Process using Self-limiting Cyclic Approach for Power Device Applications, Frédéric Le Roux, N. Possemie, P. Burtin, S. Barnola, A. Torres, Univ. Grenoble Alpes, CEA, LETI, France | | |
| 5:00pm | ALE2-MoA15 | ALE of GaN [0001] by Sequential Oxidation and H2/N2 Plasma, Kevin Hatch, D. Messina, H. Fu, K. Fu, X. Wang, M. Hao, Y. Zhao, R. Nemanich, Arizona State University | | |
| 5:15pm | ALE2-MoA16 | Comparative Study of Two Atomic Layer Etching Processes for GaN, Cédric Mannequin, C. You, University of Tsukuba, Japan; G. Jacopin, T. Chevolleau, C. Durand, University Grenoble-Alpes, France; C. Veille, LTM-UGA, France; C. Dussarat, T. Teramoto, Air Liquide Laboratories, Japan; H. Mariette, University Grenoble-Alpes, France; K. Akimoto, M. Sasaki, University of Tsukuba, Japan; E. Gheeraert, University Grenoble-Alpes, France | | |
| 5:30pm | ALE2-MoA17 | Chlorinated Surface Layer of GaN in Quasi Atomic Layer Etching of Cyclic Processes of Chlorine Adsorption and Ion Irradiation, Masaki Hasegawa, T. Tsutsumi, Nagoya University, Japan; A. Tanide, SCREEN Holdings Co., Ltd.; H. Kondo, M. Sekine, K. Ishikawa, M. Hori, Nagoya University, Japan | | |
| 5:45pm | Poster Session | | | |
ALD Fundamentals

Evergreen Ballroom & Foyer - Session AF1-MoP

Precursor Synthesis and Process Development Poster Session

5:45pm


AF1-MoP3 Atomic Layer Deposition of Lanthanum Oxide Using Heteroleptic La Precursors, Doehyeon Kim, J. Lee, W. Noh, Air Liquide Laboratories Korea, South Korea

AF1-MoP4 Synthesis and Thermal Characterization of New Molybdenum Precursors for Atomic Layer Deposition of Molybdenum Metal, Michael Land, Carleton University, Canada; K. Robertson, Saint Mary's University, Canada; S. Barry, Carleton University, Canada


AF1-MoP7 Atomic Layer Deposition of WS2 using a New Metal-Organic Precursor and H2S Molecules, Deok Hyun Kim, D.K. Nandl, S.-H. Kim, Yeungnam University, Republic of Korea


AF1-MoP9 Synthesis of Group VI Oxyhalide Adducts and Mo Metal Film Growth on TiN Surfaces, David Ernert, R. Wright Jr., T. Baum, Entegris, Inc.

AF1-MoP10 Gallium Precursor Development for ALD Film Applications, Atsushi Sakurai, M. Hotaze, N. Okada, A. Yamashita, ADEKA Corporation, Japan


AF1-MoP12 Low Temperature Plasma-Enhanced Atomic Layer Deposition of ZnO from a New Non-Pyrophoric Zn Precursor, Lukas Mai, F. Mitscher, P. Awakowicz, A. Devi, Ruhr University Bochum, Germany

AF1-MoP13 Homoleptic and Heteroleptic Yttrium Precursor: Tuning of Volatility, Reactivity and Stability for ALD Applications, Sebastian Markus Josef Beer, A. Devi, Ruhr University Bochum, Germany

AF1-MoP14 Gallium ALD Precursor Development based on Mechanistic Study, M. Foody, Y. Zhao, Adam Hock, Illinois Institute of Technology

AF1-MoP15 Fluorine Doping of Aluminium Oxide Through In-situ Precursor Synthesis: Theory, Design and Application, Ben Beeke, University of Liverpool, UK

ALD Fundamentals

Evergreen Ballroom & Foyer - Session AF2-MoP

Precursor Selection and Growth Optimization Poster Session

5:45pm

AF2-MoP1 Atomic Layer Deposition of Cyclopentadienyl Based HF Precursor With Various Oxidants, Jooho Lee, D. Kim, W. Noh, Air Liquide Laboratories Korea, South Korea

AF2-MoP2 Atomic Layer Deposition of Magnesium Oxide Thin Films by using Bis(ethylcyclopentadienyl)Magnesium Precursor and H2O, O2 Plasma and O2 Reactants, Moo-Sung Kim, S.-W. Lee, Versum Materials Korea, Republic of Korea; S. Ivanov, Versum Materials, Inc.

AF2-MoP3 Comparative Study between CpTi(OMe)2 and CpTi(NMe)2 for Atomic Layer Deposition of Titanium Oxide, Jaemin Kim, S. Kim, R. Hidayat, Y. Choi, H.-L. Kim, W.-J. Lee, Sejong University, Republic of Korea

AF2-MoP4 Tin Nitride Atomic Layer Deposition using Hydrazine, Ann Greenaway, A. Tamboli, S. Christensen, National Renewable Energy Laboratory

AF2-MoP5 Growing Polycrystalline Indium Oxide Film by Atomic Layer Deposition, Chien-Wel Chen, TRC, NARL, Republic of China


AF2-MoP9 DFT Study on Atomic Layer Deposition of Al2O3 with Various Oxidants, Seungyi Seo, T. Nam, Yonsei University, Republic of Korea; H.B.R. Lee, Incheon National University, Republic of Korea; B. Shong, Hongik University, Republic of Korea; H. Kim, Yonsei University, Republic of Korea

AF2-MoP10 Effect of Heteroleptic Structure on Atomic Layer Deposited HfO2, Using Hf[N(CH3)2]4 and CpHf[N(CH3)2]3 Precursors, Sungmin Park, B.-H. Park, S. Lee, H. Yoon, Yonsei University, Republic of Korea; M.Y. Lee, S.-H. Kim, Yeungnam University, Republic of Korea; H. Kim, Yonsei University, Republic of Korea

AF2-MoP11 Effect of Co-Reactor on the Atomic Layer Deposition of Copper Oxide, Jason Avila, N. Velpe, U.S. Naval Research Laboratory

AF2-MoP12 A Systematic Study on Atomic Layer Deposition of ZrO2 Thin Films, X. Wang, J. Cai, Xiangbo Meng, University of Arkansas

AF2-MoP13 Hydrophobic SiOx Thin Film Deposition using Low-Temperature Atomic Layer Deposition, Eunwook Nam, H. Kim, Yonsei University, Republic of Korea


AF2-MoP15 Developing Routes Toward Atomic Layer Deposition of Tungsten using Fluorine-Free W Precursor and Various Reactants with Density Functional Theory, Tae Hyun Kim, D.K. Nandl, M.Y. Lee, Yeungnam University, Republic of Korea; R. Hidayat, S. Kim, W.-J. Lee, Sejong University, Republic of Korea; S.-H. Kim, Yeungnam University, Republic of Korea

AF2-MoP16 ALD HfO2 with Anhydrous H2O2 in a 300 mm Cross-flow Reactor – Comparison with H2O and O2 Oxidants, Steven Consiglio, R. Clark, C. Wajda, G. Leusink, TEL Technology Center, America, LLC

AF2-MoP17 Atomic Layer Deposition of Copper (I) Chlorobutane Precursor, Richard Krumpolec, D. Cameron, D. Bača, J. Humlček, D. Caha, Masaryk University, Czech Republic

AF2-MoP18 Number Effect of Si Atoms Contained in Precursor for SiN Atomic Layer Deposition, Seongbae Park, H. Ji, H. Yang, S. Yoon, DUKSAN Techopia company, Republic of Korea; I.-S. Park, Hanyang University, Republic of Korea

ALD Fundamentals

Evergreen Ballroom & Foyer - Session AF3-MoP

Growth Mechanisms and In Situ Studies Poster Session

5:45pm

AF3-MoP1 Langasite Crystal Microbalance (LCM) for In-situ Process Monitoring of ALD up to 440 °C, Masafumi Kumano, Tohoku University, Japan; K. Inoue, Piezo Studio, Japan; K. Hikichi, Technofine co. Ltd, Japan; M. Shimizu, S. Tanaka, Tohoku University, Japan

AF3-MoP2 In-Situ Process Monitoring of Precursor Delivery Using Infra-Red Spectroscopic Method, Robert Wright, T. Baum, Entegris, Inc.

AF3-MoP3 Quantitative Analysis of High-k ALD Precursors for Trace Elemental Impurities by Inductively Coupled Plasma – Mass Spectrometry (ICP-MS), Jinjin Wang, L. Mey-Ami, F. Li, Air Liquide Electronics – Balzers NanoAnalysis
ALD Fundamentals

Evergreen Ballroom & Foyer - Session AF5-MoP
Plasma Enhanced ALD Poster Session
5:45pm

AF5-MoP1 Film Thickness and Trace Metal Analysis of Compound Semiconductor Stacks through Direct Film Stripping (DFS) followed by ICP-MS/OES, Vijay (Jaya) Chowdhury, J. Huang, ChemTrace; P. Sun, UCT - ChemTrace; E. Apipah, ChemTrace

AF5-MoP2 Overview of Doctoral Theses on Atomic Layer Deposition Worldwide - Outcome of the Virtual Project on the History of ALD, J. Aarik, University of Tartu, Estonia; J. Aav, E. Ahvenniemi, Aalto University, Finland; A.R. Abkhashe, Stanford University; S. Ali, Aalto University, Finland; M. Bechelany, Institut Européen des Membranes, France; M. Berdova, Aalto University, Finland; I. Bodalyov, St. Petersburg State Institute of Technology, Russian Federation; S. Boyadjiev, Bulgarian Academy of Sciences, Bulgaria; D. Cameron, Masaryk University, Czech Republic; N. Chekurov, Oxford Instruments Analytical Oy, Finland; R. Cheng, Huzhong University of Science and Technology, China; M. Chubarov, The Pennsylvania State University, University of Texas, Bengal; A. Devi, Ruhr University Bochum, Germany; V.E. Drozd, St. Petersburg State Institute of Technology, Russian Federation; L. Eniklou, Institute for Theoretical and Experimental Physics, Russian Federation; G. Gottiardi, Fondazione Bruno Kessler, Center for Materials and Microsystems, Italy; J. Ruud van Ommen, Delft University of Technology, Netherlands; R. Puurunen, Aalto University, Finland

AF5-MoP3 Nanoscale Chemical Characterization of Ultrathin Films via PIEMF, Sung Park, D. Newk, W. Morrison, Molecular Vista

AF5-MoP4 The Effect of Impurities on Film Properties in the Y(MeCp)2O3 Process, J. Kalliomäki, T. Lehto, M. Kääräjä, T. Sarnet, Jari Kivioja, Picuson Oy, Finland

AF5-MoP6 Internal Photoemission Spectroscopy Measurement of Barrier Heights between ALD Ru and Al2O3, Melanie Jenkins, M.H. Hayes, K. Holden, J.F. Conley, Jr., Oregon State University

AF5-MoP7 Growth and Characterization: Low Temperature ALD, Birø Kayel, A. Alphonse, K.P. Hong, J. Marshall, Nano-Master, Inc.

AF5-MoP8 Etch Rate Characterization of Oxide ALD Films, Martin M. Winterkorn, H.J. Kim, J. Provine, F. Prinz, T.W. Kenny, Stanford University

AF5-MoP9 Structural Aspects of Nanometer Size Amorphous Materials, Yoel Elinger-Geller, A. Katzman, B. Rakov, Technion - Israel Institute of Technology, Israel

ALD for Manufacturing

Evergreen Ballroom & Foyer - Session AM-MoP
ALD for Manufacturing Poster Session
5:45pm

AM-MoP1 Cobalt Precursor Supply Chain - Ethics and Risks, Andreas Wilk, A. Frey, O. Briel, Umicore AG & Co. KG, Germany; D. Zeng, Umicore AG & Co. KG

AM-MoP2 Homogeneous and Stress Controlled PEALD Films for Large Optics, Hassan Gargouri, F. Naumann, S. Golka, F. Naumann, S. Golka, SENTECH Instruments GmbH, Germany; K. Pfeiffer, Fraunhofer Institute for Applied Optics and Precision Engineering IOF, Germany; V. Beladiya, Friedrich Schiller University, Germany; A. Szezhalmi, Fraunhofer Institute for Applied Optics and Precision Engineering IOF, Germany

AM-MoP3 Sensing Response of ZnO Nanotube Gas Sensor Synthesized on Porous Substrate by Atomic Layer Deposition, Pengtao Lin, K. Zhang, M. Boumgard, Old Dominion University

AM-MoP4 Temperature-based Control of Liquid Precursor Delivery for ALD Processes, Egbert Wöckl, CeeVeeTech; K. Kimmerle, B. Kimmerle, NSF, National Institute of Standards and Technology, USA

AM-MoP5 Design and Manufacturing of ICP-Type Remote Plasma ALD, Dohyun Go, J.W. Shin, B.C. Yang, H.J. Kim, Seoul National University of Science and Technology, Republic of Korea

AM-MoP6 ACS™ (Atomically Clean Surface™) Cleaning and Analytical Validation of Recycled ALD Chamber Parts for the Semiconductor Industry, Russell Parise, I. Iordanov, B. Quinn, UCT - QuantumClean; P. Sun, UCT - ChemTrace

AM-MoP8 Process Control and Mass Delivery Optimization from Low Vapor Pressure Precursors, Jeffrey Spiegelman, C. Ramos, D. Alvarez, Z. Shamsi, NASIRC

AM-MoP9 Scaling Low-temperature Thermal ALD of SiO2 to Batch, J. Kalliomäki, M. Mäntyäväri, T. Lehto, S. Shukla, M. Kääräjä, T. Sarnet, Juhana Kostamo, Picuson Oy, Finland
Emerging Materials Poster Session
5:45pm

EM-MoP1 Structure and Magnetism of Electrospun a-Fe₂O₃ Nanofibers, Silica-Coated by ALD, F. Pantò, CNR-Istituto di Tecnologie Avanzate per l'Energia (ITAE), Italy; H. Raza, Humboldt-Universität zu Berlin, Germany; A.A.C. Ferrari, CNR-Istituto di Scienze e Tecnologie Molecolari (ISTM), Italy; C. Triolo, Università di Messina, Italy; A. Pantò, CNR-Istituto di Scienze e Tecnologie Molecolari, Italy; S. Patanè, Humboldt-Universität zu Berlin, Germany; Saveria Santangelo, Università Mediterranea, Italy


EM-MoP3 Fabrication and Characterization of Organic-Inorganic Hybrid Thin Films, Chu Huong, Hanyang University, Republic of Korea

EM-MoP4 High Performance Encapsulation Polymer-Al₂O₃ Hybrid Thin Layer by Atomic Layer Infiltration, Hong Rho Yoon, J. Park, N.V. Long, C. Huong, Hanyang University, Republic of Korea

EM-MoP5 ALD of Metal Oxides Fabricated by using La(NO₃)₃·6H₂O Oxidant and their Applications, In-Sung Park, S.Y. Kim, T. Lee, S. Seong, Y.C. Jung, J. Ahn, Hanyang University, Republic of Korea

EM-MoP6 Bringing Higher Etch-resistance to Metal-infiltrated Polymer, Norikatsu Sasao, K. Asakawa, S. Sugimura, Toshiba Memory Corporation


EM-MoP8 Vapor Phase Infiltration as a New Approach in the Fabrication of Advanced Hybrid Thermoelectric Materials, Jaime DuMont, M. Knez, CIC nanoGUNE, Spain

EM-MoP9 Low-temperature Atomic Layer Deposition of Aluminum Oxide on Polymeric Powder Feedstocks for Improved Powder Rheology, John Miller, C. Gillespie, J. Chesser, Lawrence Livermore National Laboratory; A. Schepp, United States Air Force Academy; A. Nelson, N. Teslich, A. Lange, S. Elhadj, R. Reeves, Lawrence Livermore National Laboratory

EM-MoP10 Atomic Layer Deposition of Molybdenum Oxide Carbide and Molybdenum Carbide Films, Michael D. Overbeek, C.H. Winter, Wayne State University


EM-MoP12 Homogenous Distribution of Dopants in ALD Films: Tin-Doped Zinc Oxide (ZTO) Case Study, Triratna Muneshwar, D. Barlage, K. Cadien, University of Alberta, Canada

EM-MoP13 Uniform, Thermal ALD of Al₂O₃ and ZnO on Zirconia Particles, Dhruv Shah, D. Patel, J. O’Tani, M. Linford, Brigham Young University

EM-MoP14 Composition Control of Ge-Sb-Te Film by Supercycles of ALD GeSb and ALD Sb Followed by Tellurization Annealing, Yewon Kim, J. Lee, Sejong University, Republic of Korea; S.J. Baik, Hankyong National University, Republic of Korea; W. Koh, UP Chemical Co., Ltd., Republic of Korea; W.-J. Lee, Sejong University, Republic of Korea

EM-MoP15 Study on The Crystallinity and The Dielectric Constant of ZrGe₁₋ₓO₁₋ₓ Films using Mixed Zr - Ge Precursor by Atomic Layer Deposition, Ju Young Jeong, Y. Han, H. Sohn, Yonsei University, Korea; H. Noh, H. Park, SK Hynix Inc

Note: ALE Posters Will Remain Posted All Week
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<tr>
<td>8:00am</td>
<td>AF1-TuM1</td>
<td>Surface Chemistry during ALD of Nickel Sulfide</td>
<td>Xinwei Wang, Peking University, China</td>
<td>Grand Ballroom A-C</td>
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<td>8:15am</td>
<td>AF1-TuM2</td>
<td>In situ and In vacuo Studies on Plasma Enhanced Atomic Layer Deposited Cobalt Films</td>
<td>Johanna Reiff, M. Knaut, S. Kilge, N.A. Hampel, M. Albert, J.W. Bartha, Technische Universität Dresden, Germany</td>
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<tr>
<td>8:30am</td>
<td>AF1-TuM3</td>
<td>Investigation of PEALD Grown HfO2 Thin Films via Near Ambient Pressure XPS: Precursor Tuning, Process Design and a New In-situ Examination Approach for Studying Film Surfaces Exposed to Reactive Gases</td>
<td>David Zanders, Ruhr University Bochum, Germany; E. Ciftyurek, Heinrich Heine University Düsseldorf, Germany; C. Bock, A. Devi, Ruhr University Bochum, Germany; K.D. Schierbaum, Heinrich Heine University Düsseldorf, Germany</td>
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<td>8:45am</td>
<td>AF1-TuM4</td>
<td>Surface Science Studies of GaN Substrates Subjected to Plasma-Assisted Atomic Layer Processes</td>
<td>Samantha G. Rosenberg, ASEE; D.J. Pennachio, University of California, Santa Barbara; E.C. Young, Y.H. Chang, H.S. Inbar, University of California Santa Barbara; J.M. Woodward, U.S. Naval Research Laboratory; Z.R. Robinson, SUNY College at Brockport; J. Grzeskowiak, University at Albany-SUNY; C.A. Ventrice, Jr., SUNY Polytechnic Institute; C.J. Palmstrøm, University of California Santa Barbara; C.R. Eddy, Jr., U.S. Naval Research Laboratory</td>
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<td>9:00am</td>
<td>AF1-TuM5</td>
<td>Infrared and Optical Emission Spectroscopy on Atmospheric-Pressure Plasma-Enhanced Spatial ALD of Al2O3</td>
<td>Maria Antonietta Mione, W.M.M. Kessels, Eindhoven University of Technology, Netherlands; F. Roozeboom, Eindhoven University of Technology and TNO, Netherlands</td>
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<td>9:15am</td>
<td>AF1-TuM6</td>
<td>Fingerprinting of ALD Reaction Products with Time-Resolved In situ Mass Spectrometry</td>
<td>Andreas Werbrouck, F. Mattelaer, J. Dendooven, C. Detavernier, Ghent University, Belgium</td>
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<td>9:30am</td>
<td>INVITED: AF1-TuM7</td>
<td>Studying Pt and Pd Nanoparticle ALD through X-ray based In situ Mass Spectrometry</td>
<td>Jolien Dendooven, J.-Y. Feng, Ghent University, Belgium; E. Solano, ALBA Synchrotron Light Source, Spain; R. Ramachandran, M. Minjaauw, M. Van Daele, Ghent University, Belgium; D. Hermida-Merino, ESRF European Synchrotron, France; A. Coati, Synchrotron SOLEIL, France; C. Detavernier, Ghent University, Belgium</td>
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<td>10:45am</td>
<td>AF3-TuM12</td>
<td>Enabling Nucleation Phenomena Studies of ALD Deposited Films by In-situ High-Resolution TEM</td>
<td>Stephanie Burgmann, A. Dadlani, A. Bin Afif, Norwegian University of Science and Technology, Norway; J. Provine, Aligned Carbon; A.T.J. van Helvoort, J. Torgesen, Norwegian University of Science and Technology, Norway</td>
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<td>11:00am</td>
<td>AF3-TuM13</td>
<td>In-situ ellipsometric analysis of plasma assisted ALD grown-stoichiometric and crystalline AlN films</td>
<td>Adrian Mohammad, D. Shukla, S. Ilhom, B. Willis, University of Connecticut; B. Johs, Film Sense LLC; A.K. Okyay, Stanford University; N. Biyikli, University of Connecticut</td>
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<td>11:15am</td>
<td>AF3-TuM14</td>
<td>Film Properties of ALD SiNx Deposited by Trisilylamine and N2 Plasma</td>
<td>Markus Bousond, E. Salmi, K. Niiranen, Beneq Oy, Finland</td>
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<td>11:30am</td>
<td>AF3-TuM15</td>
<td>Comparison of Properties of Conductive Nitride Films Prepared by PEALD using Quartz and Sapphire Plasma Sources</td>
<td>I. Krylov, X. Xu, K. Weinfeld, Valentina Korchnaya, D. Ritter, M. Eizenberg, Technion - Israel Institute of Technology, Israel</td>
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<td>11:45am</td>
<td>AF3-TuM16</td>
<td>Role of Hydrogen Radicals in the Surface Reactions of Trimethyl-Indium (TMI) with Ar/N2 Plasma in Hollow-Cathode Plasma-Assisted ALD</td>
<td>Saidjafarzoda Ilhom, A. Mohammad, D. Shukla, N. Biyikli, B. Willis, University of Connecticut</td>
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| 8:00am| ALD Applications | **ALD Applications Session AA1-TuM** | **ALD for Catalysts, Electrocatalysts, and Photocatalysts**  
**Moderators:**  
Jeffrey W. Elam, Argonne National Laboratory  
Parag Banerjee, University of Central Florida |
| 8:15am|         |                                                                     |                                                                                                                          |
| 8:45am|         |                                                                     |                                                                                                                          |
| 9:00am| AA1-TuM4| Improved Electrochemical Activity of Pt Catalyst Fabricated by Vertical Forced-Flow Atomic Layer Deposition, Tzu-Kang Chin, T.-P. Perng, National Tsing Hua University, Republic of China |
| 9:15am|         |                                                                     |                                                                                                                          |
| 9:30am| AA1-TuM5| Improved Catalyst Selectivity and Longevity using Atomic Layer Deposition, C. Marshall, Argonne National Laboratory; A. Dameron, R. Tracy, Forge Nano; C. Nicholas, L. Abrams, P. Berger, Honeywell UOP; T. Li, Lu Zheng, Argonne National Laboratory |
| 9:45am|         |                                                                     |                                                                                                                          |
| 10:00am|         |                                                                     | Break & Exhibits                                                                                                           |
| 10:15am|         |                                                                     | Break & Exhibits                                                                                                           |
| 10:30am|         |                                                                     | Break & Exhibits                                                                                                           |
| 11:00am|         |                                                                     | **ALD Applications Session AA2-TuM**  
**ALD for Batteries I**  
**Moderators:**  
Neil P. Dasgupta, University of Michigan  
Noemi Leick, National Renewable Energy Laboratory |
<p>| 11:30am|         |                                                                     |                                                                                                                          |
| 11:45am| AA2-TuM14| ALD and MLD on Lithium Metal – A Practical Approach Toward Enabling Safe, Long Lasting, High Energy Density Batteries, Andrew Lushington, Arradiance; Y. Zhao, L. GONCHAROVA, Q. Sun, R. Li, X. Sun, University of Western Ontario, Canada |
| 12:00pm|         |                                                                     | Lunch &amp; Exhibits                                                                                                           |</p>
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<th>Time</th>
<th>Session AF2-TuM</th>
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<tr>
<td>8:00</td>
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<td>Characterizing Water Delivery for ALD Processes, <em>James Maslar</em>, B. Sperling, W. Kimes,</td>
<td>National Institute of Standards and Technology; W. Kimmerle, K. Kimmerle, E. Woelk, CeeVeeTech</td>
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<td>National Institute of Standards and Technology; W. Kimmerle, K. Kimmerle, E. Woelk, CeeVeeTech</td>
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<td>8:15</td>
<td>AF2-TuM2</td>
<td>A Nickel Chloride Adduct Complex as a Precursor for Low-Resistivity Nickel Nitride Thin Films with Tert-butylhydrazine as a Coreactant, K. Väyrynen, T. Hertonmaa, M. Mattinen, M.J. Heikkilä, K. Mizoehata, J. Räsänen, University of Helsinki, Finland; J. Link, R. Stern, National Institute of Chemical Physics and Biophysics, Estonia; M. Leskelä, Mikko Ritala, University of Helsinki, Finland</td>
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<td>8:30</td>
<td>AF2-TuM3</td>
<td>Simple, Rationally Designed Aluminum Precursors for the Deposition of Low-impurity AlN Films, <em>Sydney Buttera</em>, S. Barry, Carleton University, Canada; H. Pedersen, Linköping University, Sweden</td>
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<td>8:45</td>
<td>AF2-TuM4</td>
<td>Atomic Layer Deposition of Lead(II) Sulfide at Temperatures Below 100 °C, <em>Georgi Popov</em>, University of Helsinki, Finland; G. Božić, Carleton University, Canada; M. Mattinen, M. Vehkamäki, K. Mizohata, M. Kemell, University of Helsinki, Finland; S. Barry, Carleton University, Canada; J. Räisänen, M. Leskelä, M. Ritala, University of Helsinki, Finland</td>
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<td>9:00</td>
<td>AF2-TuM5</td>
<td>Development and Characterization of a Novel Atomic Layer Deposition Process for Transparent p-Type Semiconducting Nickel Oxide using Ni(II)DAD, and Ozone, <em>Konner Holden</em>, Oregon State University; C.L. Dezelah, EMD Performance Materials; J.F. Conley, Jr., Oregon State University</td>
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<td>9:15</td>
<td>AF2-TuM6</td>
<td>Blocking Thermolysis in Diamido Plumblyenes, <em>Goran Bacic</em>, Carleton University, Canada; D. Zanders, Ruhr University Bochum, Germany; I. Frankel, Carleton University, Canada; J. Masuda, Saint Mary's University, Canada; T. Zeng, Carleton University, Canada; B. Mallick, A. Devi, Ruhr University Bochum, Germany; S. Barry, Carleton University, Canada</td>
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<td>9:30</td>
<td>AF2-TuM7</td>
<td>ALD of Sc₂O₃ with Sc(cp)₂ and a Novel Heteroleptic Precursors, T. Ivanova, Perttu Sippola, ASM, Finland; G. Vermi, D. Xie, ASM, Belgium; M. Givens, ASM, Finland</td>
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<td>9:45</td>
<td>AF2-TuM8</td>
<td>A Novel Self-limited Atomic Layer Deposition of WS₂ based on the Chemisorption and Reduction of bis(t-butylimido)bis(dimethylamino) Complexes, Nicola Pinna, Humboldt-Universität zu Berlin, Germany</td>
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<td>10:45</td>
<td>Invited talk</td>
<td>Overview of Wet And Dry Selective Processes Driven by Area Activation or Deactivation Down to Below 20nm Critical Dimensions, Silvia Armini, IMEC, Belgium</td>
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<td>11:00</td>
<td>Invited talk</td>
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<td>11:15</td>
<td>AS1-TuM14</td>
<td>Electron-Enhanced Atomic Layer Deposition (EE-ALD) of Cobalt Metal Films at Room Temperature, <em>Zach Sobell</em>, A. Cavanagh, S.M. George, University of Colorado - Boulder</td>
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<td>11:30</td>
<td>AS1-TuM15</td>
<td>Area Selective Atomic Layer Deposition on Molecular Design, Akihito Nishida, T. Yoshino, N. Ohe, A. Yamashita, ADEKA Corporation, Japan</td>
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<td>11:45</td>
<td>AS1-TuM16</td>
<td>From Surface Dependence in Atomic Layer Deposition to Area-Selective Deposition of TIN in Nanoscale Patterns, Annelies Delabie, IMEC, Belgium; D. Carabajal, UNAM; J. Soethoudt, B.T. Chan, E. Altamirano Sanchez, B. Meynerts, J.-W. Clerix, S. Van Elshocht, IMEC, Belgium</td>
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<td>12:00</td>
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**Grand Ballroom H-K**

**Session AF2-TuM**

**ALD Fundamentals**

**ALD Precursors II**

**Moderators:**

Jin-Seong Park, Hanyang University
Seán Barry, Carleton University
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<tr>
<td>8:00am</td>
<td>INVITED</td>
<td>Analyses of Hexafluoroacetylacetone (Hfac) Adsorbed on Transition Metal Surfaces, <em>Tomoko Ito, K. Karahashi, S. Hamaguchi</em>, Osaka University, Japan</td>
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<td>8:15am</td>
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<td>8:30am</td>
<td>ALE1-TuM3</td>
<td>Thermal Atomic Layer Etching of Silicon Nitride using an Oxidation and “Conversion-Etch” Mechanism, <em>Aiz Abdulagatov, S.M. George</em>, University of Colorado - Boulder</td>
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<td>8:45am</td>
<td>ALE1-TuM4</td>
<td>Thermal Dry Atomic Layer Etching of Cobalt with Sequential Exposure to Molecular Chlorine and Diketones, <em>M. Konh, C. He, X. Lin</em>, University of Delaware; <em>X. Guo, V. Pallem</em>, American Air Liquide; <em>R. Opila, Andrew Teplyakov, Z. Wang, B. Yuan</em>, University of Delaware</td>
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<td>9:00am</td>
<td>ALE1-TuM5</td>
<td>Spontaneous Etching of B$_2$O$_3$ and TiO$_2$ by HF: Removal Reaction in WO$_3$ ALE and TiN ALE, <em>Austin Cano, S.K. Natarajan</em>, Tyndall National Institute, Ireland; <em>J. Clancy</em>, University of Colorado - Boulder; <em>S. Elliot</em>, Schrödinger Inc; <em>S.M. George</em>, University of Colorado - Boulder</td>
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<td>9:15am</td>
<td>ALE1-TuM6</td>
<td>Thermal Based Atomic Layer Etching of Aluminum Oxide and Titanium Nitride, <em>Varun Sharma, ASM</em>, Finland; <em>T. Blomberg, Picosun Oy/ASM</em>, Finland; <em>M. Tuominen, S. Haukkia</em>, ASM, Finland</td>
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<td>9:30am</td>
<td>ALE1-TuM7</td>
<td>Thermal Atomic Layer Etching of Amorphous and Crystalline Hafnium Oxide, Zirconium Oxide and Hafnium Zirconium Oxide, <em>Jessica A. Murdzek, S.M. George</em>, University of Colorado - Boulder</td>
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<td>9:45am</td>
<td>ALE1-TuM8</td>
<td>Isotropic Atomic Layer Etching of Cobalt with Smooth Etched Surfaces by using Cyclic Repetition of Plasma Oxidation and Organometallization, <em>Sumiko Fujisaki</em>, Hitachi R&amp;D Group, Japan</td>
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<td>10:45am</td>
<td>ALE2-TuM12</td>
<td>Atomic Layer Etching for Germanium using Halogen Neutral Beam «Comparison between Br and Cl Chemistry», <em>T. Fuji, Daisuke Ohori</em>, Tohoku University, Japan; <em>S. Noda</em>, National Institute of Advanced Industrial Science and Technology, Japan; <em>Y. Tanimoto, D. Sato, H. Kurihara, Showa Denko K.k.</em>, <em>W. Mizubayashi, K. Enda</em>, National Institute of Advanced Industrial Science and Technology, Japan; <em>Y. Li</em>, National Chiao Tung University; <em>Y. J. Lee</em>, National Nano Device Laboratories; <em>T. Ozaki</em>, <em>S. Samukawa</em>, Tohoku University, Japan</td>
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<td>Lunch &amp; Exhibits</td>
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<td>11:15am</td>
<td>ALE2-TuM14</td>
<td>A New Etching / Passivation Process in Cyclic Mode for Spacer Etching in 3D CMOS Integrations, <em>O. Pollet, CEA-LETI</em>, France; <em>N. Posserme</em>, Univ. Grenoble Alpes, CEA, LETI, France; <em>V. Ah-Leung, Valentin Bacquie</em>, CEA-LETI, France</td>
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<td>11:30am</td>
<td>ALE2-TuM15</td>
<td>Atomic Layer Etching of Transition Metals with Gas Cluster Ion Beam Irradiation and Acetylacetone, <em>Noriaki Toyoda, K. Uematsu</em>, University of Hyogo, Japan</td>
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<td>11:45am</td>
<td>ALE2-TuM16</td>
<td>Atomic Layer Etching at Atmospheric Pressure, <em>Eugen Shkura, D. Theirich, K. Brinkmann, T. Haeger</em>, University of Wuppertal, Germany; <em>J. Schneiderwind, M. Siebert</em>, SENTECH Instruments GmbH, Germany; <em>T. Riedl</em>, University of Wuppertal, Germany</td>
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<td>1:30pm</td>
<td>AF-TuA1</td>
<td>Low Temperature High Quality Silicon Dioxide by Neutral Beam Enhanced Atomic Layer Deposition</td>
<td>Hua-Hsuan Chen, D. Ohori, T. Ozaki, Tohoku University, Japan; M. Utsuno, T. Kudota, T. Nozawa, ASM Japan K.K., Japan; S. Samukawa, Tohoku University, Japan</td>
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<td>1:45pm</td>
<td>AF-TuA2</td>
<td>Radical Surface Recombination Probabilities during Plasma ALD of SiO₂, TiO₂ and Al₂O₃ Determined from Film Conformality</td>
<td>Karsten Arts, Eindhoven University of Technology, Netherlands; M. Utriainen, VTT Technical Research Centre of Finland, Finland; R. Puurunen, Aalto University, Finland; W.M.M. Kessels, Eindhoven University of Technology, Netherlands; H. Knoops, Oxford Instruments Plasma Technology, UK</td>
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<td>2:00pm</td>
<td>AF-TuA3</td>
<td>A Robust Method for in-situ Gas Monitoring of ALD Processes using Optical Emission Spectroscopy of a Pulsed Remote Plasma</td>
<td>Joe Brindley, B. Daniel, V. Bellido-Gonzalez, Gencoa Limited, UK; R. Potter, B. Peek, University of Liverpool, UK</td>
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<td>2:15pm</td>
<td>AF-TuA4</td>
<td>Near Room Temperature Plasma Enhanced Atomic Layer Deposition of Gold Metal</td>
<td>Michel Van Daele, Ghent University, Belgium; M. Griffiths, Carleton University, Canada; A. Raza, Ghent University - IMEC, Belgium; M. Minjauw, Ghent University, Belgium; S. Barry, Carleton University, Canada; R. Baets, Ghent University - IMEC, Belgium; C. Detavernier, J. Dendooven, Ghent University, Belgium</td>
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<td>2:30pm</td>
<td>AF-TuA5</td>
<td>Low-Temperature Deposition of Gallium Oxide and Aluminum Oxide with Arrays of Microcavity Plasma Enhanced Atomic Layer Deposition</td>
<td>Jinhong Kim, A. Mironov, S.-J. Park, J.G. Eden, University of Illinois at Urbana-Champaign</td>
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<td>4:00pm</td>
<td>INVITED: AA3-TuA11</td>
<td>Doped Hi-K ALD Films of HfO₂ and ZrO₂ for Advanced Ferroelectric and Anti-Ferroelectric Memory Device Applications,</td>
<td>Nilay Mukherjee, J. Mack, S. Rothi, Givens Inc.; Z. Wang, A. Gaskell, N. Tasneem, A. Khan, Georgia Institute of Technology; M. Doppita, D. Kriegner, Charles University</td>
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<td>4:30pm</td>
<td>AA3-TuA13</td>
<td>ALD of La-Doped HfO₂ Films for Ferroelectric Applications</td>
<td>Tatiana Ivanova, P. Sippola, M. Givens, ASM, Finland; H. Sprey, ASM, Belgium; T.M. Büttner, P. Polakowski, K. Seidel, Fraunhofer IPMS-CNT, Germany</td>
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<td>4:45pm</td>
<td>AA3-TuA14</td>
<td>Characterization of Multi-Domain Ferroelectric ZrO₂ Thin Films for Negative Capacitance and Inductive Responses</td>
<td>Yu-Tung Yin, P.-H. Cheng, Y.-S. Jiang, J. Shieh, M.J. Chen, National Taiwan University, Republic of China</td>
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<td>5:00pm</td>
<td>AA3-TuA15</td>
<td>Scaling Ferroelectric Hf₃⁺:Zr⁺:O⁻ on Metal-Ferroelectric-Metal (MFM) and Metal-Ferroelectric-Insulator-Semiconductor (MFIS) Structures</td>
<td>Jaidah Mohan, H. Hernandez-Arriaga, H.S. Kim, A. Khosravi, A. Sahota, The University of Texas at Dallas; R. Wallace, University of Texas at Dallas; J. Kim, The University of Texas at Dallas</td>
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<td>5:15pm</td>
<td>AA3-TuA16</td>
<td>Interface Characteristics of MIM Capacitors using Vanadium Nitride Electrode and ALD-grown ZrO₂ High-k Dielectric Film</td>
<td>Jae Hyoong Choi, Y. Kim, H.I. Lee, H.-J. Lin, K. Hwang, S.W. Nam, H.-K. Kang, Samsung Electronics, Republic of Korea</td>
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<td>Poster Session</td>
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<td>1:30pm</td>
<td>INVITED: AA1-TuA1 Atomic Layer Deposition of Indium Gallium Zinc Oxide (IGZO) Semiconductor Thin Films: From Precursor to Thin Film Transistor Application, Jin-Seong Park, Hanyang University, Republic of Korea</td>
<td>ALD Applications Session AA1-TuA</td>
<td>Emerging Applications I</td>
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<td>Invited talk continues.</td>
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<td>Moderators: Anjana Devi, Ruhr University Bochum</td>
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<td>Han-Bo-Ram Lee, Incheon National University</td>
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<td>2:00pm</td>
<td>AA1-TuA3 ALD Growth of Ultra-thin Co Layers on the Topological Insulator SbTeS, Emanuele Longo, R. Mantovan, R. Cecchini, CNR-IMM Unit of Agrate Briaanzi, Italy; M.D. Overbeek, Wayne State University; M. longo, CNR-IMM Unit of Agrate Briaanzi, Italy; A. Tocchi, CNR-IMM, Italy; M. Manciulli, Università degli Studi di Milano-Bicocca, Italy; C.H. Winter, Wayne State University; C. Widmer, CNR-IMM Unit of Agrate Briaanzi, Italy</td>
<td>ALD Applications Session AA1-TuA</td>
<td>Emerging Applications I</td>
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<td>2:15pm</td>
<td>AA1-TuA4 Modifying Interfacial Chemistry of Cellulose-Reinforced Epoxy Resin Composites using Atomic Layer Deposition (ALD), Jamie Wooding, Y. Li, K. Kalaitzidou, M. Losego, Georgia Institute of Technology</td>
<td>ALD Applications Session AA1-TuA</td>
<td>Emerging Applications I</td>
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<td>2:30pm</td>
<td>AA1-TuA5 Atomic Layer Deposition of Au Nanoparticles on Titania, Fatemeh S. M. Hashemi, Delft University of Technology, Netherlands; F. Grillo, ETH Zurich, Switzerland; V. Ravikumar, D. Benz, A. Shekhar, Delft University of Technology, Netherlands; M. Griffiths, S. Barry, Carleton University, Canada; J.R. van Ommen, Delft University of Technology, Netherlands</td>
<td>ALD Applications Session AA1-TuA</td>
<td>Emerging Applications I</td>
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<td>2:45pm</td>
<td>AA1-TuA6 Multi-layer Protective Coatings on Silver for Protection of Historic Silver Artifacts, E. Breitung, Metropolitan Museum of Art; S. Creange, Rijksmuseum, Netherlands; G. Piili, J.A. Woolfam, A. Bertuch, Ritwik Bhatia, Veeco-CNT</td>
<td>ALD Applications Session AA1-TuA</td>
<td>Emerging Applications I</td>
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<td>3:00pm</td>
<td>AA1-TuA7 Nonlinear Optical Properties of TiO2-Based ALD Thin Films, Theodossia Gougousi, R. Kuis, I. Basoldau, P. Burkins, J.A. Kropp, A. Johnson, University of Maryland, Baltimore County</td>
<td>ALD Applications Session AA1-TuA</td>
<td>Emerging Applications I</td>
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<td>3:15pm</td>
<td>AA1-TuA8 Atomic Layer Deposition to Alter the Wetting and Thermal Properties of Lumber, Shown Gregory, C. McGettigan, E. McGuinness, D. Rodin, S. Yee, M. Losego, Georgia Institute of Technology</td>
<td>ALD Applications Session AA1-TuA</td>
<td>Emerging Applications I</td>
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<td>3:30pm</td>
<td>Break &amp; Exhibits</td>
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<td>4:00pm</td>
<td>AA2-TuA11 Tunable Electrical Properties of Lithium Fluoride Thin Films using Different Fluorine Sources, Devika Choudhury, A. Mane, J.W. Elam, Argonne National Laboratory</td>
<td>ALD Applications Session AA2-TuA</td>
<td>ALD for Batteries II</td>
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<td>4:15pm</td>
<td>AA2-TuA12 The Role of AlOx ALD Precursor Chemistry on the Electrochemical Performance of Lithium Ion Battery Cathode Materials, Donghyeon Kang, A. Mane, J.W. Elam, Argonne National Laboratory; R.F. Wurburton, J.P. Greeley, Purdue University</td>
<td>ALD Applications Session AA2-TuA</td>
<td>ALD for Batteries II</td>
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<td>4:30pm</td>
<td>AA2-TuA13 Spatial Atomic Layer Deposition of Hybrid Nanolaminates for High Capacity Li-ion Battery Electrodes, E. Balder, L. Havorkate, M. Tulodziecki, F. van den Brule, S. Unnirkrishnan, Paul Poole, TNO/Holst Center, Netherlands</td>
<td>ALD Applications Session AA2-TuA</td>
<td>ALD for Batteries II</td>
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<td>4:45pm</td>
<td>AA2-TuA14 Lithium Organic Thin Films for Various Battery Components, Juhia Heiska, M. Karppinen, Aalto University, Finland</td>
<td>ALD Applications Session AA2-TuA</td>
<td>ALD for Batteries II</td>
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<td>5:00pm</td>
<td>AA2-TuA15 ALD Infiltration of LiCoO2 for High Rate Lithium Ion Batteries, Jan Povey, M. Modreanu, S. O'Brien, Tyndall National Institute, Ireland; T. Teranishi, Y. Yoshikawa, M. Yoneda, A. Kishimoto, Okayama University, Japan</td>
<td>ALD Applications Session AA2-TuA</td>
<td>ALD for Batteries II</td>
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<td>5:15pm</td>
<td>AA2-TuA16 ALD Al2O3 and MoS2 Coated TiO2 Nanotube Layers as Anodes for Lithium Ion Batteries, H. Sopha, University of Pardubice, Czech Republic; A. Tesfaye, Ecole Nationale Superieure des Mines de Saint-Etienne, France; R. Zappe, University of Pardubice, Czech Republic; T. Djenizian, Ecole Nationale Superieure des Mines de Saint-Etienne, France; Jan Macak, University of Pardubice, Czech Republic</td>
<td>ALD Applications Session AA2-TuA</td>
<td>ALD for Batteries II</td>
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<td>5:30pm</td>
<td>Poster Session</td>
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<td>1:30pm</td>
<td><strong>AS1-TuA1</strong> Elucidating Mechanisms of Selective ALD of Al₂O₃ by a Comparative Study of Precursors, H-Kwon Oh, T.-L. Liu, Stanford University; T. Sandavol, Technical University Federico Santa Maria; R. Tonner, Philipps-Universität Marburg, Germany; S.F. Bent, Stanford University</td>
<td>Area Selective ALD Session AS1-TuA</td>
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<td>1:45pm</td>
<td><strong>AS1-TuA2</strong> Area-Selective Atomic Layer Deposition using Dodecanethiols: Comparison of Monolayer versus Multilayer, Tsu-Ling Liu, Stanford University; K. Nardi, N. Draeger, D. Hausmann, Lam Research Corp.; S.F. Bent, Stanford University</td>
<td>Area-Selective ALD by Area-Deactivation Moderators: Rong Chen, Huazhong University of Science and Tech Jessica Kachian, Intel Corp.</td>
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<td>2:00pm</td>
<td><strong>AS1-TuA3</strong> Mechanism for Breakdown in Selectivity During Area-Selective Atomic Layer Deposition of ZrO₂ on a SiO₂ Surface Functionalized with a Blocking Layer, Wanxing Xu, Colorado School of Mines; P.C. Lemaire, K. Sharma, D. Hausmann, Lam Research Corp.; S. Agarwal, Colorado School of Mines</td>
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<td>2:15pm</td>
<td><strong>AS1-TuA4</strong> Area Selective Chemical Vapor Deposition of Co from the Co (CO) Precursor: Use of Ammonia to Afford Dielectric-Dielectric Selectivity, Zhejun Zhang, S. Liu, G. Girolami, J. Abelson, University of Illinois at Urbana-Champaign</td>
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<td>2:30pm</td>
<td><strong>AS1-TuA5</strong> Area-Selective ALD of Silicon Oxide using Inhibitors in Four-step Cycles for Metal/Dielectric Selectivity, Marc Merks, R. Jongen, Eindhoven University of Technology, Netherlands; A. Mameli, TNO/Holst Center, Netherlands; D. Hausmann, Lam Research Corp.; W.M.M. Kessels, A.J.M. Mackus, Eindhoven University of Technology, Netherlands</td>
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<td>2:45pm</td>
<td><strong>AS1-TuA6</strong> Selective Area Growth of Deactivating Polymers, Rudy Wojtecki, IBM Research - Almaden; T. Pattison, University of Melbourne, Australia; A. Hess, N. Arellano, A. Fritz, IBM Research - Almaden</td>
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<td>3:00pm</td>
<td><strong>AS1-TuA7</strong> Area-Selective ALD of ZnO Films Patterned by Electrohydrodynamic Jet Printing of Polymers with Sub-Micron Resolution, Tae Cho, N. Farjam, C. Pannier, C. Huber, O. Trejo, C. Allemang, E. Kazyak, R. Peterson, K. Barton, N.P. Dasgupta, University of Michigan</td>
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<td>3:15pm</td>
<td><strong>AS1-TuA8</strong> Selective Deposition of Silicon Nitride, Han Wang, B. Hendrix, T. Baun, Entegris Inc.</td>
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<td>Break &amp; Exhibits</td>
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<td>4:00pm</td>
<td><strong>AS2-TuA111</strong> Area-Selective Deposition and Smoothing of Ru by Combining Atomic Layer Deposition and Selective Etching, Martijn Vos, Eindhoven University of Technology, Netherlands; S. Chopra, University of Texas at Austin; M. Verheijen, Eindhoven University of Technology, Netherlands; J. Ekertd, University of Texas at Austin; S. Agarwal, Colorado School of Mines; W.M.M. Kessels, A.J.M. Mackus, Eindhoven University of Technology, Netherlands</td>
<td>Area Selective ALD Session AS2-TuA1 Area-Selective ALD: Combinations with Etching Moderators: Silvia Armini, IMEC Dennis Hausmann, Lam Research Corp.</td>
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<td>4:15pm</td>
<td><strong>AS2-TuA112</strong> Single Batch Strategies for the Development of an Area Selective Deposition Process with the Deposition/Etch Approach, Christophe Vaillé, M. Bonvalot, LTM-UGA, France; R. Gassioud, CEA-List, France; V. Pesce, A. Choker, S. Belahcen, LTM-UGA, France; N. Posselme, CEA-List, France; B. Pelissier, P. Conan, A. Biesy, LTM-UGA, France</td>
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<td>4:30pm</td>
<td><strong>AS2-TuA113</strong> Surface Halogenation of Amorphous Carbon for Defect-free Area-Selective Deposition of Metal Oxides, Mikhail Kristof, EK LEUVEN, Belgium; S. Armini, IMEC, Belgium; C. De Gendt, KU LEUVEN/IMEC, Belgium; R. Ameloot, KU LEUVEN, Belgium</td>
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<td>5:00pm</td>
<td><strong>AS2-TuA125</strong> Expanding the Materials Library of Sequential Infiltration Synthesis: Conductive Indium and Gallium Oxides Grown in Polymers, Ruben Waldman, University of Chicago; N. Jeon, D. Mandia, O. Heinonen, S. Darling, A. Martinson, Argonne National Laboratory</td>
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<td>5:15pm</td>
<td><strong>AS2-TuA126</strong> Highly Efficient and Stable Organic-Inorganic Halide Perovskite Solar Cells with ALD-grown Charge Transport Layers, Hyunjung Shin, Sungkyunkwan University, Republic of Korea</td>
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<td>Poster Session</td>
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<td>1:30pm</td>
<td>ALE1-TuA</td>
<td><strong>Atomic Layer Etching Session ALE1-TuA</strong></td>
<td><strong>Modeling &amp; Instrumentation I</strong></td>
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<td><strong>INVITED: ALE1-TuA</strong> Atomic Layer Etching of Nanostructures, Sabbir Khan, Niels Bohr Institute, University of Copenhagen, Denmark; D. Suyatin, Lund University, Sweden; J. Sundqvist, Fraunhofer Institute for Ceramic Technologies and Systems IKTS, Germany</td>
<td>Ankur Agarwal, KLA-Tencor Angelique Raley, Tokyo Electron America Inc.</td>
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<td>Invited talk continues.</td>
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<td>2:00pm</td>
<td>ALE1-TuA</td>
<td>Selectivity during Plasma ALE of Si-Compounds: Reaction Mechanism Studied by in-situ Surface Spectroscopy, René Vervuurt, ASM; K. Nakane, T. Tsutsumi, M. Hori, N. Kobayashi, Nagoya University, Japan</td>
<td>Declan Scanlan, O. Stephenson, A. Stover, Edwards Vacuum, Ireland</td>
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<td>2:15pm</td>
<td>ALE1-TuA</td>
<td>Chamber Vacuum Strategies to Enable High Productivity ALE, Declan Scanlan, O. Stephenson, A. Stover, Edwards Vacuum, Ireland</td>
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<td>2:45pm</td>
<td>ALE1-TuA</td>
<td>Selective Quasi-ALE of SiO₂ over Si₃N₄ via Bottom-up Si₃N₄ Passivation: A Computational Study, Du Zhong, Y. Tsai, Y. Shi, M. Wang, TEL Technology Center, America, LLC</td>
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<td>3:00pm</td>
<td>ALE1-TuA</td>
<td><strong>INVITED: ALE1-TuA</strong> Insights of Different Etching Properties between CW and ALE Processes using 3D Voxel-Slab Model, Nobuyuki Kuboi, T. Tatsumi, J. Komachi, S. Yamakawa, Sony Semiconductor Solutions Corp., Japan</td>
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<td><strong>Break &amp; Exhibits</strong></td>
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<td>4:00pm</td>
<td>ALE2-TuA</td>
<td><strong>First-principles Understanding of Atomic Layer Etching of Silicon Nitride using Hydrofluorocarbons, Gyeong Hwang, E. Cheng, University of Texas at Austin; S. Sridhar, TEL Technology Center, America; P. Ventzek, A. Ranjan, Tokyo Electron America Inc.</strong></td>
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<td>4:15pm</td>
<td>ALE2-TuA</td>
<td>An Extended Knudsen Diffusion Model for Aspect Ratio Dependent Atomic Layer Etching, Luiz Felipe Aguiñsky, P. Manstetten, TU Wien, Austria; A. Hössinger, Silvaco Europe Ltd., UK; S. Selberherr, J. Weinbub, TU Wien, Austria</td>
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<td>4:30pm</td>
<td>ALE2-TuA</td>
<td>Thermodynamics-Based Screening Approach for Atomic Layer Etching, Nagraj Kulkarni, Consultant</td>
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<td>5:00pm</td>
<td>ALE2-TuA</td>
<td><strong>Variation of Etched Depth per Cycle and Removal of Reactive Species in Atomic Layer Etching (ALE) - Molecular Dynamics Study, Satoshi Hamaguchi, F.J. Tasnado, S. Shigeno, Y. Okada, M. Isobe, T. Ito, K. Karahashi, Osaka University, Japan</strong></td>
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<td>5:30pm</td>
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<td><strong>Poster Session</strong></td>
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ALD Applications
Evergreen Ballroom & Foyer - Session AA3-TuP
Catalysis and Sensor Applications Poster Session
5:30pm

AA3-TuP1 Highly Dispersed Uniform Pt Catalysts on Carbon Support by Atomic Layer Deposition with Fluidized Bed Reactor(FBR), Jung-Yeon Park, W.P. Hong, S.-J. Oh, Hyundai Motor Group, Republic of Korea; W.-J. Lee, S.-H. Kwon, Pusan National University, Republic of Korea

AA3-TuP2 Stabilizing Ultrasmall Colloidal Platinum Diporphide (PP) Nanocrystals with Atomic Layer Deposition Oxide for Neutral H2O Electrolysis, Maulli S. Egeru, Wake Forest University

AA3-TuP5 Synthesis of Core Shell Nanocatalysts using Atomic Layer Deposition with Fluidized Bed Reactor for PEMFC, Seung-jeong Oh, W.P. Hong, J.Y. Park, Hyundai Motor Group, Republic of Korea; W.-J. Lee, S.-H. Kwon, Pusan National University, Republic of Korea

AA3-TuP6 Porous Nanomembranes Grown by Atomic Layer Deposition: Self-Rolling in Solvent and their Sensing Applications, F. Ma, Y.T. Chen, G. Huang, Yong-Fang Mei, Fudan University, China

AA3-TuP7 Fabrication and Characterization of Atomic Layer Deposited ZnO-based Ultra-thin Films for Hydrogen Sensing, Yan-Qiang Cao, A.-D. Li, Nanjing University, China

ALD Applications
Evergreen Ballroom & Foyer - Session AA4-TuP
Protective Coatings, Barrier Films, Membranes and Flexible Substrates Poster Session
5:30pm

AA4-TuP1 ALD for Membrane Applications, Matthieu Weber, M. Bechelany, Institut Européen des Membranes, France

AA4-TuP2 Nano-Hardness of ALD Films, James Daubert, W. Sweet, J. Kellihar, Northrup Grumman

AA4-TuP3 High Acid Corrosion Resistance of NbOx Thin Film Deposited by Room Temperature ALD, Kazuki Yoshida, K. Saito, M. Miura, K. Kanomata, B. Ahmmad, S. Kubota, F. Hirose, Yamagata University, Japan

AA4-TuP4 Effects of Composition Ratios on Mechanical and Electrical Properties of AZO – Zincote Composite Thin Film Deposited on Transparent Polyimide Film Using Atomic and Molecular Layer Depositions, Seung Hong Song, B.-H. Choi, Korea University, Republic of Korea

AA4-TuP5 Room-temperature Atomic Layer Deposition of Alumino-silicate Thin Film on Flexible Films, Yoshiharu Morii, K. Yoshida, K. Kanomata, M. Miura, B. Ahmmad Arima, S. Kubota, F. Hirose, Yamagata University, Japan

AA4-TuP6 ALD Layers for Reduced Wear on Micro Cutting Tools, T. Junghans, Hans-Dieter Schnabel, Westschweizische Hochschule Zwickau, Germany

AA4-TuP7 Fabrication of Atomic Layer Deposited Alumina as Protective Coating of Silver, Gwon Deok Han, J.S. Park, J. Koo, J.H. Shin, Korea University, Republic of Korea


AA4-TuP9 Nanostructured Thin Film Deposition using Single-Phase Precursor by PEALD, Tohru Shimizu, S. Okada, T. Hiraishi, Kumamoto University, Japan

AA4-TuP10 Nanomechanical Properties of Crystalline Anatase Titanium Oxide Films Synthesized using Atomic Layer Deposition, Yousef Mohammed, P. Lin, K. Zhang, H. Baunsgart, A. Elmustafaa, Old Dominion University

AA4-TuP11 Encapsulation of Magnetic Nanostructures by ALD for Improved Stability and Performance, Devika Choudhury, Y. Zhang, K. Gao, A. Mone, J.W. Elam, Argonne National Laboratory

AA4-TuP12 Diffusion Barrier Properties of ALD TiSiN Films, Jerry Mock, J. Heo, S. Chugh, H.Y. Kim, S. Rathi, N. Mukherjee, Eugenius, Inc.

ALD Applications
Evergreen Ballroom & Foyer - Session AA5-TuP
Emerging Applications Poster Session
5:30pm

AA5-TuP1 Bottom up Stabilization of Perovskite Quantum Dots LED via Atomic Layer Deposition, Rong Chen, K. Cao, Q. Xiang, B. Zhou, Huazhong University of Science and Technology, China


AA5-TuP3 ALD for 3D Nano MEMS Applications, Dorothee Dietz, Fraunhofer Institute for Microelectronic Circuits and Systems IMS, Germany

AA5-TuP4 Tribological Properties of Plasma Enhanced Atomic Layer Deposition TiMoN, Mark Sowa, Veeco-CNT; A. Kazen, U.S. Naval Research Laboratory; B. Krick, N. Strandwitz, Lehigh University

AA5-TuP5 Thickness Optimization of Alumina Thin Film for Microchannel Plate Detector, Boojun Yan, S. Liu, Institute of High Energy Physics, Chinese Academy of Sciences, China

AA5-TuP6 Optical Coatings Deposited on Nonlinear Crystals by Atomic Layer Deposition, Ramudhi Dreddy, R. Susa, M. Dreddy, Center for Physical Sciences and Technology, Lithuania

AA5-TuP7 Atomic Layer Deposition of Nickel and Nickel Oxide Thin-Films for Astronomical X-ray Optics Applications, Hassein Salami, A. Uy, A. Vadapalli, University of Maryland; V. Dwivedi, NASA Goddard Space Flight Center; R. Adomaitis, University of Maryland


AA5-TuP9 Comparative Study of Mo, W, S, Alloy Gas Sensor by Atomic Layer Deposition, Minjoo Lee, Y. Kim, J. Park, H. Kim, Yonsei University, Republic of Korea


Area Selective ALD
Evergreen Ballroom & Foyer - Session AS-TuP
Area Selective ALD Poster Session
5:30pm

AS-TuP1 Laterally-Structured Dielectrics by Area-Selective Atomic-Layer Deposition on 3D Substrates, Philip Klement, D. Anders, F. Michel, J. Schärmann, S. Chatterjee, Justus Liebig University Giessen, Germany

AS-TuP2 Light Assisted Area Selective Atomic Layer Deposition on Plasmonic Nanoantennas, Chengwu Zhang, T. Gao, B. Willis, University of Connecticut

AS-TuP3 Area-Specific Atomic Layer Deposition (ALD) of Cobalt As Mediated by Thermally Induced Dehydrocoupled Self-Assembled Monolayers (SAMs), Barry Arkles, J. Gaff, C. Brick, Gelest, Inc.; A. Kaloyeros, Argonne National Laboratory

AS-TuP4 Investigation of In-situ Surface Cleaning of Cu Films using O2/O3 and N2H4, Su Min Huang, A.L.N. Kondusamy, Q. Zhiyang, H.S. Kim, L.F. Peña, K. Tan, J. Veyan, University of Texas at Dallas; D. Alvarez, J. Spiegelman, RASIRC; J. Kim, University of Texas at Dallas

AS-TuP5 Area-Selective Deposition of SiO2 based on Spatial ALD with Intermixed Etching Steps to Obtain High Selectivity, Alfredo Mamel, TNO/Holst Center, Netherlands; F. Roosenboom, Eindhoven University of Technology and TNO, Netherlands; P. Paodt, TNO/Holst Center, Netherlands

Tuesda Evening Poster Sessions, July 23, 2019
AS-TuP6 Defect Mitigation Solution for Area-Selective Atomic Layer Deposition of Ru on TiN/SiO₂ Nanopatterns, J. Soethoudt, KU Leuven – University of Leuven/IMEC, Belgium; F. Grillo, ETH Zurich, Switzerland; E. Marques, R. van Ommen, Delft University of Technology, Netherlands; B. Briggs, H. Hody, V. Spampinato, A. Franquet, B.T. Chan, Annelies Delabie, IMEC, Belgium

Nanostructure Synthesis and Fabrication

Evergreen Ballroom & Foyer - Session NS-TuP

Nanostructures Synthesis and Fabrication Poster Session
5:30pm

NS-TuP1 Molybdenum Disulfides and Diselenides by Atomic Layer Deposition, Raul Zazpe, J. Prikryl, M. Krba, J. Charvot, F. Dvorak, F. Bures, J. Macak, University of Pardubice, Czech Republic

NS-TuP2 Wafer-scale MoS₂ Thin Film Deposition via H₂S Plasma Sulfurization of ALD-grown MoO₃ at Low Temperature, Jeong-Hun Choi, Korea Maritime and Ocean University, Republic of Korea

NS-TuP3 ALD-based Synthesis of Few-layer Transition Metal Disulfides with Wafer-scale Uniformity for Device Integration, Tao Chen, Y. Wang, H. Zhu, L. Chen, Q.Q. Sun, D.W. Zhang, Fudan University, China

NS-TuP4 Overcoming Agglomeration and Adhesion in Particle ALD, Benjamin Greenberg, J. Wollmershauser, B. Feigelson, U.S. Naval Research Laboratory

NS-TuP5 Density Function Theory for Nucleation of MoF₆ with Oxide Surfaces in Atomic Layer Deposition of MoS₂, Matthew Lawson, Boise State University

Note: ALE Posters Will Remain Posted All Week
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<tr>
<td>8:00am</td>
<td>EM1-WeM1</td>
<td>Molecular Layer Deposition of Titanicone Films using TiCl and Fumaric or Maleic Acid: Growth Mechanism and Ambient Stability, Yan-Qiang Cao, A.-D. Li, Nanjing University, China</td>
<td>Emerging Materials Session EM1-WeM</td>
<td>Grand Ballroom A-C</td>
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<td>8:15am</td>
<td>EM1-WeM2</td>
<td>Temperature Dependent Surface Chemistry in Molecular Layer Deposition of Polyimide on Cu and Si, Chao Zhang, M. Leskelä, M. Ritala, University of Helsinki, Finland</td>
<td>Molecular Layer Deposition</td>
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<td>8:30am</td>
<td>EM1-WeM3</td>
<td>Integrated MLD Supercycle for the Direct Deposition of Zeolitic Imidazolate Framework Films, Alexander John Cruz, I. Stassen, R. Ameloot, KU Leuven, Belgium</td>
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<td>8:45am</td>
<td>EM1-WeM4</td>
<td>Understanding Molecular Layer Deposition Nucleation Mechanisms in Polyurea via Time Domain Thermoreflectance, Rachel Nye, M. Fusco, North Carolina State University; E. Radue, A. Kellner, P. Hopkins, University of Virginia; G.N. Parsons, North Carolina State University</td>
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<td>9:00am</td>
<td>EM1-WeM5</td>
<td>Molecular Layer Deposition of Indicone Thin film using Indium Precursor and Hydroquinone, Seung-Hwan Lee, G.H. Baek, J.-H. Lee, Hanyang University, Republic of Korea; T.T. Ngo Van, B. Shang, Hongik University, Republic of Korea; J.-S. Park, Hanyang University, Republic of Korea</td>
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<td>9:30am</td>
<td>EM1-WeM7</td>
<td>Molecular Layer Deposition of “Magnesicone”, a Magnesium-based Hybrid Material, as a Matrix Material for Solid Composite Electrolytes, Jeroen Kint, F. Mattelaer, M. Minjaew, Ghent University, Belgium; P. Vereecken, IMEC, Belgium; J. Dendooven, C. Detaillier, Ghent University, Belgium</td>
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<td>9:45am</td>
<td>EM1-WeM8</td>
<td>Molecular Layer Deposition of Polyamide Films on Particles Using a Rotating Cylinder Reactor, Tyler Myers, S.M. George, University of Colorado - Boulder</td>
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<td>10:45am</td>
<td>EM2-WeM12</td>
<td>Vapor Phase Infiltration: A Route for Making Insulating Polymer Fibers Conductive, Moto Knez, CIC nanogUNe, Spain; I. Azpitarte, CTEChnano, Spain</td>
<td>Emerging Materials Session EM2-WeM</td>
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<td>11:00am</td>
<td>EM2-WeM13</td>
<td>Vapor Phase Infiltration of Metal Oxides into Microporous Polymers for Organic Solvent Separation Membranes, Emily McGuinness, F. Zhang, Y. Ma, R. Lively, M. Losego, Georgia Institute of Technology</td>
<td>Organic-Inorganic Hybrid Materials</td>
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<td>11:15am</td>
<td>EM2-WeM14</td>
<td>ZnO-Infiltrated Hybrid Polymer Thin Films with Enhanced Gravimetric Water and Oxygen Vapor Sensing Properties, E. Muckley, L. Collins, A. Leveu, Oak Ridge National Laboratory; X. Ye, K. Kissinger, Brookhaven National Laboratory; B. Sumpter, N. Lavrik, Oak Ridge National Laboratory; Chang-Yong Nam, Brookhaven National Laboratory; I. Ivanov, Oak Ridge National Laboratory</td>
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<td>11:30am</td>
<td>EM2-WeM15</td>
<td>Physically Interpenetrated Organic-Inorganic Sub-Surface Layers Created via Vapor Phase Infiltration for Improved Film Adhesion, Mark Losego, S. Dwarkanath, R. Tummala, Georgia Institute of Technology</td>
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<td>11:45am</td>
<td>EM2-WeM16</td>
<td>Inorganic-Organic Thin Film Layer-Structures and Thermal Conductivity, Fabian Krahl, Aalto University, Finland; A. Giré, P. Hopkins, University of Virginia; M. Karppinen, Aalto University, Finland</td>
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<td>8:00</td>
<td>AM1-WeM1</td>
<td>Impact of Operating Parameters on Precursor Separation in “Air Hockey“ Spatial Atomic Layer Deposition Reactor</td>
<td>John Grasso, B. Willis, University of Connecticut</td>
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<td>8:15</td>
<td>AM1-WeM2</td>
<td>Plasma Enhanced Spatial ALD of Silver Thin Films at Atmospheric Pressure</td>
<td>Tim Hasselmann, University of Wuppertal, Germany; N. Boysen, Ruhr University Bochum, Germany; D. Theirich, University of Wuppertal, Germany; A. Devi, Ruhr University Bochum, Germany; T. Riedl, University of Wuppertal, Germany</td>
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<td>8:30</td>
<td>INVITED: AM1-WeM3</td>
<td>Low Temperature Spatial PEALD of Silicon Nitride Films from Aminosilane Precursors and DC Direct Plasma, Eric Dickey, Lotus Applied Technology</td>
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<td>9:00</td>
<td>AM1-WeM5</td>
<td>Development and Characterization of an Atmospheric Pressure Plasma Reactor Compatible with Open-Air Spatial ALD</td>
<td>H. Rabat, F. Zoubian, O. Aubry, N. Dumuis, S. Dozos, GREMI Université d’Orléans/CNRS, France; C. Masse de la Huerta, A. Sékkat, V.H. Nguyen, LMGP Grenoble INP/CNRS, France; M. Bonvalot, C. Vallée, LTM-UGA, France; D. Hong, GREMI Université d’Orléans/CNRS, France; David Muñoz-Rojas, LMGP Grenoble INP/CNRS, France</td>
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<td>9:15</td>
<td>AM1-WeM6</td>
<td>Fast Plasma ALD Employing de Laval Nozzles for High Velocity Precursor Injection</td>
<td>Abhishekkumar Thakur, J. Sundqvist, Fraunhofer Institute for Ceramic Technologies and Systems IKT3, Germany; S. Wege, Plasway Technologies GmbH, Germany</td>
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<td>9:30</td>
<td>AM1-WeM7</td>
<td>Development of a Meter Scale ALD Optical Coating Tool for Astronomical Mirror (and other) Applications</td>
<td>D. Fuyaf, University of California Santa Cruz; A. Phillips, University of California Observatories; A. Feldman, Structured Material Industries, Inc.; N. Kobayashi, University of California Santa Cruz; Gary Tompa, Structured Material Industries, Inc.</td>
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<td>9:45</td>
<td>AM1-WeM8</td>
<td>From Wet-lab to Cleanroom: An Integrated ALD-CVD Process for the Large-area Deposition of Ultrathin Zeolitic Imidazolate Framework Films</td>
<td>Ivo Stassen, A.J. Cruz, R. Ameloot, KU Leuven, Belgium</td>
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<td>10:45</td>
<td>EM3-WeM12</td>
<td>Atomic Layer Epitaxy of Zinc Oxide on C-plane Sapphire from Diethylzinc and Water using Pulsed-Heating Atomic Layer Deposition,</td>
<td>Brandon Piercy, M. Losego, Georgia Institute of Technology</td>
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<td>11:00</td>
<td>EM3-WeM13</td>
<td>Growth of AlN Barriers in Al/AlN/Al SIS Josephson Junctions by Low Temperature Atomic Layer Epitaxy</td>
<td>Charles Eddy, Jr., U.S. Naval Research Laboratory; D.I. Pennachio, J. Lee, A. McFadden, University of California, Santa Barbara; S.G. Rosenberg, U.S. Naval Research Laboratory; Y.H. Chang, C.J. Palmstrøm, University of California, Santa Barbara</td>
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<td>11:15</td>
<td>EM3-WeM14</td>
<td>Investigating Plasma Parameters and Influence of Argon to the Crystalinity of GaN Films Grown by Plasma-Assisted ALD,</td>
<td>Deepa Shukla, I. Saidifarzoda, A. Mohammad, B. Brian Willis, N. Biyikli, University of Connecticut</td>
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<td>11:30</td>
<td>EM3-WeM15</td>
<td>Ultrathin GaN Epilayer by Low-temperature Atomic Layer Annealing and Epitaxy,</td>
<td>Wei-Chung Kao, W.-H. Lee, Y.-T. Yin, National Taiwan University, Republic of China; J.-J. Shyne, Academia Sinica; H.-C. Lin, M.J. Chen, National Taiwan University, Republic of China</td>
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<td>11:45</td>
<td>EM3-WeM16</td>
<td>High Quality ALD Formation of Group-III Nitrides and their Applications in FTO-based Thin Film Solar Cells,</td>
<td>Xinhe Zheng, H. Wei, P. Qiu, M. Peng, Z. Liu, Y. He, Y. Song, Y. An, University of Science and Technology Beijing, China</td>
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<td>8:00am</td>
<td><strong>INVITED: AA1-WeM</strong>&lt;br&gt;A LD/ALE Process in Commercially Available Leading-Edge Logic and Memory Devices, <em>Rajesh Krishnamurthy</em>, TechInsights</td>
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<td>8:30am</td>
<td><strong>AA1-WeM</strong>&lt;br&gt;Atomic Layer Deposited Crystalline Zinc Oxide for Silver-based Ultra-Steep Threshold Switching Selector, <em>Harrison Sejoon Kim</em>, A. Sahota, J. Mohan, H. Hernandez-Arriaga, J. Kim, The University of Texas at Dallas</td>
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<td>8:45am</td>
<td><strong>AA1-WeM</strong>&lt;br&gt;ALD Ge-Se-Te OTS Selectors with Controlled Composition for PCM Applications, <em>Valerio Adinolfi</em>, L. Cheng, R. Clarke, S. Balatti, K. Littau, Intermolecular, Inc.</td>
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<td><strong>AA1-WeM</strong>&lt;br&gt;Pulsed CVD of Amorphous GeSe for Application as OTS Selector, A. Haider, IMEC, Belgium; Shaoren Deng, ASM, Belgium; E. Schapmans, IMEC, Belgium; J.W. Maes, ASM, Belgium; J.-M. Girard, Air Liquide Advanced Materials, France; G. Khalil, imec; G.S. Kor, L. Goux, R. Delhovgne, IMEC; M. CAYMAX, IMEC, Belgium</td>
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<td>9:15am</td>
<td><strong>INVITED: AA1-WeM</strong> Thin Film Challenges in 3D NAND Scaling, <em>Jessica Kachian</em>, D. Pavlopoulos, D. Kloussis, Intel Corporation</td>
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<td>10:30am</td>
<td><strong>INVITED: AA2-WeM</strong>&lt;br&gt;The Journey of ALD High-k Metal Gate from Research to High Volume Manufacturing, <em>Dina Triyoso</em>, R. Clark, S. Consiglio, K. Tapily, C. Wojda, G. Leusink, TEL Technology Center, America, LLC</td>
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<td>11:15am</td>
<td><strong>AA2-WeM</strong>&lt;br&gt;Effects of Er Doping on Structural and Electrical Properties of HfO₂ Grown by Atomic Layer Deposition, <em>Soo Hwan Min</em>, B.-E. Park, C.W. Lee, Yonsei University, Republic of Korea; W. Noh, Air Liquide Laboratories Korea, South Korea; I.-K. Oh, Yonsei University, Republic of Korea; W.-H. Kim, Hanyang University, Republic of Korea; H. Kim, Yonsei University, Republic of Korea</td>
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<td>11:30am</td>
<td><strong>AA2-WeM</strong>&lt;br&gt;Improvement of Electrical Performances of Atomic Layer Deposited ZrO₂ MIM Capacitors with Ru Bottom Electrode, <em>Jaehwan Lee</em>, B.-E. Park, Yonsei University, Republic of Korea; W. Noh, Air Liquide Laboratories Korea, South Korea; I.-K. Oh, Yonsei University, Republic of Korea; W.-H. Kim, Hanyang University, Republic of Korea; H. Kim, Yonsei University, Republic of Korea</td>
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<td><strong>AA2-WeM</strong>&lt;br&gt;Perfecting ALD-Y₂O₃/GaAs(001) Interface with Ultra-High Vacuum Annealing, <em>Keng-Yung Lin</em>, Y.-H. Lin, W.-S. Chen, H.-W. Won, L.B. Young, National Taiwan University, Republic of China; C.-P. Cheng, National Chia-Yi University, Republic of China; T.-W. Fu, National Synchrotron Radiation Research Center, Republic of China; J. Kwo, National Tsing Hua University, Republic of China; M. Hong, National Taiwan University, Republic of China</td>
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<td>8:00am</td>
<td>ALE1-WeM1</td>
<td>INVITED: ALE1-WeM1 ALD and Etch Synergy to Enable the Next Scaling Innovations</td>
<td>Angelique Raley, K.J. Lee, X. Sun, Q. Lou, Y.T. Lu, M. Edley, S. Oyola-Reynoso, P. Ventzek, R. Clark, P. Bildi, H. Masanabu, A. Ranjan, TEL Technology Center, America, LLC</td>
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<td>8:30am</td>
<td>ALE1-WeM3</td>
<td>INVITED: ALE1-WeM3 On the Role of Individual Etching Components in Selective Atomic Layer Processing: Etch and Deposit to Obtain High Selectivity, Alfredo Mameli, TNO/Holst Center, Netherlands; P. Roozeboom, Eindhoven University of Technology and TNO, Netherlands; P. Poolf, TNO/Holst Center, Netherlands</td>
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<td>9:00am</td>
<td>ALE1-WeM5</td>
<td>Area-Selective Deposition of TiO₂ on Various Surfaces by Isothermal Integration of Thermal TiO₂ ALD and ALE, Seung Keun Song, G.N. Parsons, North Carolina State University</td>
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<td>9:15am</td>
<td>ALE1-WeM6</td>
<td>Limited Dose ALE and ALD Processes for Local Film Coatings on 3D Structures, Thomas Seidel, Seitek50; M. Current, Current Scientific</td>
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<td>9:30am</td>
<td>ALE1-WeM7</td>
<td>Formation of Ohmic Contacts to Si using In-situ Chemical Cleaning of the Substrate, Sara Iacopetti, Technion - Israel Institute of Technology, Israel; R. Tarafdar, S. Lai, M. Donek, Lam Research Corp.; M. Eisenberg, Technion - Israel Institute of Technology, Israel</td>
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<td>9:45am</td>
<td>ALE1-WeM8</td>
<td>SADP Spacer Profile Engineering by Quasi-Atomic Layer Etching, Tsai Wen (Maggie) Sung, C. Yan, H. Chung, J. Lo, D. Desai, P. Lembesis, R. Pakulski, M. Yang, Mattson Technology, Inc.</td>
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<td>10:45am</td>
<td>ALE2-WeM12</td>
<td>Dynamic Temperature Control Enabled Atomic Layer Etching of Titanium Nitride, He Zhang, Y.S. Kim, D. Paeng, Lam Research Corp.</td>
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<td>11:00am</td>
<td>ALE2-WeM13</td>
<td>INVITED: ALE2-WeM13 Rapid Thermal-Cyclic Atomic Layer Etching of Thin Films with Highly Selective, Self-Limiting, and Conformal Characteristics, Kazunori Shinoda, Hitachi, Japan; H. Kobayashi, Hitachi; N. Miyoshi, M. Iizawa, Hitachi High-Technologies; K. Ishikawa, M. Hori, Nagoya University, Japan</td>
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<td>11:30am</td>
<td>ALE2-WeM15</td>
<td>Atomic Layer Etching of HfO₂ with Selectivity to Si by Utilizing Material-Selective Deposition Phenomena, Kang-Yi Lin, C. Li, University of Maryland; S. Engelmann, R.L. Bruce, E.A. Joseph, IBM T.J. Watson Research Center; D. Metzler, IBM Research - Albany; G.S. Oehrlein, University of Maryland</td>
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<td>11:45am</td>
<td>ALE2-WeM16</td>
<td>Enhancing Etch Selectivity in Plasma-Assisted ALE of Silicon-Based Dielectrics using Surface Functionalization, Ryan Gasvoda, Colorado School of Mines; S. Wang, E. Hudson, Lam Research Corp.; S. Agarwala, Colorado School of Mines</td>
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**Regency Ballroom A-C**

**Wednesday Morning, July 24, 2019**

**Atomic Layer Etching Session ALE1-WeM**

**Integration & Application of ALE**

**Moderators:**
Wei Tian, Applied Materials

**Atomic Layer Etching Session ALE2-WeM**

**Materials Selective ALE**

**Moderators:**
Fred Roozeboom, Eindhoven University of Technology and TNO
Geun Young Yeom, Sungkyunkwan University
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<tr>
<td>1:30pm</td>
<td>AA1-WeA1</td>
<td>Atomic Layer Deposited Nano-Coatings to Protect SrAl2O4 Based Long-Life Phosphors from Environmental Degradation</td>
<td>Erkul Karacaoglu, Georgia Institute of Technology; E. Ozturk, Karamanoglu Mehmetbey University, Turkey; M. Uyaner, Necmettin Erbakan University, Turkey; M. Losego, Georgia Institute of Technology</td>
<td>Invited: AA2-WeA1 Silicon-Based Low k Dielectric Materials with Remote Plasma ALD, Hyeongtag Jeon, Hanyang University, Republic of Korea</td>
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<td>2:00pm</td>
<td>AA1-WeA3</td>
<td>Atomic Layer Deposition of Pd on ZnO Nanorods for High Performance Photocatalysts</td>
<td>Jong Seon Park, B.J. Kim, G.D. Han, K.-H. Park, E.H. Kang, H.-Q. Park, J.H. Shim, Korea University, Republic of Korea</td>
<td>AA2-WeA3 SiOC Films by PEALD with Excellent Conformality and Wet Etch Resistance, Young Chol Byun, E. Shero, ASM</td>
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<td>2:15pm</td>
<td>AA1-WeA4</td>
<td>Accelerating Light Beam (ALB) Generation through Dielectric Optical Device Fabricated by Low Temperature Atomic Layer Deposition (ALD)</td>
<td>W. Zhu, C. Zhang, A. Agrawal, H. Lezec, National Institute of Standards and Technology; Huazhi Li, Arradiance LLC</td>
<td>AA2-WeA4 ALD TIN for Superconducting Through-Silicon Vias, Keastis Grigoras, S. Simbrowicz, L. Grönberg, J. Govenius, V. Vesterinen, M. Prunnila, J. Hassel, VTT Technical Research Centre of Finland Ltd, Finland</td>
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<td>2:30pm</td>
<td>AA1-WeA5</td>
<td>Tunable Plasmonic Colours Preserved and Modified by Atomic Layer Deposition of Alumina</td>
<td>J-M. Guay, A. Lesina, G. Killaire, University of Ottawa, Canada; Peter Gordon, Carleton University, Canada; C. Hahn, University of Ottawa, Canada; S. Barry, Carleton University, Canada; L. Ramunno, P. Berini, A. Weck, University of Ottawa, Canada</td>
<td>AA2-WeA5 Physical and Electronic Properties of Annealed ALD-deposited Ru from Ru(DMBD)(CO), and Oxygen, Michael H. Hayes, Oregon State University; C.L. Dezelah, J.H. Woodruff, EMD Performance Materials; J.F. Conley, Jr., Oregon State University</td>
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<td>Bongsik Kim, JUSUNG Engineering, Republic of Korea</td>
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<td>Ageeth Bol, Eindhoven University of Technology, Netherlands</td>
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<td>Md. Anower Hossain, T. Zhang, D. Lambert, University of New South Wales, Australia; Y. Zakaria, Hamad Bin Khalifa University, Qatar; P. Burr, University of New South Wales, Australia; S. Rashkeev, A. Abdallah, Hamad Bin Khalifa University, Qatar; B. Hoex, University of New South Wales, Australia</td>
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Atomic Layer Etching
Evergreen Ballroom & Foyer - Session ALE-SuP
Atomic Layer Etching Poster Session

ALE-SuP1 Mechanistic Thermal Desorption Studies of Thermal Dry Etching Reactions for Cobalt and Iron Thin Films, Mahsa Konh, A. Tepljakov, University of Delaware

Atomic layer etching of cobalt and iron has a number of important applications. The mechanisms of thermal dry etching of thin films of these metals were investigated using temperature programmed desorption (TPD) to understand surface chemistry involved in each reaction step. X-ray photoelectron spectroscopy (XPS) and microscopic investigations were used to characterize the surfaces obtained as a result of the etching process. Diketones, such as 1,1,1,5,5,5-hexafluoro-2,4-pentanedione (hfacH) and 2,4-pentanedione (acacH), were tested as etchants. It was determined that in order for the volatile etching products to be formed, the films had to be oxidized or chlorinated, since clean surfaces resulted in decomposition of the diketones. The oxidized surfaces were shown to evolve volatile transition metal-containing products at temperatures much higher compared to those on surfaces pre-exposed to Cl2. However, the mechanism of the etching process appeared to be more complicated on chlorine-exposed surfaces. For example, a number of products of a general formula of Co(hfac)xCly were followed for hfacH reaction with cobalt films, and CoCl2 was shown to participate in the process.


In semiconductor devices, the low electrical resistivity of tungsten coupled with its high resistance to electromigration have driven its use in contacts between transistor source/drain and higher layer interconnects. However, due to the diminishing dimensions of such devices, the need for precision controlled monolayer etch processes have become a necessity so as to enable current and future device architectures. Accordingly, Atomic Layer Etch (ALE) functions as a complementary process technique to well-established Atomic Layer Deposition (ALD) methodologies, such that sequential self-limiting etch processes can be targeted with the desired monolayer control for ultra-thin film material removal. Recently, thermal ALE processes for W have been reported by Parsons and co-workers in which the W is first oxidized by a pulse of O2 or Cl2 gas and then the oxidized material is subsequently removed via gas phase pulses of WF6 or WCl6. Herein, we present a first principles based computational analysis of this thermal ALE process for W metal using an oxidation step followed by introduction of WCl3 as a co-reactant. We have investigated oxidants for the first pulse in the ALE sequence including O2, NO and H2O. It is shown that bulk oxidation of W is not spontaneous, but coverage of the W surface is dependent and subject to thermodynamic barriers of approximately 2 eV. The energetic description associated with the removal of possible volatile etch species in the second ALE step such as WOCl2 and WOCl3 will be presented. Additionally, the use of Cl2 gas as an alternative to WCl3 in the second ALE step has also been explored. A full reaction mechanism for these thermal atomic layer etch processes will be discussed.

2. Xie, W., Lemaire, P., Parsons, G.N. Self-Limiting Thermal Atomic Layer Etching of Tungsten Metal Using O2 Oxidation and WCl3 or WFs: Role of Halogen Species in Temperature Dependence of ALE Reaction Rate. AVS ALE Workshop, 2018, Incheon, South Korea.

ALE-SuP3 Using Etching of the Atomic Layer to Remove Damaged Layers Obtained by Plasma-Chemical Etching with Subsequent Growth of GaAs Quantum Dots by the Method of Droplet Epitaxy, Victor Klimin, A. Rezvan, O. Ageev, Southern Federal University, Russia

The task of controlled synthesis of semiconductor self-organizing nanostructures — quantum dots, filamentous nanocrystals, metallic nanodroplets — is extremely important, first of all, to create effective sources of single and entangled photons — the basis of quantum cryptography systems, as well as functional elements based on filamentary nanocrystals, single quantum dots and / or their complexes with a given topology, on the basis of which cellular automata, memory elements, integrated photonics and functional blocks quantum computing systems are built.

At the same time, drop epitaxy, based on separate deposition of components of groups III and V, allows not only to significantly expand the range of structures formed (quantum dots, rings, disks and complex, hybrid structures based on them), but also to realize independent control of the density and size of quantum dots, as well as to use for their creation virtually any A3BS system, which is inaccessible to techniques based on the Stranks – Krasnoraev mechanism.

The use of structured GaAs and Si substrates and the features of droplet epitaxy techniques will effectively localize optical growth at given points on the surface, thereby ensuring precise positioning and control of the parameters of synthesized nanostructures — metal nanoscale droplets (catalytic centers) and quantum dots based on them (in the case of GaAs).

The structuring of the substrates was carried out by a combination of methods of focused ion beams and plasma chemical etching. However, after obtaining substrates with nanoscale relief, a broken layer was formed on the surface in the depressions caused by plasma and penetration of Ga ions after exposure to focused beams. To remove damaged layers, the best method is layer-by-layer etching of the GaAs surface [4].

To determine the penetration depth of gallium ions, a simulation was carried out and it was revealed that after treatment in chlorine plasma, 12 atomic disturbed layers remain, which were later removed using the atomic layer etching method. When using the “soft” etching mode, the angle of inclination of the nanoscale structures changed and the growth of quantum dots did not occur.

At the end of the experimental studies, samples were obtained with nanoscale surface profiling, a combination of methods of focused ion beams, plasma chemical etching, atomic layer etching, in which GaAs quantum dots were obtained by dropping epitaxy.

This work was carried out as part of a study conducted in the framework of the projects of the Russian Science Foundation No. 15-19-10006.


Silicon removal with true atomic fidelity has been shown to require fine control of reactant species concentrations, ion energies, and chamber conditioning. Such fine control of these process parameters is not straightforward to achieve, nor to verify, on legacy process equipment. This work highlights progress toward achieving atomic layer etching (ALE) of silicon wafers and packaged die in standard Cl2/Ar plasma chemistry for failure analysis applications. Wafer-scale etch experiments show an etch rate decrease to below 1 nm/cycle with decreasing substrate temperature and Cl2 surface modification step time, however the etch rate increases with the number of etch cycles due to insufficient control over Cl2 reactant supply; this is especially problematic for silicon removal depths above a few hundred nm, required for failure analysis application. We will use time-resolved optical emission spectroscopy to demonstrate best-case reactant control in this system and suggest methods for achieving ALE-like etching.

Furthermore, we observe that the D.C. voltage bias generated during the surface modification and sputter steps is significantly above target values during the first few seconds after plasma ignition for both steps. We have developed multi-step ignition schemes for both stages to ensure smooth transitions where the voltage bias remains very near zero during the Cl2 plasma generation step and below the sputter threshold of the modified surface layer(s) during the sputter desorption step. For packaged die processing, we show that silicon removal is strongly dependent on both the carrier substrate type as well as die mounting scheme. Using the best developed method, we will present cross-section microscope images showing back-side handle silicon removal to within a few hundred nanometers of the still-functional active device area.

Sandia National Laboratories is a multimission laboratory managed and operated by National Technology & Engineering Solutions of Sandia, LLC, a wholly owned subsidiary of Honeywell International Inc., for the U.S. Department of Energy's National Nuclear Security Administration under contract DE-NA0003525. This paper describes objective technical results and analysis. Any subjective views or opinions that might be expressed in the paper do not necessarily represent the views of the U.S. Department of Energy or the United States Government.

Thermal atomic layer etching (ALE) of HfO2 and ZrO2 uses sequential and self-limiting fluorination reactions using HF as the reactant. This modern approach for ALE is the reverse of atomic layer deposition (ALD) and leads to isotropic etching that removes the modified layer. Each cycle of thermal ALE consists of two precursor pulses. In the first pulse the precursor reacts with the surface atoms of the substrate material and forms a stable and non-volatile layer, this surface modification is self-limiting in nature. We present a first principles study of the hydrogen fluoride pulse in the first step in thermal atomic layer etch of monoclinic hafnium dioxide and zirconium dioxide using density functional theory (DFT) calculations. HCl molecules adsorb on the surfaces of these metal oxides by forming hydrogen bonds and may remain intact or dissociate to form, H-F and O-H for hafnium dioxide and Zr-F and O-H for zirconium dioxide. The adsorption of one HF molecule at the bare surface of both metal oxides results in dissociative adsorption at all binding sites. The adsorbed H atom can migrate to other sites on the surface depending on energetic barriers. For multiple HF adsorption at coverages ranging from 1/16 to 1 monolayer we find mixed molecular and dissociative adsorption of HF molecules at the bare surfaces. The energetic barriers involved for the formation of H2O from the HF pulse are estimated using the CI-NEB method.


Astronomical measurements in the Far Ultra-violet (FUV, 90-200 nm) require the use of aluminum thin films due to aluminum’s high reflectivity over this wavelength range. Unfortunately, the native aluminum oxide layer formed in atmosphere is strongly absorbing in this wavelength range, requiring that the aluminum films be passivated with a dielectric that inhibits oxidation. Due to the fast oxidation of aluminum, a simultaneous etch and deposition process is desirable to render the native aluminum oxide layer after growth and replace it with a different passivation coating layer. Optical measurements in the FUV range are some of the most challenging due to limited selection of low reflectivity coatings available for use on aluminum thin films. Typically magnesium fluoride (MgF2) or lithium fluoride (LiF) coatings are used for these passivation purposes but each has its problems. MgF2 has an absorption cutoff at 115 nm occluding a critical part of the FUV spectrum. LiF has a lower absorption cutoff at 102.5 nm, but it is hygroscopic and thus susceptible to degradation in ambient conditions. A promising alternative to these coating materials is AlF3, which theoretically can provide reflectivity greater than 50% down to 102.5 nm, but is hygroscopic and thus susceptible to degradation in ambient conditions. A promising alternative to these coating materials is AlF3, which theoretically can provide reflectivity greater than 50% down to 102.5 nm, but is hygroscopic and thus susceptible to degradation in ambient conditions.

References
copper patterning are being performed using conventional dry etching. Cyclic etching, as another approach to etch the copper films, can be a prospective etching technique. Cyclic etching including surface modification and its removal can provide the good etching performance of copper films by effectively inducing surface reaction and precisely controlling the etch depth. These results are attributed to the nature of self-limiting process and the removal of the film by layer-by-layer. There are possible various gas combinations in cyclic etching of copper films. In this study, cyclic etching with two sequential steps of surface modification and ion bombardment was performed. The surface modification and etch depth (etch rate) of copper film were confirmed using surface profilometer, scanning probe microscopy, and field emission scanning electron microscopy (FESEM) as a function of various parameters such as the time of surface modification (plasma exposure) and the bombardment energy of ions. Besides, the resultant etch profile and etch mechanism of copper film in the cyclic etching have been investigated by FESEM, X-ray photoelectron spectroscopy, and Raman spectroscopy.

Acknowledgments This research was supported by the MOTIE (Ministry of Trade, Industry & Energy (10080450) and KSRC(Korea Semiconductor Research Consortium) support program for the development of the future semiconductor device.


ALE-SuP11 Analysis of Mechanisms Involved in Cryogenic ALE, Thomas Tillicher, G. Antoun, P. Lefaucheux, R. Dussart, GREMI Université d’Orléans/CNRS, France; K. Yamazaki, K. Yatsuda, Tokyo Electron Limited, Japan; J. Faguet, K. Maekawa, TEL Technology Center, America, LLC

Atomic Layer Etching (ALE) has been developed almost 40 years ago, but has gained interest these last years for micro and nanoelectronic processes where high precision patterning is required. ALE consists in a sequential process relying on the self-limited adsorption of precursor radicals on the first monolayer(s) of material to be etched. Then, under a low energy ion bombardment, the etch products form and desorb until the adsorbed layer is depleted. This self-limited reaction removes a few monolayers. By repeating the cycle, the material is etched a few monolayers by a few monolayers.

ALE of SiO2 has been achieved with a 3-step process and reported in the literature [1]. The first step is an Ar/C4F8 plasma without any ion bombardment. The oxide surface is then coated with a very thin fluorocarbon layer. The second step is a pure Ar plasma still with no RF self-bias voltage where C4F8 is pumped out of the chamber. The third and final step is an Ar plasma with about 10V RF self-bias voltage. The ion energy must be kept below the sputtering threshold. If the thickness of the FC layer is accurately controlled, the etch step can be self-limited.

Although quasi-ALE of SiO2 has been demonstrated with this process, fluorocarbon contamination of chamber walls is an issue. This affects the reproducibility of ALE processes and hence chamber cleaning is required. Cryogenic Atomic Layer Etching (Cryo-ALE) is proposed as a potential solution. In this new process, the substrate is cooled to very low temperature by liquid nitrogen. The plasma phase deposition step is replaced by a physisorption step consisting in exposing the cooled substrate to a fluorocarbon gas flow. Under such conditions, species are adsorbed only at the cooled surface and hence wall pollution is mainly suppressed. Cryo-ALE of SiO2 has been shown to be effective at -120°C. The details regarding the overall process are presented in G. Antoun’s abstract.

If the temperatures is raised of a few degrees (for instance to -110°C), no etching is observed since C4F8 does not significantly physiosorb at such temperature. Therefore, understanding physisorption conditions as well as activation of etching using a physisorbed layer is relevant for a better control of the process. Desorption mass spectrometry experiments will be fully presented and discussed in this paper.


Acknowledgment The authors thank S. Tahara from Tokyo Electron Miyagi for helpful discussions.

ALE-SuP12 Study on Dry Etching Characteristics of Germanium Oxide by Atomic Layer Deposition, Donghyuk Shin, J. Jeong, H. Song, H. Park, D.-H. Ko, Yonsei University, Republic of Korea

While the Si-based electronics whose basic materials consisting of silicon substrate and silicon dioxide, have played a leading role in the semiconductor industry, germanium has also been receiving steady attention as a new channel material for its high carrier mobility. In particular, the studies on germanium oxide films of which the most are discussing mainly the Ge oxidation process on Ge substrates, have been conducted for several decades. However, the formation of GeO2 film through the oxidation process restricts its own potential for utilization because it is only applicable on Ge substrates. Oxidation process conducted on the SiGe layer causes Ge condensation at its interface where Ge atoms remain nonbonded to oxygen due to the less negative Gibbs free energy to form GeO2. In this context, the growth of GeO2 film by the atomic layer deposition (ALD) enables its utilization to be enlarged even for use on Si substrate. For example, a literature examined the applicability of ALD GeO2 film on Si substrate as a secure memory device employing its unusual film property of dissolving in water. However, the GeO2 film inevitably exhibits unstable nature under the wet etching process, which means that the fundamental study on the GeO2 film needs further explorations including dry etch characteristics.

In this talk, we discuss the growth and characterizations of GeO2 film by ALD process. Film properties of ALD GeO2 were evaluated using High-resolution X-ray photoelectron spectroscopy and Auger electron spectroscopy. We demonstrate the dry etch characteristics of ALD GeO2 films. Dry etch test was performed in the reactive ion etching chamber equipped with a direct capacitive-coupled plasma, using C/F based dry etch chemistry. In addition, the dry etch mechanism of the ALD GeO2 film was investigated in comparison with thermal oxide and silicon nitride. Basic dry etching selectivity mechanism between SiO2 and SiGeO lies on the different ability of each film to self-consume the polymer barrier layer which is formed during dry etching process using C/F based plasma. Our dry etch test results showing a faster dry etch rate for SiGeO film against SiO2 film during the reactive ion etching, are in good agreement with the experimental results reported in literatures, while the ALD GeO2 film reveals its dry etch characteristics which encompass the competing reaction between etching and polymerization.

ALE-SuP13 Laser Isotropic Atomic Removal of Germanium, D. Paeong, He Zhang, Y.S. Kim, Lam Research Corp

Pico second (ps) pulsed laser has been used to achieve isotropic atomic removal of germanium (Ge). After hydrogen (H2) plasma pre-treatment at room temperature, adsorption of O2 or Cl2 gas on the clean Ge surface is used to form germanium monoxide (GeO) or germanium chloride (GeCl) layer. Under laser irradiation, modified layer will heat up rapidly depending on the laser fluence. This surface oxide or halide desorbs thermally, and the short pulse of the ps laser suppresses heat diffusion into the material enabling surface-confined photo-thermal reactions on an ultrafast time scale without thermal budget issue. Etch rates (ER) of sub-nanometers per cycle have been achieved. We report on parametric studies showing how the laser parameters and process conditions affect the ER and the surface roughness after etching.


Atomic layer etching (ALE) is a next generation etching technique consisting of cyclic removal of a monolayer per cycle by repeating adsorption and desorption steps. ALE has advantages such as precise thickness control, high etch selectivity, surface smoothing effect, and minimization of the surface damage during the etching. For the fabrication of next generation nanoscale devices, both isotropic and anisotropic ALE techniques are required. In this study, anisotropic ALE of tungsten (W), which is used as an interconnect layer and the gate material of semiconductor devices, was investigated by sequentially exposing to F radicals by NF3 plasma to form a tungsten fluoride layer followed by the exposure to an oxygen ion beam to remove the tungsten fluoride layer by forming volatile tungsten oxyfluoride (WOxFy) compound at room temperature. The result showed that, at optimized ALE conditions, a precise etch rate of ~ 2.6 Å/cycle was obtained while increasing the W etch depth linearly with increasing the number of etch cycles. And, the W ALE mechanism was investigated by analyzing the surface roughness and surface composition of W during the adsorption step and desorption step.
experience and perspective. Topics to be discussed are: (i) the growing nanoelectronics and photovoltaics which I will discuss from my own research in industry. Application areas to be addressed are especially mechanisms has contributed to important innovations in the field, either in scale processing and discuss how understanding of the underlying presentation, I will address several recent and emerging trends in atomic processing and discuss how understanding of the underlying mechanisms has contributed to important innovations in the field, either in research or in industry. Application areas to be addressed are especially nanoelectronics and photovoltaics which I will discuss from my own experience and perspective. Topics to be discussed are: (i) the growing importance of plasma ALD, aspects such as conformality and the role (and control) of ions; (ii) the necessity of in situ metrology methods (e.g. in situ spectroscopic ellipsometry) for process monitoring and advanced surface spectroscopy for obtaining more quantitative insight into fundamental parameters; (iii) the use of ALD in nanopatterning and the interest in area-selective ALD including those combinations with intermediate etch steps; and (iv) the need for isotropic and anisotropic ALE, either thermal or plasma-based.

9:30am PS1-MoM5 Elucidating the Mechanisms for Atomic Layer Growth through In Situ Studies, Jeffrey W. Elam, Argonne National Laboratory INVITED

Atomic Layer Deposition (ALD) provides exquisite control over film thickness and composition and yields excellent conformality over large areas and within nanostructures. These desirable attributes derive from self-limiting surface chemistry, and can disappear if the self-limitation is removed. Understanding the surface chemical reactions, i.e. the ALD mechanism, can provide insight into the limits of self-limitation allowing better control, successful scale up, and the invention of new processes. In situ measurements are very effective for elucidating ALD growth mechanisms. In this presentation, I will describe investigations into the growth mechanisms of ALD nanocomposite films comprised of conducting (e.g. W, Mo and Re) and insulating (e.g. Al₂O₃, ZrO₂ and TiO₂) components using in situ measurements. These ALD nanocomposites have applications in particle detection, energy storage, and solar power. We have performed extensive in situ studies using quartz crystal microbalance (QCM), quadrupole mass spectrometry (QMS), Fourier transform infrared (FTIR) absorption spectroscopy, and current-voltage measurements. These measurements reveal unusual ALD chemistry occurring upon transitioning between the ALD processes for the two components. This results in unique reaction products that affect the properties of the films in beneficial ways. The knowledge gained from our in situ studies of the ALD nanocomposite films has helped us to overcome problems encountered when we scaled up the ALD processes to large area substrates. Beyond fundamental understanding, in situ measurements are extremely effective in ALD process development and process monitoring. I will end my talk by describing our recent work combining in situ measurements and machine learning to accelerate ALD process development.

Plenary Session
Grand Ballroom A-G - Session PS2-MoM

ALE Plenary Session
Moderators: Craig Huffman, Micron Technology, Gottlieb S. Oehrlein, University of Maryland

11:00am PS2-MoM11 Mapping the Future Evolution of Atomic Scale Processing to enable the World of Artificial Intelligence, Eric A. Joseph, IBM T.J. Watson Research Center INVITED

Advances in the semiconductor industry, historically based on Moore’s Law and Dennard scaling, have become progressively challenging as device technology moves beyond the 7nm node. The ever-continuing trend to minimize process induced device performance degradation. Examples of this paradigm shift will be discussed in detail and a vision for the future challenges of atomic scale processes will be reviewed.
dispersion properties are evaluated both in the liquid and dry state. The but non-conformal nanofilms are observed on amorphous surfaces. The and ethanol solutions, thus suggesting higher bioavailability, than the API (e.g., budesonide and salbutamol) and excipient (i.e., lactose) particles, SiO2 ALD, respectively. The deposition strongly depends on the surface of uniform and conformal nanofilms on crystal surfaces, whereas uniform and on-demand supply \cite{3}. In this presentation, we will compare the periodic table for medical radio-isotopes \cite{1} with the periodic table for ALD precursors \cite{4,5}. It will be discussed in which ways ALD can aid in the production of medical radio-isotopes. We will illustrate this by some examples, such as the production of $^{125}$I and $^{131}$I.


In this study, we combined ALD, nanoscale lithography (NSL), and electrophoresis to fabricate hollow ZnOurchin-like structures covered by Au film for surface-enhanced Raman spectroscopy (SERS) applications. The morphology of the structures was investigated using scanning electron microscope (SEM) and transmission electron microscope (TEM). These three dimensional, high-aspect-ratio organized nanostructures enabled the detection of thiopeptide with concentrations as low as 1x10^-10 M. The impact of the gold layer thickness, and annealing conditions were investigated. Samples that were not annealed had a greater overall reproducibility, whereas the ones annealed presented a stronger enhancement of the Raman signal due to the coalescence of Au into nanoparticles. Lastly, the biosensing capability of the urchin-like ZnO structures was demonstrated by successfully detecting adenosine. These proof-of-concepts enabled for a better understanding of the properties of these peculiar nanostructures, and open prospects for the biosensing community.


In-targeted radionuclide therapy a major hurdle is the dependence on a very limited number of nuclear reactors and greatly reduced powder retention in the inhaler for the ALD-coated particles. The dispersion and aerosolization properties are retained even upon different conditions of temperature (25-40 °C) and relative humidity (60-75 %) over 3 weeks. Finally, in-vitro dissolution tests and cell absorption studies reveal more sustained release with increasing film thickness.

Since the first use of the radionuclide phosphorus-32 for treatment of haematological patients in the 1930s, the use of radioisotopes in medicine has expanded into a mainstream clinical speciality. It encompasses both diagnostic imaging (exploiting the tissue penetration of gamma rays released in nuclear decay) and targeted therapy (exploiting the cellular toxicity of beta minus and alpha particles) \cite{1}. Radioisotopes are typically applied in single photon emission computed tomography (SPECT, e.g., $^{68}$Ga, $^{99m}$Tc, $^{111}$In, $^{177}$Lu and $^{188}$Re), as well as in therapeutic applications (e.g., $^{131}$I, $^{177}$Lu, $^{186}$Re, $^{212}$Bi, $^{212}$Pb, $^{225}$Ac, $^{38}$Re) \cite{2}.

In targeted radionuclide therapy a major hurdle is the dependence on a very limited number of nuclear reactors worldwide to produce these radioisotopes. Especially when some of these reactors are down due to unforeseen maintenance, critical situations for patients relying on the radionuclides can appear.

Atomic layer deposition (ALD) can provide a way to either exploit production in smaller nuclear reactors while still producing radionuclides of high specific activity (i.e. activity per unit of mass) or in some cases to prepare radionuclide generators, that can be placed in hospitals, providing on-site and on-demand supply \cite{3}. In this presentation, we will compare the periodic table for medical radio-isotopes \cite{1} with the periodic table for ALD precursors \cite{4,5}. It will be discussed in which ways ALD can aid in the production of medical radio-isotopes. We will illustrate this by some examples, such as the production of $^{125}$I and $^{131}$I.


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full 3-D conformal multilayer encapsulation, and carefully pored on to Al foil and loosely packed for transportation. Sample handling was done using plastic-tip or vacuum tweezers. Three types of substrates were coated: 500 μm x 500 μm passive silicon die, active wireless microelectronic chips, and wired interdigitated electrodes. The substrates were subjected to an accelerated aging test by immersion in saline at 87 °C. A subset of active microelectronic chips were constantly powered on using RF energy at 915 MHz. Failed samples were analyzed by scanning electron microscopy.

Results:
ALD-coated samples had an accelerated aging test survival time which can be extrapolated to > 10 years at physiologic temperatures (37°C) for passive as well as active samples (where the latter had continuous electric fields across the ALD films). Analysis of the failed samples shows areas of film breakdown at the edges, likely associated with post-encapsulation handling. There is no evidence of delamination of the ALD layer stack at the periphery of the failure, indicating that point-failure rather than a gradual degradation of the films.

Acknowledgements:
This work was supported by DARPA NESD Program Contract # N666001-17-C-4013

2:30pm AA1-MoA5 Modification of Spaceflight Radiator Coating Pigments by Atomic Layer Deposition for Thermal Applications, Vivek Dwivedi, NASA Goddard Space Flight Center; R. Adamaitis, H. Salami, A. Uy, University of Maryland; M. Hasegawa, NASA Goddard Space Flight Center
The optical and physical properties of spacecraft radiator coatings are dictated by orbital environmental conditions. For example, coatings must adequately dissipate charge buildup when orbital conditions, such as polar, geostationary or gravity neutral, result in surface charging. Current dissipation techniques include depositing a layer of ITO (indium tin oxide) on the radiator surface in a high temperature process. The application of these enhanced coatings must be such that the properties in question are tailored to mission-specific requirements.

The deposition of thin films by atomic layer deposition is a natural technological fit for manufacturing spacecraft components where weight, conformality, processing temperature, and material selection are all at a premium. Indium oxide (IO) and indium tin oxide (ITO) are widely used in optoelectronics applications as a high quality transparent conductive oxide layer. In this work, we present the thickness-dependent electrical and optical properties of IO thin-films synthesized by ALD with the aim of finding the optimum condition for coating a variety of substrates from Si(100) wafers, glass slides, and especially radiator pigments. Radiators are given surface finishes with high IR emittance to maximize surface temperature and low solar absorptance to limit heat loads from the sun. The surface finish is typically a white paint composed of nano/micron particle sized pigments with a silicate binder. It is the encapsulation of these particles that dictate the charge bleed off properties of the finished coating.

Trimmethylene and ozone were used as precursors for IO, while a tetakis(dimethylamino)tin(IV) source was used for Sn doping to produce ITO. As-deposited IO films prepared at 140 °C resulted in a growth per cycle of 0.46 Å/cycle and relatively low film resistivity.

For the case of ITO thin-films, an ALD process supercycle consisting of 1 Sn + 19 In cycles was shown to provide the optimum level of Sn doping corresponding to the 10 wt.% widely reported in the literature. By using the inherent advantage of ALD in coating high aspect ratio geometries conformally, modification of these pigments can be accomplished during coating application preprocessing. The preprocessing is rendered directly on the dry pigment/particle before binding and not on the finished coated radiator geometry thus saving reactor volume.

Samples of our coating were recently launched into space and are currently onboard the International Space Station (ISS) as part of the one-year MISSE-10 mission. The mission where the IO coated pigments are exposed to the harsh environment of space.

2:45pm AA1-MoA6 Novel Atomic Layer Deposition Process/Hardware for Superconducting Films for NASA Applications, Frank Greer, D. Cunnane, Jet Propulsion Laboratory
Future sub-millimeter telescopes and spectrometers have the potential to revolutionize our understanding of the formation of the modern universe. Sub-millimeter astronomy can probe the fine structure of the cosmic microwave background, giving glimpses into the early universe immediately following the Big Bang. Recent advances in design have enabled the production of large arrays of cryogenically cooled superconducting detectors with sufficient sensitivity for photon counting applications. Transition edge sensors (TES) and other types of detectors, fabricated from thin films of metal nitrides and such TiN, NbN, TaN, VN, and their mixtures or high temperature superconductors like MgB2, are cryogenically cooled to just below their superconducting transition temperature. Atomic layer deposition is a chemical technique that can deposit extremely conformal and uniform films with angstrom level precision that would seem ideal for deposition of films of this type. However, one significant limitation of the technique is that it is often confined to those films that can be achieved through equilibrium processes. This is a significant limitation when the material of choice, such as MgB2, which is an excellent superconducting material, is Mg deficient as deposited by conventional chemical vapor deposition and only stoichiometric MgB2 is a superconductor. Superconducting MgB2 thin films have been grown using hybrid physical/chemical vapor deposition when there is an excess of magnesium in the gas phase created by evaporation of elemental magnesium in the deposition chamber. The method for doing this is to have a charge of magnesium metal that is heated above its sublimation temperature in the very near vicinity of the substrate susceptor. Unfortunately, this method is currently only appropriate for small samples (1-2" in diameter) and for thick films (100nm or thicker). To overcome these limitations, we have built a custom lid for an existing atomic layer deposition reactor was machined to include a cavity to enable magnesium evaporation during deposition. We have subsequently used this approach to deposit MgB2 thin films detectors. This presentation will focus on our thin film results from both of the nitrides and MgB2 (composition, superconducting transition temperature, morphology, etc.) as well as the possible applicability of this generalized in situ thermal evaporation technology concept to other ALD materials.

3:00pm AA1-MoA7 Fluoride-based ALD Materials Systems for Optical Space Applications, John Hennessy, Jet Propulsion Laboratory, California Institute of Technology
In this work we describe space technology applications that plan to utilize the recent development of atomic layer deposition (ALD) processes for metal fluoride materials like MgF2, AlF3, and LiF. These materials are valuable optical thin films in the deep ultraviolet, and are being used at NASA JPL to fabricate protected-aluminum mirror coatings, anti-reflection coatings, and detector-integrated filter coatings. Such systems are currently being implemented in a variety of sub-orbital missions including sounding rockets, cubesats, and high-altitude balloons that are relevant to astrophysics, heliophysics, and planetary science observations. We describe how ALD thin film properties may offer performance advantages over conventional methods with respect to film uniformity, microstructure, and integration with back-illuminated imaging sensors. We also describe the development of mitigating approaches to enhance the environmental stability of typically-hygrosopic fluoride materials through the use of ALD nanolaminates and mixed-composition fluorides. The same fluoride-based ALD approach has also been exploited to perform low-temperature atomic layer etching (ALE) to enhance the optical performance of some of these devices, and to pursue strategies for the development of protective coatings for lithium metal anodes relevant to future Li-ion battery applications.

3:15pm AA1-MoA8 Atomic Layer Deposition of Aluminum Fluoride for use in Astronautical Optical Devices, Alan Uy, H. Salami, A. Vadapalli, C. Grob, R. Adamaitis, University of Maryland; V. Dwivedi, NASA Goddard Space Flight Center
Solid state metal halides typically have a high bandgap and low refractive index. Aluminum trifluoride (AlF3) exhibits these properties, having a band gap greater than 10 eV and a refractive index of 1.35, making it an attractive material for thin film applications that include mirrors and optical devices [1]. Techniques to deposit thin films of AlF3 include physical vapor deposition, sputtering, sol-gel, and atomic layer deposition (ALD) [2]. An important application of metal halides films in spacecraft missions has been for the protection of aluminum mirror from oxidation, which can severely affect overall reflectance in the far ultraviolet region. These coatings must maintain the underlying reflectivity of pure aluminum by having high transparency over the broad spectral range. To this end, AlF3 stands out from other metal halide protective coatings, having higher transparency at the 100-200 nm wavelength region [1]. Due to long duration missions and the inability to service observatories in orbit, coatings of aluminum fluoride are also investigated for robustness and low interactions with potential foulers such as low earth orbit atomic oxygen. These thin coatings must be pinhole free to prevent access and reaction with underlying layers.
The highly conformal dense films and thickness control by ALD are attractive for this application. In this work, the growth of AlF₃ by ALD using precursors trimethyl aluminum (TMA) and titanium tetrafluoride (TiF₄) is investigated. Deposition of AlF₃ is performed in a custom hot-wall bench-scale reactor. We have shown that our deposition system can generate growth rates of ~0.5 Å/ALD cycle at relatively low temperatures of 180 °C. Varying ALD process parameters such as the exposure and purge times of precursor were found to have interesting effects to the film growth rate, especially those concerning the precursor TiF₄. These developments also give insight into potential reaction mechanisms between TMA and TiF₄, leading towards an overall hypothesized reaction mechanism for ALD process. Furthermore, optical properties, composition, and uniformity of film are analyzed. Lastly, the generated AlF₃ film quality over months under ambient conditions for robustness also is discussed.


**ALD Applications**

**Grand Ballroom A-C - Session AA2-MoA**

**ALD for Solar Cells, Fuel Cells, and H₂ Storage**

**Moderators:** Christophe Detavernier, Ghent University, Nicholas Strandwitt, Lehigh University

4:00pm **AA2-MoA11 Nucleation Layer for Atomic Layer Deposition Enabling High Efficiency and Flexible Monolithic All-Perovskite Tandem Solar Cells, Axel F. Palmstrøm, G. Eperon, T. Leijtens, National Renewable Energy Laboratory; R. Prasanna, Stanford University; S. Nanayakkara, S. Christensen, K. Zhu, National Renewable Energy Laboratory; M. McGhee, University of Colorado Boulder; D. Moore, J.J. Berry, National Renewable Energy Laboratory**

The emergence of metal halide perovskites as high efficiency, low-cost photovoltaic materials with a tunable band-gap has led to significant interest for perovskite-based tandems. Of existing perovskite-based tandem technologies, pairing wide-gap and low-gap perovskites in a monolithic all-perovskite tandem arguably offers the greatest potential by enabling efficiencies beyond the single-junction Shockley-Queisser limit with low-cost solution processing on a flexible, lightweight substrate. As of yet, efficiency of all-perovskite monolithic tandems has lagged behind perovskites paired with silicon or CIGS despite significant improvement to low-gap perovskite materials. A barrier to effectively combining state-of-the-art wide and low band gap perovskites in a monolithic tandem is the lack of a high-quality recombination layer that sufficiently protects an underlying perovskite thin-film to enable subsequent perovskite solution processing and minimal device shunting.

In this work, we aim to understand metal oxide growth by low-temperature atomic layer deposition (ALD) on CZO to develop improved recombination layers for all-perovskite 2T tandems. The effect of CZO surface modification with ultra-thin n- or p-doped metal oxide-containing materials is studied on ALD nucleation, growth, and film properties. We show, for multiple ALD systems, nucleophilic surface modification improves the water and dimethylformamide barrier properties of the grown oxide film. This strategy enables the fabrication of improved ALD recombination layers that are thinner and less laterally conductive (reduced shunting) than currently reported strategies. We demonstrate ALD-grown aluminum-doped zinc oxide (AZO) as an effective recombination layer for two-terminal all-perovskite tandems with efficiencies over 23% for rigid devices and 21% for flexible devices.

4:15pm **AA2-MoA12 Perovskite Solar Cells Fabricated using Atomic Layer Deposited Doped ZnO as a Transparent Electrode, Louise Ryan, M. McCarthy, S. Monaghan, M. Modreanu, S. O’Brien, M. Pembble, I. Povey, Tyndall National Institute, Ireland**

Power conversion efficiencies of perovskite (PK) solar cells have rapidly improved in recent years obtaining efficiencies in excess of 20% [1]. Good absorption properties in the visible and infrared spectrum, high efficiencies and low fabrication costs have brought PK solar cells to the forefront. With single junction PK solar cells soon reaching theoretical efficiency limits a requirement for tandem cells, where materials of differing absorption characteristics convert a wider spectral range, is in demand. However, such tandem solar cells introduce fabrication complexities due to the thermal budget restrictions imposed by the complex layer structure [2].

Fluorine-tin oxide (FTO) and indium-tin oxides (ITO) are widely used transparent contacts in solar cells. However, the high deposition temperatures and energetic processes required for its production are detrimental to the fabrication of delicate perovskite based tandem solar cells and thus the need to find an alternative TCO is vital.

Here we have considered Ti-doped ZnO, produced by a ALD laminate doping method, as an alternative transparent contact and have incorporated it into perovskite solar cells in conjunction with an ALD-grown SnO₂, electron transport material. Detailed analysis of the influence of the growth process on the performance of the Ti-doped ZnO electrode is presented. Finally, the efficiency of the optimised perovskite solar cells are evaluated relative to the current state of the art.


4:30pm **AA2-MoA13 Metal Oxide Barrier and Buffer Layers by Atomic Layer Deposition and Pulsed-Chemical Vapor Deposition for Semi-Transparent Perovskite Solar Cells, Helen Heijn Park, T. Eom, R.E. Agbenyeke, S.M. Yeo, G.J. Kim, S.S. Shin, T.-Y. Yang, N.J. Jeon, Y.K. Lee, C.G. Kim, T.-M. Chung, J. Seo, Korea Research Institute of Chemical Technology (KRICT), Republic of Korea**

For n-i-p structured semi-transparent perovskite solar cells, thermal evaporation has been a common technique to deposit the sputter buffer material, such as moltenbium oxide and tungsten oxide, to protect the organic transporting layer (HTL) from damage due to sputtering of the transparent conducting oxide. However, thermal evaporation does not guarantee stoichiometric and uniform pinhole-free coverage of films, leading to inefficient protection against sputtering and poor air stability. While there have been well-established buffer materials by atomic layer deposition (ALD), such as SnO₂, for p-i-n structured semi-transparent perovskite solar cells, this is not the case for n-i-p structured devices. In addition, thermal evaporation has also been commonly used to deposit a barrier layer at the perovskite/HTL interface to improve the fill factor and open-circuit voltage, however, ALD can provide more precise control and conformal coverage for this layer. In this presentation, we demonstrate metal oxide deposition techniques by pulsed-chemical vapor deposition and ALD in perovskite solar cells for the sputter barrier and buffer layers, which result in efficiencies over 16% for semi-transparent devices. Effects of the optical and electrical properties of barrier/buffer layers on the performance of working devices will be addressed, and the mechanisms involved in the enhanced performance and stability will also be discussed.

4:45pm **AA2-MoA14 Particle Atomic Layer Deposition of Tungsten Nitride Environmental Barrier Coatings from Bis(t-butylimido)bis(dimethylamino) tungsten(VI) and Ammonia, Sarah Bull, A. Weimer, University of Colorado - Boulder**

Ultra-thin tungsten nitride (WN) films were deposited by atomic layer deposition (ALD) on zirconia nanoparticles and yttria stabilized zirconia (YSZ) micropowders using a fluidized bed reactor. The film’s intended use as a hydrogen barrier coating motivated the investigation of hydrogen diffusion in W using density functional theory (DFT) and differential thermal analysis (DTA). The lowest energy diffusion pathway was determined and the hydrogen charges at various sites along the pathway were calculated. DTA was used to investigate the efficacy of the W/WN films in preventing hydrogen attack. The temperature at which hydrogen reacts with the sample increased with film thickness, thereby indicating that the film inhibited this reaction. However, the existence of a hydrogen reaction peak in the thicker film indicated a material with greater than 2.0 eV energy barrier is necessary for a substantial decrease in hydrogen interaction with the substrate. This is the first study for ALD of WN on particles from bis(t-butylimido)bis(dimethylamino)tungsten(VI) and the use of ultrathin WN ALD films as environmental barrier coatings (EBCs) for high-temperature H₂ above 1000°C.

5:00pm **AA2-MoA15 Atomic Layer Deposition on Mg(BH₄)₂: A Route to Improved Automotive H₂storage, Noemi Leick, National Renewable Energy Laboratory; K. Gross, H. Suba<sub>2</sub>, Technology Consulting LL; T. Gennett, S. Christensen, National Renewable Energy Laboratory**

In order to meet the U.S. Department of Energy requirements for on-board solid-state hydrogen (H₂) storage in fuel-cell powered vehicles, metal borohydrides are of particular interest. However, while materials such as magnesium borohydride, Mg(BH₄)₂, have a hydrogen capacity up to ~14wt%, challenges associated with hydrogenation-dehydrogenation cyclability need to be overcome. Specifically, improve the operating...
temperatures for adsorption/desorption; increase the hydrogen adsorption-desorption kinetics; and eliminate the formation of the toxic diborane (B2H6). Prior research has indicated that nano-encapsulation (e.g., through graphene nanosheets) and chemical additives (e.g., catalysts) are areas of significance to address these challenges.

This work is the first to approach these two strategies simultaneously using atomic layer deposition (ALD). ALD coatings have been shown to protect and enhance heterogeneous catalyzed rates, as well as to precisely control the amount of chemical additive incorporated. In this project, metal-oxides (e.g. Al2O3, TiO2, CeO2), metal-nitriles (e.g. TiN, BN), pure metals (e.g. Ru, Pd) and combinations thereof were deposited by ALD on γ-Mg(BH4)2. We investigated how the deposition temperature, the use of water for some of these ALD processes and the composition of the additive affected the hydrogen storage properties of γ-Mg(BH4)2.

Compared to uncoated γ-Mg(BH4)2, we found that the ALD depositions lowered the H2 desorption temperature by 60−120 °C, doubled the desorbed gravimetric H2 capacity at temperatures below 250 °C, increased B2H6 substantially during the dehydrogenation step. The ALD-modified γ-Mg(BH4)2 was also explored with respect to the substrate, the effects of the total hydrogen capacity, and catalytic effects. In this presentation we will discuss data supporting these results from temperature programmed desorption, pressure composition temperature manometric measurements, inductively coupled plasma mass spectrometry, nitrogen physisorption measurements, nuclear magnetic resonance, transmission electron microscopy and diffraction spectroscopy.

5:15pm AA2-MoA16 Plasmonic Mediated Hydrogen Desorption from Metal Hydrides, Katherine Hurst, A. Gaulding, M. Martinez, N. Leick, S. Christensen, T. Gennett, National Renewable Energy Laboratory

Excitation of plasmonic coatings deposited by atomic layer deposition (ALD) can provide important routes for tuning the performance of gas adsorption and desorption of hydrogen storage materials. Currently available hydrogen fuel-cell vehicles systems rely on hydrogen stored in compressed tanks at 700 bar. While this hydrogen storage system is partially fostering early-market deployment, the compressed gas system presents several practical challenges and expenses related to infrastructure and delivery that could limit widespread adoption. Metal hydrides are an important class of materials that can reach DOE system capacity targets for hydrogen storage. However, the gas uptake and release of hydrogen by metal hydrides requires high pressures and temperatures, and exhibits slow kinetics. It is well known that modification of a bulk hydride to the nanoscale phase, and the addition of catalyst additives can both greatly enhance the kinetics, lower operating temperatures, and increase cycle life. This work takes a unique route to all of the processes of desorption through the incorporation of plasmonic materials into the hydride matrix. This allows for low-power-LED-illuminated systems to achieve the same rates of hydrogen desorption as radiative thermal heating.

Specifically, recent work at the National Renewable Energy Laboratory has applied ALD to enable the use of plasmonic material coatings to alter the mechanism for hydrogen desorption. Through localized heating via surface plasmon excitation, the bulk thermal signature for hydrogen release can be significantly reduced. Furthermore, hydrogen desorption induced via plasmonic heating offers a completely new approach to using hydride materials. Temperature programmed desorption spectroscopy is used to monitor the kinetic changes associated with desorption by varying the conditions and type of plasmonic material introduced. The effects of partial coverages, ALD film thickness and crystallinity on the resonant plasmonic frequencies are examined. This presentation will discuss advancements in enabling gas desorption via plasmonic excitation especially with respect to hydrogen carrier applications. These exciting results also point towards new applications for ALD in nano-scale photo-thermal processes.

5:30pm AA2-MoA17 Surface Modification of Solid Oxide Fuel Cell Cathodes by Atomic Layer Deposition, Dong Hwan Kim, H.J. Choi, J. Koo, Korea University, Republic of Korea; J.H. Park, J.-W. Son, Korea Institute of Science and Technology (KIST), Republic of Korea; J.H. Shim, Korea University, Republic of Korea

Development of high-performance cathode is key to the commercialization of solid oxide fuel cells (SOFCs). Doped perovskite-type oxides including lanthanum strontium cobaltite (LSC) and lanthanum strontium cobalt ferrite (LSCF) are the most typical materials in practical SOFCs. However, degradation of LSC and LSCF from dynamic on-off operation at high temperature (600-1000 °C) has been considered as the most serious technical obstacle. Many kinds of literature have reported that segregation of cations near the cathode surface leads to this degradation. Specifically, the A-site element of the cathode perovskite is subjected to electrostatic attraction to the surface due to excess oxygen vacancies on the cathode surface, which brings out the A-site element to segregate on the surface [1]. To solve this problem, we have proposed surface modification by atomic layer deposition (ALD) [2]. In this study, 1-4 cycles of ALD Al2O3 has been deposited on porous LSC to suppress the cation segregation and improve the surface redox kinetics. Performance of SOFCs with the ALD Al2O3-treated LSC cathodes has been evaluated in I-V-P and impedance. Finally, long-term stability at 500-600 °C has been examined in the potential-static mode. In this presentation, the progress of this research will be shared in details.


ALD Fundamentals
Grand Ballroom H-K - Session AF1-MoA

ALD Growth Mechanisms I
Moderators: Simon Elliot, Schrödinger, Inc., Angel Yanguas-Gil, Argonne National Laboratory

1:30pm AF1-MoA1 Hybrid Computational Fluid Dynamics / Machine Learning Approaches to Reactor Scale Simulations and Optimization of ALD, ALEt, and LPCVD Processes, Angel Yanguas-Gil, S. Letourneau, A. Lancaster, J.W. Elam, Argonne National Laboratory

As the range of potential applications of atomic layer deposition increases, it is becoming increasingly important to understand how processes scale up to large area substrates and complex substrate geometries. Compared to the number of processes available, there is still a scarcity of tools to explore the interaction between surface kinetics, gas phase transport, and thin film growth at a reactor scale. These tools can help us answer not only key questions regarding the economics or scalability of a given process in terms of throughput or precursor utilization, but they can help us develop a better understanding and intuition of processes and simulate the output of commonly used in-situ techniques such as quartz crystal microbalance or mass spectrometry.

In this work we describe an open source code developed at Argonne to simulate processes based on self-limited and non-self limited surface kinetics at a reactor scale. This code, which is freely available, is built on top of OpenFOAM, a free, open source Computational Fluid Dynamics software. In combination with open source mesh generators such as GMESH, our code provides a simple workflow to explore the role of surface kinetics and the scale up of ALD, ALEt, and LPCVD processes.

To validate our model, we have established a comparison between simulations and experimental results obtained at two different cross-flow ALD reactors. We have then used synthetic growth profiles as a starting point to explore the ability of machine learning approaches to extract relevant information from growth profiles and other experimental datasets. In particular, we have explored the use of artificial neural networks to extract relevant kinetic data from reactor profiles and extrapolate saturation profiles based on a reduced set of experiments.

1:45pm AF1-MoA2 Scalable Kinetic Monte-Carlo Model for Parasitic Reactions in Silicon Nitride Growth using 3DIMAS Precursor, Gem Shoute, T. Muneshwar, Synthergy Inc., Canada; D. Barlage, K. Cadien, University of Alberta, Canada

Atomic layer deposition (ALD) is a cyclical self-limiting reaction deposition technique that heavily depends on the characteristics of the chosen precursor. Currently, there are a limited number of ALD models that can give insight into key growth characteristics of a precursor such as ideal growth per cycle (GPC). Whether a self-limiting reaction can be achieved is determined by several factors related to the precursor itself, including its exposure and purge times and substrate temperature (Tsub), all which affect the GPC of the desired material. For instance, the silicon nitride (Si3N4) precursor, tris(dimethylamino)silane (3DMAS), saturates at Tsub up to ~150 °C but beyond this temperature window, it exhibits dependence on its exposure time resulting in a non-saturated growth. While saturation indicates ideal ALD behavior, the latter observation implies the presence of parasitic reactions that are concurrent with ALD reactions, resulting in non-ideal ALD growth. These non-idealities are especially prominent in aggressive topologies such as high aspect-ratio structures which are a
that previously-inert ligand remnants on the surface can become reactive co-adsorbed fragments or molecules, which otherwise take no part in the reactions have been previously computed to be strongly influenced by the ‘cooperative effect’ [1]. The activation energy at a reactive site has its local environment on the surface around the reaction site, which is called for forward is to sample the chemical space by automating the systematic enumeration of reaction pathways for modeling ALD, can be used to relate the evolution of experimental observables such as the island-size distribution to well-defined growth mechanisms. For example, I will show how dynamic coalescence can govern nanoparticle growth during ALD of noble metals and how different surface diffusion rates can have a dramatic effect on the extent of the “nucleation delay”. Finally, I will present KMC simulations showing how surface diffusion can induce topology-dependent growth in area-selective ALD.


The deposition or etching of solid films by ALD or ALE proceeds via reactions between gas-phase molecules and surfaces. The kinetics of such reactions have been previously computed to be strongly influenced by the local environment on the surface around the reaction site, which is called the ‘cooperative effect’ [1]. The activation energy at a reactive site has been shown to be affected by, or even dictated by, the presence of nearby co-adsorbed fragments or molecules, which otherwise take no part in the reaction and so may be termed ‘spectators’. In the case of ALD, this means that previously-inert ligand remnants on the surface can become reactive once sufficient numbers of other ligands adsorb in their neighborhood. This has been experimentally verified in the case of low-temperature ALD of Al₂O₃ from TMA+H₂O [2].

Including a proper description of the cooperative effect is a serious challenge for first principles simulations of surface reactivity. One way forward is to sample the chemical space by automating the systematic investigation of the factors contributing to the cooperative effect. Specifically, we show how spectator Lewis acids and bases at various coverages and distances affect the activation energy for adsorption and proton transfer on the functionalized surfaces that are typically present during ALD of Al₂O₃.

To study the surface reactivity, we have generated an [Al₂O₂]₄⁺-based cluster model of the (1 0 0) bilayer structure of q-Al₂O₃. We computed the activation energy for adsorption of H₂O onto an open Al site at the center of the cluster and for its dissociation into H⁺ and OH⁻. The cluster is terminated with OH groups on its sides, but has space on top for up to 32 spectator molecules to surround the reactive site at distances ranging 2-6 Å. As spectator molecules we have considered various sizes of alkyl, alkoxyl, hydroxyl and halide groups, so as to probe both electronic and steric effects. All possible arrangements of spectator adsorbates were generated and enumerated with the tools in the Schrödinger Materials Science Suite [3]. The reaction pathway for dissociative adsorption of H₂O was then re-computed for each new spectator environment revealing how the activation energy changes with spectator identity and proximity.

We discuss the importance of the results for our understanding of thin film deposition and related fields such as heterogeneous catalysis. We also look forward to the prospects for efficient and systematic computation of complex surfaces.


2:45pm AF1-MoA6 An Immiscible Fluids Approach for Correctly Predicting Agglomerate Dynamics during Particle Atomic Layer Deposition (Particle ALD), Julia Hartig, A. Weimer, University of Colorado - Boulder

Particle agglomeration can significantly impact performance of fluidized bed reactors when running particle atomic layer deposition (Particle ALD). The fine powders frequently used in Particle ALD tend to agglomerate due to large interparticle forces, blocking surface sites and inhibiting surface coating uniformity. By modeling the agglomeration process during coating, steps can be taken to facilitate agglomerate breakup and mixing, thereby enhancing surface coating uniformity. However, current models of gas-solid flows which preserve the gas-solid interface, an important component for modeling ALD, have several limitations when incorporating agglomeration. Many of these approaches fail to address agglomerate size distributions or the dynamic formation and breakup process of fluidized agglomerates, shortcomings which remain a significant challenge to studying fluidized bed Particle ALD. In this work, we propose an alternative modeling approach which naturally accounts for the dynamic nature of fluidized agglomerates by treating the fluidizing gas and particles as two immiscible (non-interpenetrating) fluids. Agglomerates are modeled using dynamic “bubbles” whose interior consists of many primary particles from the solids phase. The position, shape and formation/breakup of these agglomerate “bubbles” are allowed to change with time as dictated by the corresponding transport equations. With this model, we can investigate the formation and breakup of agglomerates without prior knowledge of the agglomerate size characteristics. This study provides some preliminary agglomerate size distribution results from fluidized bed Particle ALD simulations and compares these results to experimental data from previous literature studies.

3:00pm AF1-MoA7 The Time-Resolved Interface between ALD and CVD, Henrik Pedersen, Linköping University, Sweden

INVITED

ALD (atomic layer deposition) is possibly the most important evolution of CVD (chemical vapor deposition). To a first approximation, ALD can be described as CVD where the precursor flows are separated in time. In other words, ALD is a time-resolved form of CVD. Despite this, CVD typically has a negative connotation in the ALD community. The phrase “CVD-component” is used to point to a process deviating from the idealized ALD behavior, where continual growth occurs.

The time-resolved precursor supply in ALD enables the self-limiting surface chemistry, rendering the very high degree of surface control which is the hallmark of ALD. However, CVD does not need to be time-resolved to have a very high degree of surface control. There are several examples in the literature of continuous CVD filling deep trench structures. A time-resolved precursor supply is a self-limiting surface chemistry is another important evolution of CVD as it can be used for growing semiconducting nanowires on a patterned surface without the need for a catalyst and can afford deposition of ternary or quaternary materials in some materials systems.

CVD can also be made time-resolved by controlling the amount of energy available to the process over time. While this is difficult to do with a thermally activated CVD process, a process driven by the energy provided...
in a plasma discharge can easily be time-resolved in energy. This has allowed self-limiting processes with constant flow of precursors and an enhanced ability to use ionic species for film deposition.

This talk will discuss the time-resolved interface between CVD and ALD but also how continuous CVD can outcompete time-resolved CVD for some films: a recent example is nearly conformal B-C films in a 2000:1 structure by continuous CVD at 700 °C and 5 kPa. The talk will also seek to nuance the view of a “CVD-component” in ALD processes and discuss how the time component can be used as a process knob in ALD.

References:

ALD Fundamentals
Grand Ballroom E-G - Session AF2-MoA

ALD Precursors I
Moderators: Daniel Alvarez, RASIRC, Charles H. Winter, Wayne State University

1:30pm AF2-MoA1 The Materials Supplier Challenge: Flawless Execution from Precursor Design to High Volume Manufacturing, Madhukar B. Rao, Versum Materials

INVITED
Advancements in scaling and architecture in logic and memory devices are driving the development of new precursors which provide more precise control of film thickness, composition, morphology and electrical properties. The challenge for materials suppliers is to design new precursors that can meet the performance requirements, and scale-up the precursors to high volume, while meeting the cost of ownership targets. At Versum Materials, the process starts with defining technical requirements of the precursor through close collaboration with the customer and equipment vendor. We use our in-depth understanding of the structure-property relationships between precursor and final film to identify and synthesize promising new precursors on the laboratory scale and rapidly test new precursors using our in-house deposition capabilities to confirm the film performance. These results are validated with our collaboration partners and this defines the potential candidates for further scale-up.

Converting promising laboratory discoveries into viable commercial products is a complex and resource-intensive effort. The product development work must scale up and validate a low-cost synthetic route and purification methods, identify and quantify EH&S risks (e.g., toxicity, stability, reactivity), develop analytical methods to fingerprint incoming raw materials and ensure final product quality, design and validate suitable containers for delivery, ensure supplier quality and supply-chain readiness and prepare for container life-cycle management. This presentation highlights the key steps and technical challenges in the product development process and highlights the importance of close collaboration with customers, suppliers, and equipment manufacturers to make new products HVM ready.

2:00pm AF2-MoA3 Precursor and Co-Reagent Selection: A Figure of Merit, Séan Barry, M. Griffiths, Carleton University, Canada

Developing novel precursors for atomic layer deposition (ALD) processes is a complicated task: the selected chemical compounds must be volatile and thermally stable, yet reactive with a surface, and perhaps even demonstrate selective reactivity among several different surfaces. Additionally, it is helpful if the precursors are liquid (for handling and to improve the kinetics of evaporation) and robust to a change in the chemical environment.

To initially study a compound for potential use as a precursor, one must understand both the volatility and thermal stability. We have recently established a Figure of Merit (FoM) for potential precursor compounds based on volatility and decomposition. Conceptually, this FoM alters the ratio in temperature between a judiciously chosen onset of decomposition and onset of thermal decomposition modifies that with respect to the residual mass left behind in a standard thermogravimetric ramp experiment. In this way, the larger the value for the FoM, the better the precursor, with negative values representing compounds that decompose before acceptable volatility is achieved.

Selection of the onset of volatility and decomposition, as well as the construction of this Figure of Merit will be examined with respect to potential precursors for transition metals (Ni, Co, W, Mo, Au, Ag, Cu) as well as main group metals (Al, Ga, In, Sn, Pb) that are presently being developed in our group.

2:15pm AF2-MoA4 Designing Thermal Atomic Layer Deposition Processes for Gold Metal using New Organogold Precursors and Co-reactants, Matthew Griffiths, G. Bačić, A. Varga, S. Barry, Carleton University, Canada

Gold nanoparticles have been studied extensively by virtue of their plasmonic properties and their ability to act as photocatalysts for CO2 reduction and hydrogenation. In 2016, our group showed that (PMe3)AuMe3 would deposit gold nanoparticles by atomic layer deposition (ALD) using oxygen plasma and water as co-reactants. Recently, Van Dale et al. showed that the same compound could deposit gold with hydrogen plasma as a co-reactant at temperatures as low as 50 °C. The development of a process that uses thermal co-reactants is ongoing in our laboratory in order to circumvent the use of harsh co-reactants.

Bimolecular reductive coupling is believed to catalyze the on-surface decomposition of (PMe3)AuMe3 on Au. Thus, increasing the steric bulk of the alkyl ligand should increase the activation energy of this process and produce a surface species that resists decomposition to metallic gold. We synthesized a series of (PMe3)AuR compounds (R = Me, CH3SiMe3, CH(SiMe3)2, and (SiMe3)3) with a stepwise increase in steric bulk. We then developed a screening process to test their ability to form self-limiting surface monolayers with an in situ quartz crystal microbalance (QCM). At equal vapour pressures and equal deposition temperatures, the rate of CVD decreased with increasing steric bulk, but was never fully prevented.

A-heterocyclic carbenes (NHCs) are ubiquitous ligands in modern chemistry, and they also form robust self-assembled monolayers on gold. We envisioned a second strategy where an NH ligand bound to Au(l) in the general formula (NHC)AuCl could play the role of the self-limiting ligand in an ALD process. All that would be needed is a co-reactant which could remove the NHC from the metallic gold surface to complete the cycle. A series of alkylgold(l) NHCs were synthesized and tested with a focus on small alkyl groups and stable, sterically unhindered NHCs to facilitate efficient packing on the surface. Using our QCM methodology, we compared the various compounds for their ability to form self-limiting monolayers, and we analyzed the gas-phase products of the ALD reactions using in situ quadrupole mass-spectrometry (QMS).

Finally, exploration of a third strategy was initiated by our discovery that a thermally stable A-heterocyclic silylene (NHSi) reacted with our previously reported and stubbornly inert gold ALD precursor (PMe3)AuMe3. We identified a highly reactive silylgold(l) silylene species by solution-phase NMR spectroscopy and set out to develop an ALD process using these two compounds. The surface chemistry was studied using our combined QCM and QMS methodology, and the final film properties were evaluated ex-situ by 4-point probe, XPS, and XRD.

2:30pm AF2-MoAS A New Carbene Based Silver Precursor Applied in APP-ALD Yielding Conductive and Transparent Ag Films: A Promising Precursor Class for Ag Metal ALD, Nils Boysen, Ruhr University Bochum, Germany; T. Hasselmann, D. Theirich, T. Riedl, University of Wuppertal, Germany; A. Devi, Ruhr University Bochum, Germany

The realization of transparent electrodes for solar cells and light-emitting devices based on metals like silver still remains a challenge due to a preferred Volmer-Weber growth mode in the initial stages of thin film growth. This results in a typically observed metal island formation with a high sheet resistance (Rsh) at a low film thickness. Atomic layer deposition (ALD) can be the method of choice to effectively lower the percolation threshold and to afford electrically conductive but at the same time optically transparent silver thin films. While the influence of different reducing agents in thermally- and plasma-activated silver ALD processes was studied in the past, the employment of different silver precursors and their influence on the growth behavior and percolation threshold of silver
thin films was not coherently studied before due to the limited number of volatile and thermally stable silver precursors. To overcome this issue and to set a starting point for further comprehensive studies, we herein report the synthesis and evaluation of a new fluoro-, oxygen- and phosphorous-free volatile N-heterocyclic carbene (NHC)-based silver precursor.[1] The successful synthesis of the new NHC-based silver amide compound 1,3-diphenyl-imidazolin-2-ylidene bis(trimethylsilylamide) [(NHC)Ag(hmds)] was confirmed via 1H- and 13C-NMR spectroscopy, elemental analysis and EI-MS, while the thermal characteristics of the compound were determined via thermogravimetric and isothermal thermogravimetric analysis. Subsequently, the volatile silver precursor [(NHC)Ag(hmds)] was employed in spatial atmospheric plasma-enhanced ALD (APP-ALD) yielding high purity conductive silver thin films at temperatures as low as 100 °C and with a low resistivity of 10^8 Wcm utilizing an Ar/H2 plasma. The growth characteristics were investigated, and the resulting thin films were analysed via SEM, XPS, optical transmittance (UV-Vis) and RBS. Compared to a nominally identical process employing the commercially available silver precursor [Ag(fod)(PEt3)], [(NHC)Ag(hmds)] was able to considerably enhance the growth rate and prohibit unwanted contaminants like fluorne, oxygen and phosphorous. This renders the new precursor as a promising alternative to the currently established [Ag(fod)(PEt3)]. The current study marks the first example of a carbene stabilized Ag complex that was successfully employed for ALD applications of Ag metal layers. In addition, these promising results create a basis for the development of new metal ALD precursors as there is only a very limited number of ALD precursors known, especially for silver metal ALD.

2:45pm AF2-MoA6 Transition Metal β-ketoiminates: A Promising Precursor Class for Atomic Layer Deposition of Binary and Ternary Oxide Thin Films, Dennis Zytwitzki, A. Devi, Ruhr University Bochum, Germany

Due to their abundance in the earth’s crust and promising characteristics in (photo-) electrocatalysis and energy storage devices, binary and ternary oxide films of first row transition metals such as Fe, Co, Ni, Zn have gained increasing attention in recent years. ALD is a promising technique for such applications, as it guarantees excellent interface quality to the underlying substrate and enables the conformal coating of large and nanostructured surfaces. Precursors for these metals however remain limited especially for water assisted processes. While ALD processes for ZnO are dominated by the pyrophoric alkyl compounds such as diethyl zinc, few other precursors were reported thus far. On the other hand, for Fe, Co and Ni, metal cyclopentadienyls and β-diketones, which require strong oxidizing agents like ozone, have often been used. Water assisted process were realized by utilizing the amidinate ligand system for Fe, Co and Ni. In order to find a compromise between the stable but less reactive metal β-diketones and the highly reactive metal β-ketimines, metal β-ketoiminates have been found to be a promising precursor class, which can easily be tuned in terms of volatility and reactivity by employing different substitutions at the imino moiety.

A series of new β-ketoiminato precursors, suitable for ALD have been developed for transition metals. As representative examples, Fe, Co, Ni and Zn β-ketoiminates have been synthesized in good yields and were thoroughly characterized with regard to their purity, composition and molecular structure by NMR spectroscopy, elemental analysis, EI-MS and single crystal XRD. The spectroscopic data and monomeric compounds were reactive toward water. Their volatility and decomposition behavior was evaluated by thermal analysis and were found suitable for ALD. The introduction of etheric sidechains led to lower melting points, ensuring a steady evaporation rate. Subsequently, water assisted ALD processes with Fe and Zn β-ketoiminato precursors were developed. The typical ALD characteristics were confirmed in terms of ALD window, saturation and thickness dependence. Lastly, the resulting films were analyzed for their structure, morphology, composition and the optical properties were investigated.

With the successful synthesis and characterization of transition metal β-ketoiminates, the library of potential precursors for first row transition metals was expanded. As representative examples, the successful development of water assisted ALD processes for iron and zinc oxide is demonstrated. The similarity in the physico-chemical properties of these precursors is an advantage to grow ternary metal oxides.

3:00pm AF2-MoA7 A New and Promising ALD Process for Molybdenum Oxide Thin Films: From Process Development to Hydrogen Gas Sensing Applications, Jan-Lucas Wree, Ruhr University Bochum, Germany; M. Mattinen, University of Helsinki, Finland; E. Ciftyürek, K.D. Schierbaum, Heinrich Heine University Düsseldorf, Germany; M. Ritała, M. Leskela, University of Helsinki, Finland; A. Devi, Ruhr University Bochum, Germany

The oxides of molybdenum are well known for their versatile properties and therefore serve as excellent materials for a wide range of applications like photocatalysis, optoelectronics, and gas sensors for a variety of gas species. Molybdenum oxide can occur in several oxidation states that exhibit very different properties. The different oxides can be distinguished by their crystalline structures as well as by their mechanical and electrical properties. While the different crystalline phases of MoO3 (α, β, h) are semiconducting with wide band gaps between 2.7 eV and 3.5 eV, the less common suboxides such as Mo2O5 exhibit higher electrical conductivity and the dioxide MoO2 is even known as pure metallic conductor.[1] Recent studies have shown that α-MoO3 is a promising material for gas sensing applications owing to its high activity towards gases such as ammonia, nitrogen dioxide and hydrogen at moderate temperatures.[2] Although various oxides of Mo have been tested for the sensing of hydrogen, which is an important source for an energy, the suboxides of Mo are not well explored for hydrogen sensing.

In this study, we have investigated the feasibility of using the bis(tertbutylimido)bis(N,N'-disopropyl-acetamidinate) compound of molybdenum [Mo(NBu2)(dpamdi)] as a potential precursor for atomic layer deposition (ALD) of MoOx films. In the first part of the study, the focus was to optimize a new ALD process using this precursor together with ozone as the oxygen source. The phase and composition of the layers could be tuned by varying the process parameters which resulted in amorphous (≤250 °C), crystalline suboxide (275 °C), a mixture of suboxide and α-MoO3 (300 °C), or pure α-MoO3 (≥325 °C) films. The evaluation of the layers using synchrotron-based surface enhanced photoemission spectroscopy revealed a high amount of oxygen vacancies on the surface of MoOx suboxide films deposited at 275 °C, which is relevant for sensing applications. Owing to the high oxygen content that could be achieved, the second part of this study focused on evaluating the electrical properties of the MoOx layers. The temperature dependent resistivity of the MoOx films suggested them to be suitable for gas sensing applications. In this context, a simple hydrogen gas sensor device was built using 50 nm suboxide MoOx films which showed reversible and fast response to hydrogen gas at low temperatures.[3] The results derived from this study are very encouraging and form a solid foundation for in-depth studies on tuning the crystallinity of the suboxides for applications beyond gas sensing such as catalysis and energy storage.

3:15pm AF2-MoA8 Atomic Layer Deposition of Gallium Oxide Thin Films using Pentamethylcyclopentadienyl Gallium and Combinations of H2O and O2 Plasma, Fumikazu Mizutani, S. Higashi, Kojundo Chemical Laboratory Co., Ltd., Japan; M. Inoue, T. Nabatame, National Institute for Materials Science, Japan

Pentamethylcyclopentadienyln gallium (GaCp*) was synthesized as a new precursor for atomic layer deposition of Ga2O3 thin films. GaCp* has higher vapor pressure compared with ethylcyclopentadienyl indium (InEtCp), which we reported previously [1, 2]. GaCp* is a cyclopentadienyl compound having a pentahapto half-sandwich structure as well as the InEtCp. Therefore, GaCp* thin films could be deposited in a similar way. In this paper, we investigated the role of the combinations of oxidant gases, H2O followed by O2 (plasma) with O2 (with) and solely O2 plasma (pO2) on deposition mechanism of Ga2O3 films by the ALD process with GaCp* precursor.

During WpO process at 200 °C, linear growth with no nucleation delay and with a growth rate (GPC) of approximately 0.06 nm/cycle was observed, when 0.1 s GaCp*, 3 s H2O, and 50 s O2 plasma pulse times were applied. For the WpO process, a self-limiting surface reaction occurred when an GaCp* pulse time of 0.1-0.3 s, a H2O pulse time of 1-5 s and an O2 plasma pulse time of 40-90 s were applied at 200 °C. At this time, with a short O2 plasma pulse time of less than 40 s, the oxidation reaction insufficiently carried out and resulted in thinner Ga2O3 films.

To understand the role of the surface oxidation step in the ALD process on the GPC, GPCs at 200 °C for WpO process with shorter O2 plasma pulse time of 14 s (0.1 s GaCp* and 3 s H2O) and WO process (0.1 s GaCp*, 3 s H2O, and 50 s O2) were examined. The GPC for the WO and for the pO2 process were 0.04 nm/cycle and 0.003 nm/cycle, respectively. If the O2 plasma pulse time is shortened for WpO process, the GPC becomes slightly
smaller. On the other hand, GPC becomes negligibly small without plasma (WO).

Next, the role of the H2O step on the GPC was investigated. The GPC at 200 °C for PO process (0.1 s GaCp* and 50 s O2 plasma) was 0.05 nm/cycle, indicating that the oxidation is insufficient compared with WpO process. The Ga2O3 films by plasma-enhanced ALD using a new GaCp* precursor was demonstrated. Based on these experimental data, note that the Ga2O3 surface oxidation step is found to be extremely important.

References

ALD Fundamentals
Grand Ballroom E-G - Session AF3-MoA

Growth and Characterization I

Moderators: Somilkumar Rath, Eugenius, Inc., Sumit Agarwal, Colorado School of Mines

4:00pm AF3-MoA11 Understanding Elementary Steps of ALD on Oxidation Catalysts, Kristian Kneemeier, M. Piernavieja Hermito, R. Naumann d’Alincourt, Technische Universität Berlin, Germany; A. Trunschke, R. Schlagl, Fritz Haber Institute of the Max Planck Society, Germany; M. Driess, Technische Universität Berlin, Germany; F. Rosowski, BASF SE, Germany

Since the invention in the 1970s, Atomic layer deposition (ALD) has been extensively studied. Over the course of 40 years, its benefits for the microelectronic industry have been spread to numerous different fields such as medicine, batteries and catalysts[1]. Despite being applied and investigated for such a long time the deposition mechanism is barely understood. Typically, ALD is applied by performing hundreds of cycles to grow layers in the range from nanometers to micrometers and most of the times the first cycles show different growth behavior than the following ones. The first cycles might not be of interest for depositing films but they are crucial for us, as our aim in catalyst synthesis and modification is a film thickness in the nm range which is achieved with only few cycles.

We focused on understanding the first cycles of ALD on vanadium pentoxide as oxidation catalyst. Phosphorous oxide ALD on V2O5 was conducted with two different precursors (P3+ and P5+) and then compared to the highly investigated mechanism of TMA/H2O. ALD was performed in a magnetic suspension balance to track the mass gain in situ[2]. Surface species were analyzed not only by 31P-NMR but also by in-situ DRIFTS measurements of the second half cycle. XPS was conducted to determine oxidation states of bulk and surface species after each half cycle. STEM-EDX shows highly distributed P on the surface and no additional phases were found. With the combination of these analytics we will show that the ALD mechanism depends heavily on the substrate and that ALD on oxidation catalysts is clearly different than on typical catalyst supports, such as SiO2 or Al2O3.


4:15pm AF3-MoA12 Advanced Lateral High Aspect Ratio Test Structures for Conformality Characterization by Optical Microscopy, Oili Ylivaara, P. Hyytinne, VTT Technical Research Centre of Finland Ltd, Finland; K. Arts, Eindhoven University of Technology, Netherlands; F. Gao, VTT Technical Research Centre of Finland Ltd, Finland; W.M.M. Kessels, Eindhoven University of Technology, Netherlands; R. Puurunen, Aalto University, Finland; M. Utriainen, VTT Technical Research Centre of Finland Ltd, Finland

Atomic Layer Deposition (ALD) is a key technology in 3D microelectronics enabling conformal coatings into deep microscopic trenches and high aspect ratio cavities. However, conformality characterization in 3D trench walls is challenging and requires sample preparation. The MEMS-based all-silicon Lateral High Aspect Ratio (LHAR) test structure, developed at VTT, named PillarHall™ [1-3], provides a fast and accurate substrate and characterization concept for the thin film conformality analysis [4,5]. The most important outcome from the PillarHall™ characterization is the film saturation profile, which provides valuable data for reaction kinetics modelling and quantifying conformality. Since the LHAR enables utilization of planar metrology instruments, multiple approaches are compatible.

In this study, we focus on characterization methods suitable to extract the saturation profile and show the advantage of simple optical microscopy image analysis. Studied material was prototypical ALD Al2O3 (40-50 nm thick layers) made in two separate research facilities. The study consisted of SEM/EDX planar view, micro-spot reflectometry and ellipsometry and optical microscopy image analyses. These experiments were carried out by two research labs and supported by leading edge optical metrology tool vendors, Semilab Ltd, JA Woollam and Filmetrics.

We also introduce advanced LHAR 4th generation design, which enables characterization of the penetration depth profile with distinct advantages. Namely, the pillar design enables employment of optical line scanners up to 50 µm spot sizes. Furthermore, internal distance indicators support positioning the characterization tools more accurately. These features are illustrated in Supplementary Material Fig S1.

The results show that the gray-scale optical microscopy image analysis with the thickness determination in opening area gives similar results as the reflectometry or ellipsometry line scans, within the accuracy limits. Optical thickness/A of the film is a limitation for the image analysis, but designing the experiments properly, the grayscale optical micrograph can be a powerful, widely compatible and easy method for conformality analysis.

Support from Semilab Ltd is gratefully acknowledged.

References

4:30pm AF3-MoA13 Dopant Concentration Analysis of ALD Thin Films in 3D Structures by Tof-SIMS, A.M. Kia, Wenke Weinreich, Fraunhofer-Institut fur Photonische Mikrosysteme (IPMS), Germany; M. Utriainen, VTT Technical Research Centre of Finland Ltd, Finland; R. Puurunen, Aalto University, Finland; N. Haufe, Fraunhofer-Institut fur Photonische Mikrosysteme (IPMS), Germany

Self-limiting nature of atomic layer deposition (ALD) proposes a unique deposition mechanism which can produce extremely good step coverage within high aspect ratio (HAR) structures. This layer-by-layer deposition method also provides fine control on different features of deposition techniques such as controlling the dopant distribution in the direction of growth.

The quantity of dopant per layer is controlled, by applying saturation coverage delivering adequate dose rate for each precursor/reactant mixture. There are different parameters that contribute to control the dopant concentration in both 2D and 3D structures. To understand the reasons and characterize the precursors’ behavior in deep trench structures, we used dynamic SIMS. Time of flight secondary ion mass spectrometry (ToF-SIMS) is a well-known method due to high detection sensitivity for the measurement of concentration levels of the dopant materials. Nevertheless, due to the geometry of the vertical HAR structures, it is challenging to characterize samples by ToF-SIMS. The absence of a simple and immediately available 3D structure for analyzing thin films produced by ALD has led most studies being made on flat surfaces.

A potential approach to circumvent the challenges is a MEMS-based all-silicon lateral high aspect ratio (LHAR) test structure, PillarHall™ developed at VTT[1-2]. After removal of the top membrane (Fig.a-c) the LHAR test chip enables utilization planar characterization tools to examine the properties of deposited thin film on the 3D trench wall. This study focuses on semiquantitative characterization of different doping concentrations of La-doped HfOx with using LHAR. The LHAR Test Chips (LHAR3-series, AR2:1-10000:1, 500nm gap height) were used on carrier wafers in a 12 in wafer ALD process (Jusung Eureka 3000).

The findings show that the main difficulties with respect to the geometry for elemental analysis in non-planar structures can be resolved with LHAR. In particular, with the power of ToF-SIMS in data imaging (Fig.d) and integrating of data point from interested area (Fig.e), we are able to quantify doping profile along with understanding the properties of the trench wall in depth penetration.
E. Solano, conductivity (resistivity of Ru ~ 7.4 μΩ.cm) and high work function (4.7 eV). For various applications, such as metal-insulator-metal capacitors (MIMCAP), diffusion barriers, and electrodes for dynamic random access memory (DRAM), due to its good thermal and chemical stability, high conductivity (resistivity of Ru ~ 7.4 μΩ.cm) and high work function (4.7 eV).

Most of the ALD Ru films reported were deposited by the oxidants such as O₂ and O₃, and the main mechanism of Ru deposition was combustion reactions by the oxidant. So, Ru oxide phases were unintentionally formed under overexposure condition of oxidant. In this study, we used H₂O as a reactant to deposit metallic Ru film by ALD. We proposed an abnormal reaction mechanism between H₂O and the new beta-diketonate Ru precursors (5-methyl-2,4-hexanediketonato) Ru(II), Carish, Cu₂H₂O₄Ru) led to the formation of Ru metallic film without the appearance of oxide phase under overexposure condition of the reactant. The formation of metallic Ru film by H₂O was analyzed with experimental and theoretical approaches, including the X-ray photoelectron spectroscopy (XPS), transmission electron microscopy (TEM) and Density functional theory (DFT). Also, the cyclic voltammetry (CV) testing was performed on ALD Ru on SiO₂ powders.

We show how the monolayer surface sensitivity of LEIS enables the precise quantification of the element composition of the first atomic layer energy spectrum of noble gas ions scattered from the sample surface is recorded. The evaluation of elemental peaks in the resulting spectra allows the quantification of the elemental composition of the first atomic layer. This extreme surface sensitivity of just a single atomic layer, combined with composition analysis, is unique to LEIS and makes it especially useful in the study of nanoscale systems. In addition, sub-surface scattering signal from deeper layers gives information about sample composition and layer thickness up to depths of 10 nm.

We show how the monolayer surface sensitivity of LEIS enables the precise determination of the areal density of the deposited nanoparticles and the particle surface coverage of sub-monolayer Al₂O₃ shells. Furthermore, cracking of the shells by annealing has been observed. By measuring layer thickness values, average particle sizes are determined, which give insight into coarsening processes. The thickness of Al₂O₃ shells can be determined precisely over a wide range of values, including ultra-thin sub-monolayer shells after just five cycles of Al₂O₃ deposition.

The results demonstrate that the effectiveness of the Al₂O₃ shell depends on the process conditions during the deposition of the Pt nanoparticles. MeCpPdMe₂ was used as a precursor, with either O₂ or N₂ plasma as reactants. In the former case, a sub-monolayer Al₂O₃ shell can completely prevent particle coarsening. In the latter case, the N₂ plasma based Pt process results in a denser collection of smaller Pt nanoparticles and stabilization with an Al₂O₃ overcoat is proven to be more difficult.

REFERENCES
[2] Puurunen et al., AF-SuA15, ALD 2017 Denver,USA.


In three-dimensional memory integration schemes, like those used for current NAND flash memory technologies, the active layers of the memory device are typically filled into vias with aspect ratios of 4:1 or greater. It is important for the deposited films to demonstrate consistent properties all the way through the depth of the via. Recently, novel ALD chalcogenide materials have emerged [1-3] that could be used as phase-change memory (PCM) and on-chip switch technologies (OTS) selectors. ALD chalcogenides are attractive because they could be compatible with 3D integration schemes; however, the properties of these films in high-aspect ratio structures have not been extensively investigated.

In this study, we use PillarHall® Lateral High Aspect Ratio (LHAR) test chips [4-6] to elucidate the properties of ALD chalcogenides on a trench wall using standard in-plane metrology techniques without fabricating full device stacks. The PillarHall all-silicon LHAR test chip includes multiple trenches in the aspect ratio range 2:1 - 10000:1 with constant 500 nm gap height [6]. LHAR chips are used as substrates for ALD binary and ternary chalcogenide films using H₂Ge(O)₆, (CH₃)₂Si(Ch₃)₂Se, (CH₃)₂Si(Ch₃)₂Te, and (C₅H₉O)₆Te as precursors. Using optical microscopy, scanning electron microscopy with energy-dispersive x-ray spectroscopy, and scanning-probe techniques, we describe the chemical, physical, mechanical, and electrical properties of these films. We show that the thickness and atomic composition of certain chalcogenide films changes dramatically inside of high-aspect ratio features [Fig. S1]. Furthermore, we perform optical profilometry on silicon micro-membranes on the PillarHall test chips (Fig. S2) to rapidly estimate the ALD film stress on the microscopic level, which is not directly measurable in devices today despite its importance in 3D architectures. We use these results to comment on the ALD reaction kinetics and discuss implications for future research on ALD chalcogenide films.

Combining high-aspect ratio and stress measurements on a single test chip can accelerate R&D of ALD chalcogenides for applications in PCM and OTS as well as other microscopic 3D applications of ALD thin films.

References

5:30pm AF3-MoaA17 The Tailoring of the Single Metal Atom-Oxide Interface, Bin Zhang, Y. Qin, Institute of Coal Chemistry, Chinese Academy of Sciences, China

The metal-oxide interface plays important roles in the metal-based heterogeneous catalyst. By sample tailoring the types of interface, size and crystal structure of metal and oxides, etc, the catalytic performance of the catalyst changes dramatically. Thus, the precisely tailoring the metal-oxide interface in atomic scale is a key and most important strategy to design a selective metal-based catalyst. Atomic layer deposition (ALD) is a promising and controllable approach to precisely design and tailor the metal-oxide interface because of its atom-level thickness control, excellent uniformity and conformality and good repeatability in film or particle deposition. Recently, we have developed new strategies for the tailoring of the interface structure by building a serial of nanostructures, such as the core-shell structures, inverse oxide/metal structure, porous sandwich structure, multiple confined metal nanoparticles in oxide nanotubes, and tube-in-tube structure with multiple metal-oxide interfaces. In many cases, the metal-oxide interface forms at the cost of metal surface sites through ALD overcoating or modification. In order to increase the ratio of metal-oxide interface and utilization of metal, the building of single metal atom-oxide interface with high loading of metal is a good but challenge strategy since the unstability of single atoms. We have realized this in many ways, such as developing new ALD deposition approaches, depositing oxide site in advance, and changing the deposition dynamic conditions etc.
TiO₂ and Pt-CeO₂ single metal atom-oxide interface showed high catalytic performance in selective hydrogenation with high efficiency.

**References**


**ALD Fundamentals**

**Grand Ballroom H-K - Session AF4-MoA**

**Growth Mechanisms II**

Moderators: Viljami Pore, ASM, Mikko Ritala, University of Helsinki

4:00pm **AF4-MoA11 Monolithic Integration of Single Crystal Perovskites on Semiconductors with ALD, John Ekerdt**, University of Texas at Austin

**INVITED**

The semiconductor industry faces new challenges in the sub-10 nm era as scaling will no longer dominate performance improvement. New materials provide opportunity to improve performance with minimal architectural overhead. For example, high-mobility channels of Ge and III-V semiconductors can provide both lower power consumption and faster computing speeds. In certain applications significant advantages are gained by monolithic integration of the oxides directly on the substrates that will host other devices/components. Perovskite oxides offer a wide range of properties from high-k to multiferroic affording the device designer a suite of possibilities and are particularly important due to their common structure and lattice-matching with common semiconductors.

Here, we report the fabrication of monolithically integrated, single crystal, metal-ferroelectric-semiconductor structures. This talk demonstrates the possibilities through the monolithic integration of perovskite oxides on Si(001) for applications in silicon nanophotonic devices and low-power transistors. Barium titanate (BTO) films, and BTO/La₀.₅Sr₀.₅TiO₃ (x ≤ 0.15) perovskite heterostructures are grown on strontium titanate (STO)-buffered Si(001) using atomic layer deposition at 225 °C. Film strain and c-axis orientation are manipulated by growth and annealing conditions. Piezoresistive force microscopy (PFM), electrical and electro-optic measurements establish BTO film ferroelectric (FE) behavior at the µm-scale. The La₀.₅Sr₀.₅TiO₃ (x ≤ 0.15) perovskite heterostructures sandwiched between Si(001) and BTO permits examination of a quantum metal between Si and a FE film.

It is possible to grow crystalline perovskites directly on Ge(001) by ALD and we have used this to deposit STO, BTO, SrHfO₃, Sr(HfO₂)₀.₅Sr₂O₃, and SrSnO₃ directly on Ge(001). We will also present the growth and properties of these perovskites layers directly on Ge(001) and will discuss the how the interface chemistry and structure control the interfacial reactions that allow for crystalline film formation during ALD, and how they affect film properties.

4:30pm **AF4-MoA13 - Introducing the Concept of Pulsed Vapor-Phase Copper-Free Surface-Click Chemistry using the ALD Technique, Ivo Saric, R. Blažek**, University of Rijeka, Croatia; C. Roger, Materials Physics Center (CSIC-UPV/EHU), Spain; M. Iljin, Donostia International Physics Center (DIPC), Spain; M. Knez, CIC nanoGUNE, Spain; G. Ambrozic, University of Rijeka, Croatia

While ALD allows deposition of a broad variety of inorganic materials, MLD typically relies on very few basic organic reactivity concepts and therefore is not yet as versatile as it could or should be. Given the great promise of ALD/MLD, it is highly demanded to extend the choice of available chemistries, providing a greater choice of suitable organic precursors. The idea behind our work is to extend the range of possible surface chemical reactions by introducing click chemistry as an additional option into the organic chemical vapor phase deposition concept. Click chemistry, initially developed for drug delivery, has recently gained increasing attention in surface-pattern with important applications in biotechnology and in development of nanomaterials. Here we report for the first time on a model gas-phase copper-free azide-alkyne click reaction performed in an ALD instrumentation [1]. The newly developed process is based on in-situ two-step pulsed vapor-phase sequence consisting of initial exposure of ZnO to propionic acid as the first precursor, followed by gas-phase click-chemistry coupling of benzyl azide as the second precursor. The organic phase compositions were analyzed by XPS and FTIR, while the preservation of ZnO surface morphology was investigated by SEM and STEM. When compared to known state of the art ex-situ gas phase click reactions [2,3], the present MLD/ALD processing conditions ensure reproducibility and improve the time and surface coverage efficiency. The resulting hybrid material exhibits no surface contaminations with physiosorbed organic precursors and/or by-products deriving from organic precursor degradation. This study offers great potential toward the development and fabrication of complex functional organic layers on metal oxide surfaces by selective azide-alkyne cycloadditions performed in an ALD/MLD instrument and broadens the variation range of applicable chemistry in MLD. Variation of the functionalities of the organic precursors will allow MLD type of polymer growth based on click chemistry and add degrees of freedom for the design of functional polymeric coatings.

(HFO$_2$) and zirconium oxyfluoride (ZrO$_2$F$_2$). Techniques were developed to obtain tunable stoichiometry of the metal oxyfluoride films.

The metal oxyfluoride ALD films were deposited at 150°C. H$_2$O and HF-pyridine were used as the oxygen and fluorine sources. Al(CH$_3$)$_3$ was used as the Al source and Hf and Zr amides precursors were used as the Hf and Zr metal sources. The metal oxyfluorides were deposited using either (1) the halide-exchange method (see Supplemental Figure 1) or (2) the nano-laminate method (see Supplemental Figure 2). Both methods were evaluated using in situ quartz crystal microbalance (QCM) measurements and ex situ X-ray photoelectron spectroscopy (XPS) analysis.

The halide-exchange method is based on the facile exchange of oxygen by fluorine from HF. HF exposures after deposition of the metal oxide easily replaced oxygen with fluorine. In addition, the fluorene also diffused into the underlying metal oxide film. The oxygen/fluorine exchange and fluorine diffusion complicates the control of the stoichiometry of the metal oxyfluoride film.

Compositional control was achieved by the halide-exchange mechanism using either metal oxide layers with various thicknesses or different HF pressures. The stoichiometry could also be tuned using the nano-laminate methods with different numbers of metal oxide ALD and metal fluoride ALD cycles. These two methods gave rise to tunable stoichiometry from pristine metal oxide to adjustable oxyfluoride to pristine metal fluoride.

5:15pm AF4-MoA16 Fundamental Study on the SiO$_2$ Growth Mechanism of Electronenegativity Difference of Metal-O in the High-k Underlayers by PE-ALD Method, Erika Maeda, Shibaura Institute of Technology, Japan; T. Nabatame, National Institute for Materials Science, Japan; M. Hirose, Shibaura Institute of Technology, Japan; H. Kiyono, Shibaura Institute of Technology, Japan

To fabricate silicate films such as HfSiO$_x$ and AlSiO$_x$ as gate insulator of GaN; M. Takahashi, K. Ito, Institute for Materials Science, Japan Shibaura Institute of Technology, Japan

Tris(dimethylamino)silane (TDMAS) precursor and O$_2$ plasma gas, and we T. Nabatame, SiO$_2$ growth mechanism, we should pay attention to the difference of (0.036 nm/cycle) < Al$_2$O$_3$ (0.090) < TiO$_2$ (0.11) < HfO$_2$ (0.13). Here, we pay films were varied on Metal-O by changing ALD cycles during PEALD at 300 °C. These two methods gave rise to tunable stoichiometry from pristine metal oxide to adjustable oxyfluoride to pristine metal fluoride.

5:30pm AF4-MoA17 Low Temperature Aluminium Nitride Deposition: Comparing Hydrazine and Ammonia, Aswin L.N. Kundosamy, S.M. Hwang, A.T. Lucero, Z. Qin, X. Meng, The University of Texas at Dallas; D. Alvarez, J. Spiegelman, RASIRC; J. Kim, The University of Texas at Dallas

Aluminium nitride is a wide bandgap material having high thermal conductivity [1]. Depositing thin films of high thermal conductivity such as Aluminium nitride as a capping layer or a passivation layer by a CMOS compatible method is a viable approach to tackle the heat management issue that arises with scaling down of devices. Compatibility demands lower deposition temperature (<300 °C) and improved conformality over high-aspect ratio structures. AlN, ALD using low reactive NH$_3$ results in incomplete reaction below 300 °C [2], resulting in carbon and hydrogen impurities and Plasma enhanced ALD (PEALD) frequently exhibits poor conformality. Thermal ALD (t-ALD) with a more reactive nitrogen precursor such as hydrazine is expected to overcome these problems. Newly available ultra-high purity hydrazide sources have been successfully used to deposit metal nitrides at low temperature [3]. In this work we study the low temperature t-ALD growth characteristics of aluminium nitride using hydrazide and trimethylaluminium (TMA) and evaluate the properties of the films. t-ALD results with hydrazide will be compared to films grown by t-ALD with NH$_3$ and PEALD with NH$_3$, plasma, all using the same ALD reactor in the same temperature range.

AlN films were deposited using a custom-made ALD reactor from 175-350 °C. Hydrazide is supplied from a BRUTE hydrazide source. Growth with hydrazide shows saturation behavior, with growth per cycle (GPC) saturating at hydrazide exposure as low as 0.1 s ("10$^4$L). High GPC of 2.8-3.2 Å/cycle is observed at 300 °C with refractive index of 1.890 whereas t-ALD with NH$_3$ shows lower GPC (1.1 Å/cycle) for similar exposure, which is expected due to superior reactivity of hydrazide. AlN growth using hydrazide shows high temperature dependence in the range 175-300 °C. X-ray photoelectron spectroscopy is used to confirm film stoichiometry; films with low carbon (1%) impurities can be achieved. Films deposited below 250 °C get oxidized easily under air due to low film density. A novel densification method is proposed to obtain denser films at these temperatures to overcome this problem. The denser films are expected to have higher thermal conductivity. The detailed experimental results will be presented.

J. Szornel, demanding atomic scale process controllability to further decrease critical Single digit nanometer semiconductor manufacturing is increasingly demanding atomic scale process controllability to further decrease critical dimensions and pitches. High etching precision and material selectivity become essential in the atomic scale era. Plasma based atomic layer etching (ALE) shows promise to attain atomic etch precision, enhancing energy control and reaction chemistry control. Here we study a Fluorocarbon-based process for controlling the etching of silicon dioxide at the atomic level. Figure 1 shows the schematic of atomic layer etching process using Ar plasma and CHF$_3$ gas. In this technique, the Ar plasma is maintained continuously through the process, below the energy threshold for SiO$_2$ sputtering. A fluorocarbon chemistry is then introduced via CHF$_3$ pulsing to provide the reactant absorption. Subsequently, once the gas pulse has concluded, bias power is introduced to the Ar plasma, to provide enough energy to initiate reaction of the FC with the SiO$_2$. In ideal ALE, each of the steps is fully self-limiting for over exposure to increase uniformity on the microscale (wafer) and atomic scale. With the goal of achieving self-limiting FC-based ALE, we investigated theetch step using low energy Ar ion bombardment. By carefully tailoring the energy of ion bombardment, it is possible to control the etching depth to approach a self-limiting behavior. The impact of various process parameters on the etch performance is established. We demonstrated that the SiO$_2$ amount etched per cycle (EPC) is strongly affected by the forward bias plasma power, as well as the substrate temperature (Figure 1(a)). The substrate temperature has been shown to play an especially significant role, at -10 °C the contributions of chemical etching coming from fluorine and fluorocarbon compounds on the chamber walls are minimized and a quasi-self-limiting behavior ALE is observed. Figure 1(b) showed the Cr features after being etched for 60 ALE cycles with the optimal ALE self-limiting conditions. Feature trenches vary from 20-200 nm and were defined using metal lift-off. Overall, using the cyclic CHF$_3$/Ar plasma at -10 °C, we reduced geometric loading effects during etching and reached aspect ratio independent etching, with great potential for significant improvement in future etching performances. The impact of continuous-wave plasmas in realizing a pattern transfer process with a Ar/fluorocarbon composition on photoresist etching behavior and surface roughness development has been extensively studied. However, the characteristics of photoresists under atomic layer etching (ALE) processes have not been well established. Specifically, the structure and morphology of the photoresist layer is dependent on the interplay between energetic ion bombardment and the diffusion of reactive species at the surface. For evaluating these photoresist properties, we used an ALE process with an Ar carrier gas and a fluorocarbon (FC) precursor gas, for example C$_4$F$_8$. For sample characterization, we utilized a combination of real-time, in situ ellipsometry and post-process surface roughness and surface chemistry analysis using atomic force microscopy (AFM) and x-ray photoelectron spectroscopy (XPS). Based on the ellipsometric characterization, we find that the 193 nm photoresist initially develops a surface dense amorphous carbon (DAC) layer from Ar ion bombardment of both the native photoresist and deposited FC, which contributes additional carbon to the DAC layer, increasing its thickness. Upon the FC deposition step in the ALE process, the refractive index of the DAC layer decreases due to fluorine diffusing into the layer structure. Corresponding AFM analysis shows a reduction in both the surface roughness magnitudes and the surface roughness. Once the DAC layer becomes saturated with fluorine, a discrete FC layer forms on the surface. Subsequently, in the etching step, the discrete FC layer is removed, the DAC layer recovers its thickness, and the cycle repeats. The authors gratefully acknowledge Eike Beyer for assistance with the experimental setup, R. L. Bruce, S. Engelmann, and E. A. Joseph for supplying the EUV materials, and financial support of this work by the National Science Foundation (NSF-DMR-1449309) and Semiconductor Research Corporation (2017-NN-2726).
The experiments were carried out in an inductively coupled plasma reactor. To follow the layer thickness evolution of the central sample, the other samples were characterized ex-situ after the experiment. Surface smoothing effect was observed after the etch process with the novel gas molecule. Because of these advantages, the proposed novel hydrofluorocarbon etch gas is a very promising candidate for spacer patterning, to enable further CD and pitch downscaling of the CMOS device.

3:30pm ALE1-MoA8 Atomic Layer Etching of Silicon Nitride with Ultrahigh Etching Selectivity over Silicon and Oxide Materials by Utilizing Novel Etch Gas Molecule, Xiangyu Guo, American Air Liquide; N. Stafford, Air Liquide; V. Pallem, American Air Liquide

Silicon nitride etching with high selectivity over silicon and silicon oxide material, without or with minimal damage to the exposed surfaces, is one of the most critical processes in the fabrication of complementary metal-oxide-semiconductor (CMOS) devices. In this work, the authors propose a novel hydrofluorocarbon etch gas molecule for Si3N4 etching with ultrahigh etching selectivity over Si materials (p-Si, SiO2, SiON, SiCN, etc.) based on atomic layer etching (ALE) cyclic process. Each cycle of the ALE process consists of two independent unit process reactions: step A - polymer deposition and step B - removal step. The process was conducted in a home-built capacitively coupled plasma (CCP) chamber and was optimized on planar thin films first. CH3F was used as the process baseline. The authors show that novel gas molecule demonstrates significant improved performance in several aspects comparing to CH3F - ultrahigh selectivity, minimal damage, smoother surface after etching, higher ALE synergy, etc. The new molecule was also evaluated on patterned structure - Si3N4 gate spacer. The authors demonstrate the ALE process utilizing proposed novel hydrofluorocarbon molecule outperforms typical spacer process, in particular, with better etch profile control - the spacer footing can be reduced more than 70%, and with minimal nitride sidewall thinning. The authors also show that due to the ultrahigh etch selectivity, damages to Si substrate was minimized, as evidenced by further surface elements characterization - no formation of Si-C/SiO. Surface smoothing effect was also observed after the etch process with the novel gas molecule. Because of these advantages, the proposed novel hydrofluorocarbon etch gas is a very promising candidate for spacer patterning, to enable further CD and pitch downscaling of the CMOS device.

3:15pm ALE1-MoA7 Atomic Layer Etching of Silicon Nitride with Ultrahigh Etching Selectivity over Silicon and Oxide Materials by Utilizing Novel Etch Gas Molecule, Xiangyu Guo, American Air Liquide; N. Stafford, Air Liquide; V. Pallem, American Air Liquide

The authors gratefully thank S. Tahara for his helpful discussions.


Atomic Layer Etching
Regency Ballroom A-C - Session ALE2-MoA
ALE of Compound Semiconductors
Moderators: David Boris, U.S. Naval Research Laboratory, Ishi Yohei, Hitachi High Technologies

4:00pm ALE2-MoA11 Developments of Atomic Layer Etch Processes and their Applications in Fabricating III-V Compound Semiconductor Devices, Xu Li, Y.-C. Fu, S.-I. Cho, D. Hemakumara, K. Floros, D. Moran, I. Thyney, University of Glasgow, UK

In recent years, atomic layer etch (ALE) to precisely remove very thin layers of materials using sequential self-limiting reactions has attracted extensive attention in semiconductor processing. Our work has indicated that ALE processes have versatile potential in the fabrication of III-V compound semiconductor devices, a number of which will be discussed in this presentation. One example is the use of an ALE process for precise control of the threshold voltage of GaN-based power transistors. This enables both normally off and normally on devices to be realised on the same wafer, which is a candidate for the realisation of an integrated cascode transistor (Fig 2). Another application example is the realisation of III-As and III-Sb nanowires and finfets for low power logic applications using a lateral ALE process to minimize the wire diameter and fin width. A further example is using a lateral ALE process to selectively etch gate metal stacks to form nanometer scale T-gates required for low noise for RF devices (Fig 3). This has been achieved using Si industry compatible subtractive processes and without the need for complicated resist stacks.

In our ALE processes, Cl2, HBr, and SF6 have been used as the reactive gases for surface modification, with the details depending on the etched materials and target applications. The etching chemistries are based on the formation of self-limited Ga, In, Al, and Sb halides in the case of III-V materials or Mo, W and Pt in the case of T-gate metal stacks. The modified surfaces are then removed using an Ar plasma formed with optimized RF and/or ICP power. The impact of all ALE process parameters on etch induced electrical damage has been an important aspect of our work (Fig 4)

To gain insight into the etching mechanisms, in-situ surface analyses have been carried out using Auger spectroscopy and XPS techniques. The ALE processes and surface analyses which will be described in this presentation are carried out in a cluster tool from Oxford Instrument Plasma Technology, which includes an ICP etching chamber with repeat loop function and a Scienta Omicron NanoSAM surface analysis tool with Auger spectrometer and XPS (Fig 1). The clustered arrangement enables samples to be subjected to plasma processing and then transferred, under vacuum, into the analysis chamber. This flexibility enables each step of the ALE cycle to be evaluated (Figs S&6).

4:30pm ALE2-MoA13 GaN and Ga2O3 Thermal Atomic Layer Etching Using Sequential Surface Reactions, N. Johnson, Y. Lee, Steven M. George, University of Colorado - Boulder

Atomic layer etching (ALE) of GaN and Ga2O3 is important for the fabrication of power electronics devices. Thermal ALE of GaN and Ga2O3 was performed using sequential, self-limiting surface reactions. The thermal ALE was accomplished using fluorination and ligand-exchange reactions. XeF2 and HF were used as the fluorination reactants. BCl3 was the main metal precursor for ligand-exchange. Ga2O3 was also etched using AICl3, AICl5, AlCl3, TiCl4 or Ga(N(CH3)2)3 as the metal precursors for ligand-exchange.

Crystalline GaN samples prepared using MOCVD techniques were etched with sequential XeF2 and BCl3 exposures. GaN etch rates varied from 0.18 to 0.72 Å/cycle at temperatures from 170 to 300°C, respectively (see Supplemental Figure 1). Because the GaN etch rates were self-limiting versus BCl3 exposure and BCl3 pressure, the GaN etching mechanism is believed to involve XeF2 fluorination of GaN to GaF3 and then ligand-exchange between BCl3 and GaF3 to yield volatile BCl3F3 and GaF3Cl3 species. GaN fluorination using a NF3 plasma was also successful for etching crystalline GaN at 250°C.
Ga$_2$O$_3$ samples deposited using ALD techniques were etched with sequential HF and BCl$_3$ exposures. Ga$_2$O$_3$ etch rates varied from 0.59 to 1.35 Å/cycle at temperatures from 150 to 200°C, respectively. The Ga$_2$O$_3$ etch rates were self-limiting versus HF and BCl$_3$ exposure. Ga$_2$O$_3$ ALE was also performed using HF for fluorination and a variety of metal precursors for ligand-exchange. Ga$_2$O$_3$ etch rates at 250°C were 0.2, 0.8, 1.1 and 1.2 Å/cycle for Ga(N(CH$_3$)$_2$)$_3$, TiCl$_4$, Al(CH$_3$)$_3$ and AlCl(Ch$_3$)$_3$; as the metal precursor was varied, respectively (see Supplemental Figure 1). The wide range of metal precursors that can etch Ga$_2$O$_3$ argue that the ligand-exchange reaction with GaF$_3$ is facile.

4:45pm ALE2-MoA14 Selective GaN Etching Process using Self-limiting Cyclic Approach for Power Device Applications, Frédéric Le Roux, N. Posseme, P. Burtin, S. Barlona, A. Torres, Univ. Grenoble Alpes, CEAX LETI, France

Formation of the two-dimensional electron gas (2DEG) in AlGaN/GaN heterostructures is the key-point for successful development of GaN-based power-electronics such as High Electron Mobility Transistors (HEMT) and diodes. Plasma-etching steps are considered as critical in fabrication for such devices. Indeed standard chlorine plasma$^3$ can lead to surface roughness degradation$^2$ and surface state modifications (non-stoichiometric layers, surface potential modifications and dangling bonds)$^3$.

This is why Atomic Layer Etching (ALE) and Digital Etching (DE) are developed to limit the material degradations and to have a better etch depth control$^4$. The aim of this study is first to evaluate a self-limited GaN etching process using DE for power devices. This DE consists in two steps. First an O$_2$ plasma oxidizes the GaN surface. Then, the oxidized layer is removed using BCl$_3$ plasma selectively to the non-oxidized GaN.

Experiments have been carried out on 200mm wafer using the following stack: GaN (80 or 20nm)/Al$_{0.22}$Ga$_{0.78}$N (24nm)/AlN (<1nm)/GaN (1.8um)/buffer layers/Si substrate.

The development and optimization of the DE process will be presented. The etch mechanism of the self-limited process has first been understood thanks to XPS analyses performed on blanket wafers. It will be demonstrated that the O$_2$ plasma oxidizes the surface until a saturation level, which enable the self-limitation. Then the BCl$_3$ plasma removes the oxidized film selectively to the non-oxidized GaN film. This selectivity has been explained by the deposition of BCl$_3$ layer on non-oxidized GaN. Small amount of boron oxide by-products is also detected at the surface after the DE.

Then DE O$_2$/BCl$_3$ cyclic process has been compared to standard chlorine based plasma. It will be shown that the roughness and the uniformity are similar for both processes, while the cyclic process present better performances in term of electrical and material degradation. The benefit of the self-limited GaN etching process has finally been validated on patterned wafers for power device integration.

In the second part of this study, the first results of a Cl$_2$/Ar ALE process for GaN etching will be presented and compared to the DE O$_2$/BCl$_3$ cyclic process.


5:00pm ALE2-MoA15 ALE of GaN (0001) by Sequential Oxidation and H$_2$/N$_2$ Plasma, Kevin Hatch, D. Messina, H. Fu, K. Fu, X. Wang, M. Hao, Y. Zhao, R. Nemorch, Arizona State University

Atomic layer etching of GaN may be used to reduce the high surface defect concentrations produced during inductively coupled plasma (ICP) etching and other processing methods. We have demonstrated a new method for plasma enhanced atomic layer etching (PEATLE) of GaN (0001) using sequential surface modification by remote O$_2$ plasma, followed by removal of the surface oxide through H$_2$/N$_2$ plasma etching. The efficacy of etching the surface oxide via H$_2$/N$_2$ plasma exposure was confirmed by deposition and removal of several nm of plasma enhanced atomic layer deposited (PEALD) Ga$_2$O$_3$ epilayers on GaN. The composition of the H$_2$/N$_2$ plasma was investigated, and a H$_2$/N$_2$ volumetric flow ratio of 2:1 was found to produce sufficient etch rates at 500°C. Anetch per cycle (PEC) of 2 nm was achieved and is attributed to the oxidation rate of GaN. This PEATE process was performed on “as-grown” unintentionally doped GaN (UIG-GaN) deposited on a GaN substrate by metalorganic chemical vapor deposition (MOCVD), which also underwent Ar/Cl$_2$/BCl$_3$ ICP etching prior to the PEATE process. Application of several PEATE cycles resulted in improved surface stoichiometry, which was attributed to removal of Ga-rich layers created during ICP etching. After the PEATE process the N:Ga ratio increased from 0.5 to 0.8, and the surface roughness improved from $R_{max}$ = 0.3 nm to $R_{ms}$ < 0.2 nm, as measured by AFM. This ALE process has been performed on ICP-etched samples prior to research and the XPS characteristics have been measured, showing improved voltage breakdown observed.

Research supported by the ARPA-E PNDIODES program through grant DE-AR0001691.

5:15pm ALE2-MoA16 Comparative Study of Two Atomic Layer Etching Processes for GaN, Cédric Mannequin, C. You, University of Tsukuba, Japan; G. Jacobin, T. Chevolleau, C. Durand, University Grenoble-Alpes, France; C. Vallée, LTM-UGA, France; C. Dussarot, T. Teramoto, Air Liquide Laboratories, Japan; H. Mariette, University Grenoble-Alpes, France; K. Akimoto, M. Sasaki, University of Tsukuba, Japan; E. Gheeraert, University Grenoble-Alpes, France

Drastic reduction of defect density after etching in nitride semiconductor-based devices becomes a pressing requirement to improve further device performance. Defects introduced by etching process during the formation of the recess gate at AlGaN/GaN or during the fabrication process of GaN displays based on µ-Light Emission Diodes are the main sources issues of devices reliability degradation. Atomic Layer Etching (ALE) processes relying on two or more separated half reactions: adsorption step and activation step are of great interests for solving these issues.

In this work, we propose a comparative study of two ALE processes for undoped c-oriented Ga-polar GaN, relying both on Cl$_2$-based plasma for the absorption step but using different gases for the activation step. The two ALE processes were developed in an Inductively Coupled Plasma etcher (RIE-200ip from SAMCO). In-situ Optical Emission Spectroscopy (OES) was used to monitor gas dissociation for the adsorption, activation and purge steps, allowing identification of active species. Additionally, OES monitoring were used to calibrate Cl$_2$ dosing time and purging time to ensure complete separation of the Cl$_2$ dissociation by-products and the gas used for the activation step. The ICP source power ($RF_{source}$) and pressure for the adsorption step were varied in the 5—120 W range and 0.65—2 Pa range, respectively. For set adsorption step conditions, the self-bias ($V_{DC}$) of the activation step was varied in the range of 11—40 V by changing the ICP Bias power ($RF_{bias}$). For each condition, the Etching Rate Per Cycle (ERC) was estimated from the etched depth of GaN submitted to 200 ALE cycles using Scanning Electron Microscopy images and reported as a function of $V_{DC}$ (from the activation step).

In the case of the first activation gas, we report an ALE mode with an ERC of 0.276 nm, corresponding to 1.3 monolayer (ML) of GaN wurtzite structure in the c-direction. For this first activation gas, a constant ERC were observed for $V_{DC}$ in the 15—17 V range consistent with ALE process. For $V_{DC}$ > 17 V, the ERC rapidly increases for $V_{DC}$ > 17 V. For the second activation gas, we report an ALE mode presenting an ERC of 0.567 nm corresponding to 2 ML. A constant ERC for $V_{DC}$ in the 16—22 V range were observed. From Atomic Force Microscopy observations of 500 x 500 nm$^2$, we report significant decrease of the RMS roughness from 0.18 nm for as-deposited GaN surface to 0.07 nm after ALE processing.

Finally, we will discuss and tentatively propose mechanisms to explain the significant differences observed between our two ALE approaches.

5:30pm ALE2-MoA17 Chlorinated Surface Layer of GaN in Quasi Atomic Layer Etching of Cyclic Processes of Chlorine Adsorption and Ion Irradiation, Masaki Hasegawa, T. Tsutsumi, Nagoya University, Japan; A. Tanide, SCREEN Holdings Co., Ltd.; H. Kondo, M. Sekine, K. Ishikawa, M. Hori, Nagoya University, Japan

In fabrication of the next-generation power electronic devices of gallium nitride (GaN), an atomic layer etching (ALE) technique with cyclic processes of ion irradiation and Cl adsorption steps has been attracted for reduction of plasma induced damage. To control the ALE of GaN, we have studied the chlorinated surface layer of GaN at each Ar and Cl reaction step using the beam experiments with in situ X-ray photoelectron spectroscopy (XPS).

Samples were GaN films grown on sapphire substrate by Hydride Vapor Phase Epitaxy (HVPE) method. Prior to the beam experiments, native oxide on GaN surface was removed by wet cleaning (5% HF) and Ar ion sputter. The as-cleaned surface was exposed by Cl radicals with a dosage of 10$^{13}$ cm$^{-2}$ generated in Cl$_2$ gas (flow rate 0.5 sccm) plasma by application of RF power of 400 W. Next, Ar ions with a dosage of 10$^{16}$ cm$^{-2}$ and the
accelerating voltage of 100 V or 200 V. The one cycle consisted of these Ar ion irradiation and Cl radical exposure. To stabilize the GaN surface, five cyclic processes were carried out. Then, the GaN surface at each step was analyzed by angle-resolved XPS with take-off-angles of 20, 30, 40, 60, and 90 degrees with respect to the wafer plane. Depth profiles were analyzed by the maximum entropy method.

The Ar ion bombardments change the GaN surface to Ga-rich. Subsequently, as the ion-bombarded Ga-rich surface exposes to the Cl adsorption step, the surface stoichiometry recovers to high N/Ga ratio, resulting to form Ga chlorides as a volatile. The depth profiles obtained from XPS data after the 7th Cl radical exposure were compared with the different Ar ion energies. In the depth profiles of Cl concentration after Cl radical exposure after irradiation with 100-eV-ion (a) and 200-eV-ion (b), the Cl amount and penetration with a depth of approximately 2 nm during the Cl radical exposure were in details observed quantitatively. In the Ar ion bombardments, the formation of non-bonded Ga (dangling bond) and disordered structure was dominated by the ion energies. The resultant etching depth per cycle and the surface stoichiometry were depended on the non-bonded Ga amounts that resulted to desorb Ga chlorides during the Cl radical exposure. This indicates that the surface chlorination layer determined the ALE-properties of real layer-by-layer etching and self-limiting reaction. Not only the ion energy but also the chlorination layer depths should be taken account for the ALE cyclic processes.

ALD Fundamentals
Evergreen Ballroom & Foyer - Session AF1-MoP
Precursor Synthesis and Process Development Poster Session


The lower resistivity WL (Word Line) material is very attractive to the 3DNAND device makers, because they could reduce the cell stack height while maintaining the device speed. Current POR material of 3DNAND WL is tungsten made by tungsten hexafluoride ALD. However, it is well-known that fluorine results in fatal defects in the device critical layer. Fluorine free tungsten precursors such as tungsten pentachloride has been evaluated recently worldwide not only for 3DNAND application but also other memory and logic devices application. Molybdenum is considered as an attractive WL material for next generation 3DNAND devices. Molybdenum has almost same level of low bulk resistivity comparing to tungsten, but it has smaller EMFP (Electron Mean Free Path), so the effective resistivity, a product of bulk resistivity and EMFP, is expected to be lower compare to tungsten for films less than 10nm. Molybdenum chlorides are considered as potential precursors for deposition of molybdenum films from fluorine free precursors.

Here, we report thermal ALD of molybdenum films on PVD titanium nitride substrates up to 500°C from heated solid high-purity molybdenum pentachloride precursor. Hydrogen was used as a reactant gas under cyclic CVD and ALD conditions. Thickness of molybdenum and titanium nitride films was measured with XRF. Sheet resistance of molybdenum films was measured using 4-point probe technique. The films have been also characterized with TEM and XPS for conformality at aspect ratio 15 trench size, traditional metallization materials (e.g., Cu, Al) begin to fail. When microelectronic interconnects – the wiring of integrated circuits – become smaller than 10 nm, the resistivity of the material increases due to electromigration of the metal atoms within the interconnect. Promising metals to replace copper are molybdenum, osmium, iridium, ruthenium, rhodium, and tungsten, because they all have high melting temperature and relatively low bulk resistivities (~4-10 μΩcm), leading to lower electromigration.

AF1-MoP4 Atomic Layer Deposition of Lanthanum Oxide Using Heteroleptic La Precursors, Daeyeon Kim, J. Lee, W. Noh, Air Liquide Laboratories Korea, South Korea

Rare earth-based oxides are of interest for their potential application in future logic and memory technologies, and lanthanum oxide (La2O3) is a well-known high-k material for metal gate transistors and a dopant for high-k materials. In past studies, heteroleptic precursors which have alkycyclopentadényl and amide ligands, La(RCp)(R’-amd), have been developed to aim to be liquid and to enhance volatility and thermal stability. In this work, three heteroleptic precursors, La(MeCp)(ip- amd), La(EtCp)(ip-amd), and La(PrCp)(ip-amd), were synthesized, and their physical properties were compared. La(EtCp)(ip-amd) and La(PrCp)(ip-amd) were liquid at RT, and very thermally stable. ALD evaluation of La(EtCp)(ip-amd), which is more promising than La(PrCp)(ip-amd) in terms of the vapor pressure and the viscosity, was performed with O3 and H2O as a co-reactant. Both processes had two plateaus in the ALD windows which were at low and high temperature, respectively. The desired ALD window will be the plateau at higher temperature (>350 °C), because of low C impurity. The plateau at lower temperature might be useful for another processes. Carbon impurity at the low temperature was drastically decreased below detection limit, after post annealing in N2 atmosphere. In case of oxygen process, the cubic phase was observed at 400 °C while all films with water process showed amorphous phase even at 400 °C.

AF1-MoP3 Atomic Layer Deposition of Lanthanum Oxide Using Heteroleptic La Precursors, Michael Land, Carleton University, Canada; K. Robertson, Saint Mary's University, Canada; S. Barry, Carleton University, Canada

To keep pace with “Moore’s Law” (i.e., the number of transistors in an integrated circuit doubles every 18 months), the size regime of high-performance transistors has now shrunken to <10 nm. With this decrease of size, traditional metallization materials (e.g., Cu, Al) begin to fail. When microelectronic interconnects – the wiring of integrated circuits – become smaller than 10 nm, the resistivity of the material increases due to electromigration of the metal atoms within the interconnect. Promising metals to replace copper are molybdenum, osmium, iridium, ruthenium, rhodium, and tungsten, because they all have high melting temperature and relatively low bulk resistivities (~4-10 μΩcm), leading to lower electromigration.

A method of choice that can be used for the preparation of these small interconnects is atomic layer deposition (ALD). The goal of this project is to develop a chemical precursor compound for the ALD of molybdenum metal. To date, there has only been one reported ALD process for molybdenum metal, however that process utilized harsh co-reagents, and the resulting films had high resistivities. We have chosen the known bis(tert-butylimido)molybdenum(VI) dichloride as a synthetic starting material, and it has been derivatized with various neutral coordinating ligands, such as ethers, phosphines, amines, and carbenes. The ligands were found to have varying effects on the thermal stability of the precursors (up to 300 °C for the 2,2'-bipyridine adduct), which sometimes came at the cost of poor volatility. However, complexes incorporating less Lewis basic ligands, such as the 1,2-dimethoxyethane adduct, was found to have a large thermal range, with an onset of volatilization of 80 °C and thermal decomposition at 180 °C.

These compounds have been characterized in the condensed state, using traditional spectroscopic techniques, and their solid-state structures have been determined using single crystal X-ray diffraction. Their mechanisms of volatilization will also be proposed, based on results from thermal gravimetric analysis (TGA), differential scanning calorimetry (DSC), and the resulting sublimation products. Finally, the thermal stabilities of these compounds have been studied using DSC and thermolysis in flame sealed N2 tubes, and non-volatile decomposition products were characterized using a scanning electron microscope (SEM) with energy-dispersive X-ray spectroscopy (EDS). From these results, mechanisms of thermal decomposition will also be proposed, including methods to prevent low temperature decomposition pathways and furnish viable vapour deposition precursors.
Atomic layer deposition (ALD) has gained significant attention from the research community and industry due to the distinct advantages in terms of precursor and film properties of the ALD HfO thin films were analyzed with considerable S-deficiency but can be crystallized as WS₂ films with in the film significantly as confirmed by the X-ray photoelectron spectroscopy. Further characterizations of the as-deposited and annealed films are performed using several other spectroscopic measurements like Raman, Rutherford backscattering, and UV-vis spectroscopy. The current study thus establishes a new and efficient route to obtain WS₂ thin films which could find several potential applications in future.

Acknowledgements
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Atomic layer deposition (ALD) has gained significant attention from the research community and industry due to the distinct advantages in terms of uniform and conformal coating with precisely tunable stoichiometry and thin film thickness. Since ALD is a chemical vapor phase technique, one of the important parameters governing the process is the precursor employed, which most often is in the form of a metal organic complex. The precursor must be volatile and at the same time it must possess a certain thermal stability to avoid decomposition. Furthermore, due to the surface driven reactions the precursor has to be reactive toward the reactive surface sites and in the second reaction step toward co-reactants to achieve a self-limiting behavior to obtain the desired material. However, the library of precursors for various material systems is not very large and for certain metals there are limited precursors commercially available.

This prompts researchers to develop new precursors or fine tune the characteristics of the already adopted precursors to improve upon the properties relevant for ALD. Over the years, our research group focused on developmental precursor chemistry spanning the periodic system and identified several ligand systems bound to the metal center that are well suited for ALD conditions. Herein, we present an overview of our research work including the synthetic strategies for various ligands, namely guanidinates, amidinates, b-ketoimines, cyclopentadienyls, diazadienes, N-heterocyclic carbones and alkyamines. Potential precursor solutions for group III, IV and V transition metals as well as lanthanides are presented employing guanidinates and amidinates among which Y, Ho, Mo, W, Gd and Er were already successfully used in ALD processes. For the fourth period transition metals ranging from Fe to Zn, employing b-ketoimines and diazadienes resulted in promising precursors. Noble metals like Cu and Ag can be deposited using N-heterocyclic carbene complexes. Precursors for main group III metals such as Al, Ga and In, were fine tuned for both, low and high temperature ALD processes employing either alkyamines, amidinates or guanidinates. Furthermore, we identified and developed ligand systems which were combined with Sn, Pb for main group IV metals and Sb for main group V, resulting in potential ALD precursors.

In this presentation, precursor systems covering a range of metals will be presented alongside representative examples for the application in ALD processes. We will also demonstrate that this large library is not only suitable for inorganic oxides, or nitrides but also compatible with organic co-reactants in ALD/MLD processes.

AF1-MoP9 Synthesis of Group VI Oxyhalide Adducts and Mo Metal Film Growth on TiN Surfaces, David Ernert, R. Wright Jr., T. Baum, Entegris, Inc. Molybdenum and tungsten metal films are being widely considered for logic and memory (DRAM/NAND) devices, a result of their low-resistivity and high melting points (low electromigration). Challenges to more widespread adoption of group VI film growth using chemical vapor deposition (CVD) and atomic layer deposition (ALD) stem, in part, from the availability of suitable metal-containing precursors. When considering materials for CVD/ALD applications, halide-saturated MX₃, species (e.g. MoCl₅, WF₅) offer suitable volatility and can deposit high-quality metal films, but may not be compatible with neighboring films within the device. For example, the resulting HCl or HF byproducts may be detrimental to diffusion barrier performance within the device.

Zero-valent metal carbonyls are logical choices for metal deposition as they display suitable vapor pressures and do not require chemical reduction during thermal decomposition on a surface. Barriers to adoption of these precursors include prohibitively high decomposition temperatures, the formation of metal carbides via incorporation of carbon in the films, and the release of toxic carbon monoxide by-products. In general, volatile organometallic precursors that can be deposited at low temperatures offer attractive alternatives for film deposition provided the deposited films are carbon-free.

Here, we describe a general approach to CVD/ALD precursor design and subsequent growth of molybdenum metal films, at moderate surface temperatures, using a molybdenum oxyhalide species and H₂ co-reactant. Group VI oxychlore adducts of the general formula MoOCI₃L₃ (where M = Mo, W with L = Lewis base adduct and n = 1, 2) are prepared and screened as potential ALD candidates. Precursor characterization and use in thermal deposition studies will be described. Deposited metal film resistivity approaching 50 μΩ-cm were observed at temperatures below 500 °C. Film composition studies, carried out by XRF spectroscopy, demonstrated a strong substrate temperature-dependence on film identity.

AF1-MoP10 Gallium Precursor Development for ALD Film Applications, Atsushi Sakurai, M. Hatase, N. Okada, A. Yamashita, ADEKA Corporation, Japan

Gallium-based films such as gallium oxide and gallium nitrile have been attracting the world’s attention of those who are looking at future power electric devices with high power, high breakdown voltage, and energy-saving benefit. Although ALD process could be useful for producing many kinds of metal oxide, nitride, carbide thin films with excellent quality and conformality, many studies have not yet been done regarding gallium precursor screening for ALD applications.
Trimethylgallium (TMG) is the well-known gallium precursor to make various kinds of Ga-based thin films such as gallium nitride and gallium arsenide. However, TMG with remote oxygen plasma ALD process still left over some carbon impurity in the gallium oxide film [1]. Furthermore, it has been pointed out that TMG has undesirable pyrophoric nature when exposed to air.

We are looking for various kinds of gallium precursors which have non-pyrophoric nature, good volatility, enough thermal stability, and high ALD reactivity to produce gallium-based thin film even with gentle ALD process conditions. Fig.1 indicates that our new precursor of GNP-7 has the highest vapor pressure of all the kinds of N-based gallium molecules. Therefore, this ALD process using GNP-7 and H₂O co-reactant produced the amorphous gallium oxide film with good ALD process window at low temperature domain (Fig.2). We are also demonstrating gallium nitride films using GNP-7 and NH₃, whose results will be shown in our presentation then.


The stack capacitor of DRAM is continuously developed by decreasing the horizontal dimension, increasing the aspect ratio, and adopting dielectric materials with higher dielectric constants (k). Zirconium oxide (ZrO₂) is a high-k material currently in use in dynamic random access memory (DRAM) devices. The deposition of high-k dielectric materials with excellent conformality and accurate thickness control is required, and the atomic layer deposition (ALD) technology is the best choice. The high-temperature ALD process is desirable for the high dielectric constant and low leakage current density of the deposited film, so the thermal stability of the precursor should be excellent. The reactivity of the precursor is an essential factor to obtain a better conformal film. Also, the precursors must have excellent reactivity for conformal deposition of the film on high-aspect-ratio patterns. A new heteroleptic zirconium precursor for ALD of ZrO₂ has been developed to meet these requirements, and the deposition process and thin film properties using this precursor were presented [1]. The result showed a wide ALD temperature window and excellent step coverage. In the present work, we present the design and optimization of the zirconium precursors by using density functional theory (DFT) calculations. We compared zirconium compounds with different numbers of triamine and dimethylamine ligands to determine the most stable structure. Then, we optimized the alkyl groups in the triamine ligands in terms of thermal stability, reactivity, and viscosity. The optimized zirconium compound with a trimine ligand showed better reactivity and stability as compared with the cyclopentadienyldimethylaminezirconium (C₅Zr[N(CH₃)₂]), which is in a good agreement with deposition experiments. DFT calculation is a powerful tool for designing new precursors for ALD process to obtain the desired thermal stability, reactivity, and viscosity.

Figure 1. Lewis base indices and zirconium charge densities of triamine-type zirconium compounds with different combinations of alkyl groups.

[1] H.-D. Lim et al., ALD 2018, AF2-TuA13

AF1-MoP12 Low Temperature Plasma-Enhanced Atomic Layer Deposition of ZnO from a New Non-Pyrophoric Zn Precursor, Lukas Mai, F. Mitschker, P. Awakowicz, A. Devi, Ruhr University Bochum, Germany

With its high transparency to visible light and tunable conductivity, zinc oxide (ZnO) is a transparent conductive oxide (TCO) and promising candidate for all-electronic applications such as thin film transistors (TFTs), solar cells or chemical sensors. Furthermore, with a direct band gap of Eₗ = 3.37 eV it can not only be used for electrical but optical applications e.g. in UV-light emitting diodes (LEDs), too. Owing to its high density, ZnO layers can be employed as protective coating as well and could serve as conductive and protective gas barrier layer (GBl) at the same time on polymers in flexible electronics. For high quality GBLs, the thin films should be very uniform, dense and conformal over the whole surface. With atomic layer deposition (ALD), it is possible to fabricate such thin films at low temperatures with a precise thickness control. For the ALD of ZnO, diethylzinc ([ZnEt₂]), DEZ is the most commonly used precursor. Despite the inherent advantages of DEZ in terms of high volatility and reactivity towards a range of co-reactants at low temperatures, there are certain issues with DEZ such as its pyrophoric behavior and not well-defined ALD window. Thus, we attempted the synthesis of an alternative Zn precursor. Here, we present the synthesis and detailed characterization of bis-3-(dimethylamino)propyl zinc, [Zn(DMAP)₂] as an alternative precursor for ALD of ZnO. As already demonstrated for aluminum precursors, the DMAP ligand stabilizes the zinc center atom by a dative bond from the amine to the metal. This yields a favored 18 electron complex, causing a thermally stable, non-pyrophoric solid compound with a melting point at only 46 °C. The thermal properties are thoroughly characterized showing a high evaporation rate at only 55 °C. Using this precursor, a new plasma enhanced (PE)ALD process employing O₂ plasma was developed. The process is self-limiting at substrate temperatures between 60 °C and 140 °C on Si[100] with growth rates of 0.44 Å cycle⁻¹ at 60 °C and 0.72 Å cycle⁻¹ at 140 °C. The resulting ZnO thin films are conformal, uniform, smooth, dense and of high purity even at low deposition temperatures and were analyzed regarding their optical and electrical properties. For the investigation of the ZnO films as GBLs, thin films of various thicknesses were deposited on PET substrates at 60 °C and the improvement of the gas barrier of the PET by a factor of 60 for a 10 nm thin film obtained by oxygen transmission rate (OTR) measurements. The thin film properties are of the same quality as for layers obtained from DEZ, rendering the new intramolecular stabilized precursor to be a promising and safe alternative for ALD of ZnO coatings.

AF1-MoP13 Homoleptic and Heteroleptic Yttrium Precursor: Tuning of Volatility, Reactivity and Stability for ALD Applications, Sebastian Markus Josef Beer, A. Devi, Ruhr University Bochum, Germany

Rare-earth (RE)-based materials in the form of thin films have gained significant attention due to their unique functional properties rendering them suitable for a broad variety of applications. Especially yttrium oxide (Y₂O₃) has been intensively studied for optics, protective coatings or high-k dielectrics. Furthermore, the ability to dope Y into other oxide material systems opens up new avenues for the development of high-performance materials as for instance yttrium doped zinc oxide (Y:ZnO), yttria stabilized zirconia (YSZ) or yttrium doped SrO. Atomic layer deposition (ALD) serves as a superior thin film processing technique enabling precise layer thickness control paired with conformal growth and uniformity fulfilling the main requirements for the fabrication of high-quality thin films. However, ALD processes strongly depend on the performance of the applied precursors. Therefore, the rational design and development of metalorganic compounds comprising optimal physico-chemical characteristics remains a key factor for ALD-based research. Over the years, various Y metalorganic precursors have been developed for ALD processes mainly focusing on homoleptic complexes such as ß-diketones [Y(thd)], silylamides [Y(tmsa)]3, amidinates [Y(dpam)], guanidinates [Y(dpdmg)] or cyclopentadienyls [Y(Cp)]. Some of these compounds have high melting points, low volatility, reactivity or thermal stability which, in most cases, can be tuned through side-chain variations of the ligand moieties.

Another promising approach is to employ mixed ligand systems to form heteroleptic substituted compounds, ideally combining the characteristics of the respective homoleptic analogues. In earlier reports, RE precursor systems with combination of ligands were demonstrated by Leskelä et al. and Lansalot-Matras et al. where liquid precursors were successfully employed for RE oxide thin films. These approaches encouraged us to design and develop new metalorganic Y complexes with advantageous physico-chemical properties such as a high volatility, reactivity and stability thus ensuring applicability in ALD processes.

In our study, we focused on the guanidinate and amidinate ligand classes which provide pronounced reactivity towards co-reactants such as water through their Y-N bonds in combination with the cyclopentadienyl ligand, possessing good thermal stability due to the formation of robust leaving groups. In the present work, we present the synthesis and detailed characterization of new, spectroscopically pure heteroleptic and monomeric yttrium cyclopentadienyl guanidinate and yttrium cyclopentadienyl amidinate precursors for ALD processes of Y-based thin film materials.

AF1-MoP14 Gallium ALD Precursor Development based on Mechanistic Study, M. Foody, Y. Zhao, Adam Hock, Illinois Institute of Technology

Low temperature deposition of Ga₂O₃ remains a challenge, particularly in the presence of energetic oxygen sources e.g. plasma or ozone. This is somewhat surprising given the close chemical relationship of aluminum to gallium. For example, trimethylaluminum is an incredibly well-behaved ALD precursor combined with a variety of oxygen sources, trimethylgallium requires the energetic reagent oxygen as an ALD partner. We have synthesized a variety of gallium precursors that span the potential chemical space for gallium, e.g. 4, 5, and 6-coordinate complexes, alkyl amide, and...
other ligands, etc. and conducted in depth mechanistic analyses of the potential ALD chemistry.

In this talk we discuss the effect of ligand coordination number, identity (N vs C, etc), and ALD partner reagent on nucleation and growth of gallium oxides. This includes QCM measurements under ALD conditions, solution model reactions, and synchrotron studies conducted at the Advanced Photon Source (APS) located at Argonne National Laboratory. The surface reaction of Ga precursors and half-reaction with oxygen sources were also observed by X-ray absorption spectroscopy (XAS). We have found that nucleation of GaOx growth can be achieved on a variety of substrates, however sustained growth of Ga2O3 requires forcing conditions for some precursors. The results of these studies were applied to improved gallium oxide processes, including doping strategies. Film characterization will also be discussed as time allows.

**AF1-MoP15 Fluorine Doping of Aluminium Oxide Through In-situ Precursor Synthesis: Theory, Design and Application. Ben Peek, University of Liverpool, UK**

Fluorine doped metal oxides are technologically important as conducting thin films, for applications in photovoltaics, flat panel displays, mem resistive devices and power semiconductors. Conventional precursor sources for F-doping involve the use of harmful or toxic reagents such as hydrofluoric acid. Use of these precursors presents challenges in terms of handling and disposal.

Here we report a novel method to synthesise a fluorine precursor, FAI(CH3)2 in-situ, using mechanisms like those found in atomic layer etching. The method involves a pre-reaction between Al(CH3)3 and AlF3 powder to generate the FAI(CH3)2 immediately before it is injected into the ALD reactor chamber. The intermediate fluoride product has been isolated and analysed using 19F NMR. The effects of key process parameters, including the Al(CH3)3 dosing and AlF3 powder bed temperature have been assessed and optimised. The design and fabrication of a system to generate the precursor is presented.

We demonstrate how the precursor has been exploited for the fluorine-doping of aluminium oxide grown by atomic layer deposition. The F-doped Al2O3 films have been characterised using low energy ion scattering as a probe of the surface and through-thickness distribution of fluorine in the doped films. This approach is used to elucidate the incorporation mechanisms and the composition of deposited materials.

This in-situ precursor generation technique, potentially opens new routes to doping of a wider range of ALD thin film materials. The full potential of the approach is discussed and other doped systems are considered.

**ALD Fundamentals**

**Evergreen Ballroom & Foyer - Session AF2-MoP**

**Precursor Selection and Growth Optimization**

**Poster Session**

**AF2-MoP1 Atomic Layer Deposition of Cyclopentadienyl Based Hf Precursor With Various Oxidants, Jooho Lee, D. Kim, W. Noh, Air Liquide Laboratories Korea, South Korea**

In electronic devices, a hafnium based oxide film has drawn a lot of attention, because it is a potential High-k material that can replace SiO2 in a conventional transistor. Recently, hafnium based oxide films can be used for other applications, such as next generation DRAM capacitors and NAND flash memories. HfC14 was one of the best precursor candidates for a HFO2 film, however, there are some issues related to corrosive halide ligands, low vapor pressure, difficulty in delivering a solid precursor. In order to solve those issues, Hf(Rcpc)(NMe3) (R = H, Me), which are chlorine free precursors, were proposed. In this work, these precursors were evaluated for physical properties and ALD processes. Both precursors showed high thermal stability and clean evaporation in TG. Hf(Cp)(NMe3)2 and Hf(MeCp)(NMe3)2, have high vapor pressure (1 Torr at 900oC) and low viscosity (9 cP at 300oC). According to ALD evaluation, both precursors obtained high ALD windows up to 360-370oC with a growth rate of 0.9-1.0 Å/cycle with ozone and a growth rate of around 0.5 Å/cycle with water. X-ray photoelectron spectroscopy (XPS) showed that deposited thin films were pure, carbon and nitrogen impurities were below the detection limit. Step coverage of the film was excellent (~100%, AR=1:40) at 360oC.

**AF2-MoP2 Atomic Layer Deposition of Magnesium Oxide Thin Films by using Bis(ethylcyclopentadienyl)Magnesium Precursor and H2O, O2 Plasma and Os Reactants, Moo-Sung Kim, S.-W. Lee, Versum Materials Korea, Republic of Korea; S. Ivanov, Versum Materials, Inc.**

Since MgO has high temperature stability, wide band gap, insulating, and diffusion barrier properties, it has been studied to use as a cathode coating layer in Li-ion battery, buffer layer for superconductors, high-k gate dielectric and ferroelectric non-volatile memory, a dopant for High K capacitors, etc.

In this work, deposition of magnesium oxide (MgO) thin films was conducted with liquid precursor Bis(ethylcyclopentadienyl) magnesium (Mg(EtCp)2) and various reactants such as H2O, O2 plasma and O3 by using atomic layer deposition (ALD) method. The MgO films were analyzed by ellipsometry, transmission electron microscopy (TEM), X-ray photoelectron spectroscopy (XPS), X-ray diffraction (XRD) and X-ray reflectivity (XRR) to compare step coverage, chemical composition, crystallite orientation as well as film density of the films deposited with three different reactants.

ALD characteristic saturation behavior was observed for H2O and O2 plasma processes between 200 and 300°C with Mg saturation pulse time 1 sec and 1.5 sec, respectively. GPC of MgO at 250°C was 1 A/cy with H2O and O2 plasma processes. In the case of O3 process, however, ALD characteristic saturation behavior was only observed above 250°C. MgO deposition rate was constant between 200°C and 300°C for O2 plasma process only. MgO deposition rate was decreased with temperature in the case H2O process, and was increased with the temperature in the case O3 process.

MgO films deposited with water thermal ALD and O2 PEALD exhibited good stoichiometric composition about MgO = 1 : 1 with low carbon content and excellent step coversages at the deposition temperatures between 200 and 300°C. MgO film density with XRR was ~3.6 g/cc at most deposition conditions. However, in O2 process at 200°C, a large amount of carbon (~13%) was detected, which also led to poor step coverage (~68%). XRR density was less than 2.5g/cc, lower than other deposition conditions. In addition, it showed no MgO XRD peak suggesting deposition of amorphous film. On the contrary, O3 process at 300°C showed sharp and strong MgO XRD peak with (200) dominant orientation, and film density was ~3.5g/cc, similar to H2O and O2 plasma processed MgO films.

In summary, we have demonstrated MgO ALD with Mg(EtCp)2 and 3 types of reactants, H2O, O2 plasma, and O3. Most conditions showed stoichiometric film composition, and good step coverage. Only O2 plasma process showed constant ALD rate between 200 and 300°C. O3 process below 250°C showed high carbon and oxygen content in the film, lower film density and poor step coverage. However, at 300°C, similar films were deposited with all three reactants.

**AF2-MoP3 Comparative Study between Cpti(O(Me)3) and Cpti(NMe3) as Atomic Layer Deposition of Titanium Oxide, Jaemin Kim, S. Kim, R. Hidayat, Y. Choi, H.-L. Kim, W.-J. Lee, Sejong University, Republic of Korea**

Titanium oxide (TiO2) and titanium-based perovskites have been attracting attention as capacitor dielectric materials for the next-generation DRAM. Atomic layer deposition (ALD) is used as a deposition method because it can prepare conformal films over high-aspect-ratio capacitor structures. Titanium precursors capable of high-temperature ALD process were studied to produce high-quality TiO2 films with excellent step coverage. The most common ALD precursors, tetrakis(dimethylamino)titanium and titanium tetraisopropoxide, showed low ALD temperatures due to their insufficient thermal stability. Heteroleptic titanium precursors having a cyclopentadienyl (Cp) ligand that binds strongly to titanium have been reported to increase the ALD process temperature [1]. There are two types of the titanium precursors with a Cp ligand: alkylamines having dimethylamino (NMe2) ligands and alkoxides having methoxy (OMe) ligands. However, no direct comparison between two types of precursors and ALD processes using them has been reported. In the present study, an alkylamine-type heteroleptic precursor, tris(dimethylamino) cyclopentadienyl titanium [Cpti(NMe3)3], and an alkoxide-type heteroleptic precursor, trimethoxy cyclopentadienyl titanium [Cpti(OMe)3]1, were comparatively studied. Ozone was used as an oxidizing agent for ALD TiO2. The saturation doses of both precursors were measured at different temperatures to determine the ALD temperature window. The results showed that Cpti(OMe)3 has better reactivity and thermal stability compared to Cpti(NMe3)3, which is explained by density functional theory calculations. Both precursors showed excellent step coverage and relatively wide bandgap at the temperature at which the thin film grows only by the ALD reaction. However, the poor step coverage and narrow bandgap were
observed at temperatures at which the CVD reaction occurred due to the thermal decomposition of the precursor. Therefore, a titanium precursor capable of a high-temperature ALD process is essential, and the alkoxide-type titanium precursor is superior to the amine-type titanium precursor.


AF2-MoP4 Tin Nitride Atomic Layer Deposition using Hydrazine, Ann Greenaway, A. Tamboli, S. Christensen, National Renewable Energy Laboratory

There is substantial lag in the development of atomic layer deposition (ALD) processes for nitrIdedecomposition to the high-quality, conformal oxides for which ALD has become the standard. A major factor in this disparity is the ready availability of highly reactive oxygen sources (mainly H2O, O2, and H2O2). High-energy nitrogen precursors are similarly required for the efficient incorporation of nitrogen in a film. Ammonia has often been used in conjunction with metal chlorides but requires relatively high temperatures for thermal ALD. Plasma-enhanced ALD can utilize molecular nitrogen as a precursor but can reduce film conformity on complex supports and damage the underlying substrate.

Hydrazine (N2H4) is an alternative precursor which has been rarely explored for the fabrication of nitrides in ALD, but which is experiencing a surge in popularity due to its high reactivity, which enables the deposition of nitrides as-yet undemonstrated by ALD. The added reactivity and volatility of liquid hydrazine may enable new reaction mechanisms, lower deposition temperatures, and conformity for high aspect ratio applications.

Sn3N4 is a metastable semiconductor which shares a crystal structure with its analog, Si3N4; unlike Si3N4, Sn3N4 has only recently been grown by ALD, despite films being substantially Sn-rich. Identification of ALD growth precursors, respectively. The Sn3N4 growing temperature is between 100 Å and the growth rate per cycle (GPC) increases and the surface roughness reduces with the temperature increasing. The GPC of Sn3N4 film increased to about 2.5 Å/cycle as the substrate temperature was decreased to 50 °C. Top-view SEM image in Fig. 2 shows uniform Sn3N4 thin films were deposited on Si wafer. Cross-section HRTEM image in Fig. 3 shows that the dense and continuous Sn3N4 thin films of 32.4 nm at very low substrate temperature (50 °C).


ALD of dielectrics requires new precursor chemistries. Development efforts have focused on new Organometallic, Organosilicon and Organoaluminum precursors. Our research focus has been on oxidents, specifically hydrogen peroxide reactivity. Due to this reactivity, hydrogen peroxide use may allow lower deposition temperatures and achieve distinct properties in the resulting film when compared to other oxidents. Our research study uses:

- Gas-phase hydrogen peroxide, delivered from an anhydrous, amouple-based formulation by use of a membrane delivery system.
- High concentration H2O2/H2O delivery by in situ concentration methods and use of a membrane vaporizer as a gas generator.

For Al2O3 ALD, initial results show that anhydrous H2O2 generates higher density films with better initial nucleation as measured by in situ XPS. The presentation will compare Al2O3 film characterization for anhydrous H2O2, H2O2/H2O mixtures and water. Data will be reported on wet etch rates, refractive index and capacitance.


Atomic Layer Deposition (ALD) of silicon oxide is commonly used in the semiconductor industry for its excellent thickness control and conformality. For some applications, films deposited at low temperatures with low wet etch rate or low dielectric constant (k) are required. Carbon doping is a known method to reduce the wet etch rate as well as the k value of the silicon oxide film. In this paper, ALD SiOxC films were studied. The impact of oxidant concentration and deposition temperature on the carbon content, WER, k value and other properties of the deposited film, with and without post deposition annealing and post deposition hydrogen plasma treatment is discussed.

In ALD conference 2017, the impact of the precursor design for the number of Si-CH3, Si-N and Si-H bonds on the reactivity, carbon content, and dHF WER of the deposited films were reported. It was demonstrated that precursors with only one Si-CH3 bond substitution, eg. di-isopropylammoniumsilane (DIPAMS), could deposit silicon oxide film with a relatively high GPC and carbon doping up to 10 at. %. In this report, a new
organosilane precursor “Precursor V” is designed and it provides higher reactivity and higher carbon content and lower WER than DIPAMS, films with up to ~20 at. % C are obtained. With thermal annealing at 600 °C, film k value reduced from ~6 to < 4, almost no etch after 10min in 0.5% dHF dip, while film carbon content showed no change, and film shrinkage was < 2%. FTIR spectra show decreased Si-OH peak, and increased Si-O-Si network peak, indicating that Si-OH to Si-OH crosslinked to form Si-O-Si linkage at 600 °C. In contrast, by annealing at 800 °C, the film carbon content is reduced significantly, from 17 at. % to 6 at. %, and the film density is increased from 1.5 g/cm³ to 2.0 g/cm³. A high shrinkage of ~25% was also observed from the 800 °C anneal, indicating a significant densification of the film with carbon removal. Direct hydrogen plasma treatment on the film was also studied. The film k value reduced from around 6 to < 4. The film develops a dense surface layer with higher WER, between 10-40 fl. However, WER of the bulk film remains unchanged compared to as-deposited film. Corresponding to this observation, the film surface carbon is reduced, but the bulk film carbon content is kept constant. FTIR shows Si-OH decrease, Si-O-Si increase, and Si-H increase, indicating crosslinking of Si-OH bonds to form Si-O-Si network and generation of Si-H bonds during H₂ plasma treatment. The hydrogen plasma treatment forms a densified SiOₓ layer with removal of carbon near surface region and protecting the bulk film from carbon depletion.


AF2-MoP9 DFT Study on Atomic Layer Deposition of Al₂O₃ with Various Oxidants, Seunggi Seo, T. Nam, Yonsei University, Republic of Korea; H.B.R. Lee, Incheon National University, Republic of Korea; B. Shang, Hongik University, Republic of Korea; H. Kim, Yonsei University, Republic of Korea

Atomic layer deposition (ALD) is a vapor phase thin film deposition technique, which enables deposition of thin films with high material quality, good uniformity, high conformity, and sub-nanometer thickness controllability. Therefore, ALD has been regarded as one of the most suitable deposition technologies for semiconductor device fabrication. Since ALD is based on sequential self-limited reactions on surfaces, understanding the surface chemical reaction mechanism is crucial for development of ALD process.

ALD of Al₂O₃ has been widely investigated owing to its wide ALD temperature window, high vapor pressure of Al precursors such as trimethylaluminum (TMA), and wide applicability of Al₂O₃. It is known that the reaction between surface adsorbed precursors and reactants, and the resulting material properties of deposited Al₂O₃ are affected by the type of the oxidant. However, relatively small research effort has been focused on the chemical reaction mechanisms of each oxidants during ALD.

In this study, we investigate the reaction mechanism of various oxidants such as H₂O, H₂O₂ and O₃ during ALD of Al₂O₃ with TMA. Density functional theory (DFT) calculations at B97D3/6-311+G* level of theory were performed using Gaussian 09 suite of programs. Our results show that the method of groups adsorbed on the surface can be oxidized into hydroxyls with all considered oxidants with ease. The number of oxidant molecules required for the reaction is one for H₂O, and two for O₃ or H₂O₂. According to the activation energy of the considered reactions, it is suggested that O₃ is the most reactive oxidant for Al₂O₃ ALD with TMA.

AF2-MoP10 Effect of Heteroleptic Structure on Atomic Layer Deposited HfO₂, Using Hf[N(CH₃)₂]₄ and CpHf[N(CH₃)₂]₃ Precursors, Sungmin Park, B.-E. Park, S. Lee, H. Yoon, Yonsei University, Republic of Korea; M.Y. Lee, S.-H. Kim, Yeungnam University, Republic of Korea; H. Kim, Yonsei University, Republic of Korea

With scaling down of complementary metal-oxide semiconductor (CMOS), atomic layer deposition of HfO₂ is a key technology for ultra-thin and high-k gate dielectrics. To obtain high-quality HfO₂ and good devices performances, various Hf precursors, such as Hf halides, alkylamides, and alkoxides, have been employed. However, these precursors have clear limitations such as low reactivity of halides and alkoxides and poor thermal stability of alkylamides. Recently, heteroleptic precursors have been investigated as alternatives to the existing homoleptic precursors. Among them, partial substitution with a cyclopentadiene (Cp)-based ligand has been reported to control volatility and thermal stability of the precursor. Despite of the promising usages, there is still lack of systematic studies on the film properties associated with growth characteristics of ALD HfO₂ using Cp-containing precursors. This could be due to the complexity of the Cp-containing precursors, which makes difficult to conduct theoretical studies to support the growth mechanism.

In this study, we investigated the effects of substituting Cp ligands for high-k properties of ALD HfO₂ by using Hf[N(CH₃)₂]₄ and CpHf[N(CH₃)₂]₃. The Cp ligand improved the thermal stability of precursor to withstand thermal decomposition up to 350 °C, but decreased the saturated GPC in the ALD window. The growth characteristics were discussed with the theoretical calculations utilizing geometrical information on the precursor and density functional theory. In addition, we analyzed the chemical composition such as Cu implantations and oxygen vacancies through XPS and the microstructure such as crystallinity, density, and interlayer through XRD, XRR and TEM. These results were comparatively studied in relation to the electrical properties of ALD HfO₂. This study can provide researchers with a broad insight to select proper precursor for the fabrication of high quality dielectric layer in future nanoscale devices.

AF2-MoP11 Effect of Co-Reactant on the Atomic Layer Deposition of Copper Oxide, Jason Avila, N. Nepal, V. Wheeler, U.S. Naval Research Laboratory

Atomic layer deposition (ALD) of copper oxide presents a powerful opportunity to grow p-type semiconductor material for a wide variety of applications such as transparent conducting oxide, solar fuels catalysis, and power devices. There are, however, very few ALD processes to facilitate the growth of copper oxide. Cu(II) bis(dimethylamino-2-propoxide) (Cudmap) has previously been used to grow copper metal using a reducing source such as tetrabutyl hydrazine. Cudmap has also been demonstrated to grow CuO using water as a co-reactant, self-reducing from Cu(II) to Cu(I) in the presence of water. This study will examine the effect of ALD co-reactants, ozone and water, on the copper oxidation state of copper oxide films grown using Cudmap.

Copper oxide films were grown in a Veeco Savannah ALD reactor using Cudmap and ozone or water at 150 °C on Si and c-plane sapphire. This is the first experimental demonstration of CuO films using Cudmap and ozone. Using ozone, a growth rate of 0.18 Å/cycle was achieved at 150 °C, far higher than the measured growth rate of 0.04 Å/cycle when growing with water. Additionally, XPS was able to confirm only the Cu(II) oxidation state with a Cu/O ratio of 1 verifying CuO films. For comparison, films grown with water show the presence of only Cu(II) oxidation state and have a nearly stoichiometric with a Cu/O ratio of 2.1. AFM also indicated uniform film growth as low as 2 nm independent of co-reactant, with CuO films grown with ozone being weaker than CuO films grown with water. Initial optical and electrical properties of the films will be examined for p-type semiconductor applications.

References


AF2-MoP12 A Systematic Study on Atomic Layer Deposition of ZrO₂ Thin Films, X. Wang, J. Cai, Xiangbo Meng, University of Arkansas

Zirconium oxide (ZrO₂) is an attractive material with many applications because of its excellent mechanical, thermal, optical, and electrical characteristics. ZrO₂ can present three crystalline structures, i.e., monoclinic (below 1170 °C), tetragonal (1170-2370 °C), and cubic (above 2370 °C). To synthesize ZrO₂ nanomaterials, there have to date many methods developed. ALD is a unique thin-film technique, featuring its tremendous capabilities for depositing conformal and uniform thin films with the atomic precisions. Using Tetraakis(dimethylamido)zirconium and water as precursors, previous studies have deposited ZrO₂ on carbon substrates in the range of 100 – 250 °C. However, these studies have not fully investigated the growth mechanism and film characteristics of the ALD ZrO₂. Applying in situ quartz crystal microbalance (QCM), in this study we optimized growth parameters and then further studied the growth characteristics in the range of 50 – 275 °C. We found that the growth rate of the ALD ZrO₂ decreases with increasing temperature in the range of 50 – 225 °C, but the growth of the ALD ZrO₂ at 250 and 275 °C terminated after the first several ten cycles. Furthermore, we applied synchrotron-based techniques to study crystallinity and film thickness of the ALD ZrO₂ deposited at different temperatures, including X-ray diffraction and X-ray reflectivity. In addition, we studied the films’ composition using X-ray photoelectron spectroscopy, observed the films’ morphology using scanning electron microscopy, and analyzed the films’ structure using transmission electron microscopy. These studies provided
us an integral understanding on the growth mechanism and films’ characteristics of ALD ZrO.


**AF2-MoP13 Hydrophobic SiO Thin Film Deposition using Low-Temperature Atomic Layer Deposition, Taewook Nam, H. Kim, Yonsei University, Republic of Korea**

A hydrophobic coating has been widely used in various applications from passivation coating on electronics to medical or even pharmaceutical devices. In many applications, organic material coatings such as fluorocarbon or hydrocarbon compounds have been used for hydrophobic coating due to their low material cost, simple coating process, and chemical stability. However, organic coatings have several disadvantages in practical applications, chiefly their inherently poor mechanical durability and thermal stability. Hydrophobicity was also found in a few inorganic materials. However, hydrophobicity using inorganic metal oxides was not retained after high-temperature annealing or UV exposure because of the generation of the surface hydroxyl group. To overcome these problems, hydrophobic coating using rare-earth oxide (REO) was reported. Although its superior thermal and chemical stability, however, REO is expensive because of its scarcity and has some deleterious effects on the human body. In addition, the relatively high process temperature is an obstacle for coating on a thermally fragile substrate, such as fabric or polymer substrate. Therefore, it is highly required to fabricate a hydrophobic surface with low cost and safety material at low temperature.

Silicon oxide (SiOx) is a well-known material in semiconductor industries. Since it can be easily formed by using vapor deposition, exhibiting good chemical, mechanical, and electrical properties, it has been greatly investigated for various applications. SiOx is inherently hydrophilic material because of the presence of silanol (Si-OH) groups on the surface. Therefore, it is hard to make a hydrophobic surface of SiOx without surface treatment or functionalization.

In this study, hydrophobic ALD SiOx was obtained at the low growth temperature without any post-treatment. The water contact angle of ALD SiOx grown at 50 °C is 94 °. However, when the growth temperature is 100 and 150 °C, the water contact angles were decreased to 74 and 53 °, respectively. This hydrophobic characteristic of ALD SiOx was retained after the annealing at 300 °C. To analyze this phenomenon, various analysis including XPS and AFM had proceeded. To obtain superhydrophobicity, ALD SiOx was coated on the silicon nanowire (SiNW) at 50 °C. On SiOx-coated SiNW, superhydrophobicity is observed for water, blood, and 10 wt% ethanol solution. Owing to its low process temperature, hydrophobic SiOx can be also coated on the thermally fragile cloth, cotton or spandex, for instance, enhancing the waterproof characteristics. The detailed experimentation and origin of hydrophobicity of low-temperature ALD SiOx will be discussed.


In recent years, technologies for stacking semiconductor devices in three dimensions have been introduced as a method for overcoming the limitations of the two-dimensional scaling of devices. Thus, there is an increasing interest in atomic layer deposition (ALD) which can deposit thin films with excellent conformity in high-aspect-ratio three-dimensional patterns. In particular, SiOx and SiN thin films used as tunneling oxide, trap layer, and blocking oxide in 3-dimensional vertical NAND devices must have excellent step coverage in channel hole as well as good physical and electrical characteristics. In the conventional ALD processes of silicon oxide, the physical and electrical properties of the deposited thin film are improved as the deposition temperature increases, however, at high temperatures above 500°C, the thermal decomposition of the Si precursor occurs, resulting in poor step coverage and film properties [1]. In the present work, we developed an ALD process using a Si precursor with excellent thermal stability, which does not cause a step coverage degradation due to thermal decomposition up to 750°C. The thermal decomposition of the Si precursor was evaluated by examining the growth rate change with the feeding time of Si precursor at 600°C or higher temperatures. The step coverage, composition, density, and leakage current of silicon oxide films deposited at different temperatures were investigated and compared with thermal oxide. The effects of the oxidizing agent on the deposition kinetics and the film properties were also investigated and discussed.


**AF2-MoP15 Developing Routes Toward Atomic-Layer Deposition of Tungsten using Fluorocine Free W Precursor and Various Reactants with Density Functional Theory, Tae Hyun Kim, D.K. Nandi, M.Y. Lee, Yeungnam University, Republic of Korea; R. Hidayat, S. Kim, W.-J. Lee, Sejong University, Republic of Korea; S. H. Kim, Yeungnam University, Republic of Korea**

The W-ALD process using WF₆ is applied to the fabrication of the nucleation layer for W-plug and W gate or bit line in the current semiconductor device manufacturing. However, the highly corrosive nature of the F containing in the precursor, damages the underlying oxide and metal film, and degrade the electrical characteristics and reliability of the device. Therefore, it is necessary to develop an ALD process with F-free W (FTW) precursor. In this study, DEAB(WCOH) is selected as a F-alt metal-organic precursor, while suitable reactants (reducing agents) among various ones, molecular H₂ plasma (which provides highly reactive H radical), trimethyl aluminum triethyl aluminum, TBF₄ (tet butyl hydradine), diethyamineborane (DEAB), dimethylamineborane (DMAB), NH₃ etc. are adopted based on the density functional theory (DFT) calculation. Following the DFT predictions, successful ALD-W films are prepared using the reducing agents diethyamineborane (DEAB) and H₂ plasma at a deposition temperature of 325°C. The growth rate observed using DEAB reactant is ~1.3 Å/cycle. On the other hand, H₂ plasma, as a reactant, offers relatively lower growth rate of ~ 0.4 Å/cycle. The crystalline and amorphous phase of the as-deposited W films are confirmed using X-ray diffraction (XRD) for H₂ plasma and DEAB, respectively. Furthermore, the XRD reveals a mix-phase of H₂ plasma and tungsten carbide (WC) for the films grown by H₂ plasma and the X-ray photoelectron spectroscopy analyses confirm considerable impurities (Boron, Carbon, Nitrogen, Oxygen) in the films grown by DEAB. However, a post annealing could further improve the properties of these films.

**AF2-MoP16 ALD HfO₂ with Anhydrous H₂O₂ in a 300 mm Cross-flow Reactor – Comparison with H₂O and O₃ Oxidants, Steven Consiglio, T. Clark, C. Wajda, G. Lesunik, TEL Technology Center, America, LLC**

HfO₂-based dielectrics deposited by ALD have been utilized in CMOS manufacturing since the 45 nm node [1]. In addition to applications of ALD HfO₂-based dielectrics in CMOS and DRAM, the recent discovery of ferroelectricity in HfO₂-based dielectrics [2] shows promise for applications in emerging non-volatile memory [3] and neuromorphic computing [4]. Thus, improving and modifying the growth of ALD HfO₂ is of significant industrial interest.

For ALD growth of HfO₂, H₂O and O₃ are the most commonly used oxidants. The drawbacks of H₂O include low oxidative reactivity and strong adsorption to surfaces in the deposition chamber which requires long purge times. Although the use of the strong oxidant O₃ in ALD typically uses reduced cycle times compared to H₂O, O₃ exposure can lead to unwanted oxidation of the underlying substrate which can significantly impact final device properties. In this regard, HfO₂, which has an oxidation potential greater than H₂O, but less than O₃, is an attractive candidate as an alternative oxidant for ALD growth of metal oxides.

In this study we evaluated a source for anhydrous H₂O₂ delivery which eliminates some of the drawbacks of H₂O₂/H₂O solutions, which have a low concentration of H₂O₂ in the vapor phase. The novel source and delivery system (RASIRC® BRUTE™ Peroxide) consists of ~ 99% H₂O₂ dissolved in > 99% H₂O₂.[5-7]

By optimizing the hardware and delivery setup to minimize vapor phase H₂O₂ decomposition and depletion effects, we were able to demonstrate uniform ALD HfO₂ growth across a 300 mm wafer in a cross-flow deposition system (RASIRC® BRUTE™ Peroxide) consists of ~ 99% H₂O₂ dissolved in > 99% H₂O₂.[5-7]
chamber. In order to compare the performance of H2O with the other commonly used oxidants, we compared ALD H2O growth with well-established processes using H2O and O2 [8]. Dose dependence of H2O was investigated to determine reactant saturation. Using a saturated H2O pulse we obtained >50% increase in growth-per-cycle compared to both H2O and O2 while also significantly improving within-wafer-uniformity. Further optimization of purge times and carrier Ar flow rate achieved a reduced cycle time for H2O process which was >50% less than the cycle time required for H2O process and approaching the optimized cycle time for the O2 process.

References
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AF2-MoP17 Atomic Layer Deposition of Copper (I) Chloride using Liquid 1-Chlorobutane Precursor, Richard Krumpolec, D. Cameron, D. Baça, J. Humliček, O. Caha, Masaryk University, Czech Republic.

Zinc blende-structure γ-copper (I) chloride is a wide, direct bandgap semiconductor with the potential for applications in UV optoelectronics. Atomic layer deposition has previously been applied to deposition of copper chloride CuCl thin films and nanocrystals [1,2]. The ALD-like process was reported using solid precursors [Bis(trimethyliyl)acetylene]- (hexafluoroacetylacetone) copper(I) and Pyridine HCl [3]. In this paper, we worked with anhydrous 1-Chlorobutane as a Cl precursor for deposition of CuCl thin films. The advantage of this liquid precursor is high vapour pressure enabling short pulsing times. The CuCl films were deposited on crystalline silicon with different pretreatment protocols and also on flexible polyimide polymeric substrates. The structural, chemical, optical and photoluminescence properties of CuCl thin films were studied by SEM, XRD, AFM, XPS, optical reflectance and photoluminescence. Figure 1 shows the SEM images of a layer of CuCl crystallites on a silicon substrate cleaned by RCA protocol and deposited using liquid 1-Chlorobutane. The deposition using a liquid 1-chlorobutane precursor is compared to the process using previously reported solid Pyridine hydrochloride precursor.

Figure 1: SEM images of a layer of CuCl crystallites on a silicon substrate cleaned by RCA protocol.

References:

AF2-MoP18 Number Effect of Si Atoms Contained in Precursor for SiN Atomic Layer Deposition, Seungbae Lee, H. Ji, H. Yang, S. Yoon, DUKSAN Techopia company, Republic of Korea; I-S. Park, Hanyang University, Republic of Korea.

Silicon nitride (SiN) films have been widely applied to the in solid-state devices as functional and process layers. The examples include charge trap layer in flash memory, gate dielectric layer in thin film transistors, gate spacer in FinFET transistor, etch stop layer in CMP, and capping layers in interconnection. The requirements of thin and smooth film, its uniform thickness and composition distribution, and high conformal coating on complicated structure have allowed ALD method to be widely introduced to make SiN films. In SiN-ALD process, the selection of Si precursor is significant because of the variability of film characteristics such as growth rate and material/dielectric/electrical properties. In this work, the number of Si atoms in precursor has focused on fabricating SiN-ALD films to investigate its linkage to growth and materials properties of SiN films.

Three precursors of SiC14, SiC16, and SiC18 were used as Si source for ALD for the model materials with the 1, 2, and 3 Si atoms. The ALD-SiN were performed at plasma system with NH3 reactant. For the growth rate of SiN, SiC16 has the highest value of 1.44 Å/cycle at the deposition temperature of 400 °C. The Si: N ratio of all SiN films was analyzed by using XPS measurement, which was the same with 1:1.16 near the surface, and kept constant with depth. The contamination of Cl and C was under the limit of XPS resolution for SiN. With these results, the ALD-SiN was introduced to the deposition system with diluted HF solution was reduced from 0.55 Å/sec to 0.36 Å/sec for SiC14 to SiC18. The SiN film properties compared with Si numbers in precursor presented in this work will be useful for the fast and robust film formation.

ALD Fundamentals

Evergreen Ballroom & Foyer - Session AF3-MoP

AF3-MoP1 Langasite Crystal Microbalance (LCM) for In-situ Process Monitoring of ALD up to 440 °C, Masafumi Kumano, Tohoku University, Japan; K. Inoue, Piezo Stock, Japan; K. Hikichi, Technofine co. Ltd, Japan; M. Shimizu, S. Tanaka, Tohoku University, Japan.

A quartz crystal microbalance (QCM) is often used as an in-situ monitoring tool for ALD process. The piezoelectric constant of quartz crystal starts to decrease at 300 °C and disappears at 573 °C. In addition, it’s temperature coefficient of frequency (TCF) around the turn temperature increases above 300 °C. Therefore, QCM is generally limited in use under 300 °C. In a higher temperature range, GaPO4 is only a material practically used for a microbalance[4]. However, the crystal growth of GaPO4 is not industrially established like quartz, and the crystal size is limited.

Langasite CaTaGa3Si2O14 is a new candidate for a high temperature microbalance. It keeps piezoelectricity in a wide temperature range without any phase transition, and a large crystal can be potentially grown in an industrial scale. Around the turnover temperature range, a Langasite crystal microbalance (LCM) shows a much smaller TCF than the conventional QCM (Fig. 1).

The Langasite has a dielectric constant about 5 times as larger as that of quartz. This must be taken into account of to use an available QCM oscillator circuit. As shown in Fig. 2, the active area of the LCM, i.e. the center part where the electrodes on both sides overlap, is smaller than that of the QCM. Fig. 3 shows the resonance impedance characteristic of the LCM. The resonance frequency is 6 MHz, and the electromechanical coupling factor is 2.6%. A weak spurious mode remains in Fig. 3, but it can be swept out by polishing the crystal surface to a convex shape.

The LCM was applied for TMA/H2O cycle up to 440°C. The inside of a LCM holder is purged by pulsed pressure synchronized to the ALD cycle to avoid internal deposition. Transient temperature fluctuation is repetitive and reproducible over the ALD sequence and can be separated from a mass change by averaging over sequence numbers. The measured LCM frequency change by a mass change of each cycle is 1.6 Hz at 395 °C and 2.2 Hz at 280 °C, which is smaller than that of the QCM (3.5 Hz/cycle at 285 °C). The sensitivity is improved using a larger active area of LCM in conjunction with a dedicated oscillator circuit.


AF3-MoP2 In-Situ Process Monitoring of Precursor Delivery Using Infra-Red Spectroscopic Method, Robert Wright, T. Baum, Entegris, Inc.

ALD processing is an increasingly critical deposition method for conformally coating high-aspect ratio features in advanced logic and memory devices. Accurate, consistent and controllable delivery of precursor materials to the deposition system is a necessity. To achieve reliable, low-cost deposition processes, a sensitive and non-destructive real-time method for monitoring the precursor concentration is increasingly important. An IR method offers chemical specific information for both the reactant and the reaction by-products. An IR based system was developed and used to measure the ‘direct’ flux from a solid source in real time. The real-time measurement of precursor concentrations in the gas-phase can be applied to process monitoring, process control and towards the detailed characterization of key variables in the precursor delivery. Further, this method can be used to characterize ampoule performance under different pressure, temperature and flow conditions for a specific chemical precursor.
AF3-MoP3 Quantitative Analysis of High-k ALD Precursors for Trace Elemental Impurities by Inductively Coupled Plasma – Mass Spectrometry (ICP-MS), Jinjin Wang, L. Mey-Ami, F. Li, Air Liquide Electronics – Balazs NanoAnalysis

The scaling of logic technology node following Moore’s law has reached <10 nm. Consequently, high-k dielectrics are prevalent in modern microelectronic devices. They are insulating thin films of metal oxides, metal nitrides or other types of metallic compounds with much higher dielectric constant k ranging from 8 to 32, in contrast to SiO2 with a k of 3.9. These thin films are deposited from high-k dielectric precursors, which are organometallic or inorganic compounds, via atomic layer deposition (ALD) technology. The ALD allows growth of thin films of high conformity and uniformity downscaled to single nm. In order for these thin films to function in micro devices, the films must be free of contamination that causes defects of microelectronic devices. Therefore, for quality control of the ALD process, all high-k precursors used must be completely free of elemental impurities. As a result, each batch of high-k precursors is now analyzed for elemental impurities before it can be used in the ALD process.

ICP-MS is the preferred technique for analysis of high-k precursors for trace metals at sub ppb and ppt level. High-k dielectric precursors generally contain a metal atom bound to a ligand or other organic components, and often react violently with water and moisture in atmosphere. Both metal and organic components create various matrix effects and mass interferences, both of which affect the accuracy of the precursor analysis. One of the matrix effects is known as “space-charge-effects” due to high metal concentration present in the precursor sample. The “space-charge-effects” suppresses the signal of many elements of interest and causes low spike recovery and poor analytical accuracy. In addition, there are two other types of mass interferences that can be formed due to high concentration of metal and organic components. These mass interferences generally exist in the form of polyatomic molecular ions and isobaric ion species. The polyatomic molecular ions include and are not limited to metal oxide, metal argide and metal carbide, formed by high concentration metal ions reacting with organic components and other species in the plasma. Doubly charged ions are another form of mass interferences that affect the analysis.

ICP-MS methods have been developed to reduce and eliminate all these matrix effects and mass interferences. The method development strategy enables us to develop low detection limits, which allow process engineers to set lower quality control specification limits for their process. Our method capability analysis (MCA) shows the low detection limits that we have achieved, excellent repeatability and accuracy as demonstrated by spike recovery experiments. The MCA also shows that the matrix effects and the mass interferences have significantly been reduced or eliminated.

AF3-MoP4 Numerical Studies of the Fluid Dynamics and Chemical Kinetics of Spatial Atomic Layer Deposition of Al₂O₃, Dongqing Pan, University of North Alabama

Low-throughput is a major limitation for industrial level atomic layer deposition (ALD) applications. Spatial ALD is regarded as a promising solution to this issue. With numerical simulations, this paper studies an in-line spatial ALD reactor by investigating the effects of gap size, temperature, and pumping pressure on the flow and surface chemical deposition processes in Al₂O₃ ALD. The precursor intermixing is a critical issue in spatial ALD system design, and it is highly dependent on the flow and material distributions. By numerical studies, it’s found that larger gap, e.g., 3 mm, results in less precursor intermixing, but generates slightly lower saturated deposition rate. Water temperature is shown as a significant factor in both flow and surface deposition processes. Higher temperature accelerates the diffusive mass transport, which largely contributes to the precursor intermixing. On the other hand, higher temperature increases film deposition rate. Well-maintained pumping pressure is beneficial to decrease the precursor intermixing level, while its effect on the chemical process is shown very weak. It is revealed that the time scale of in-line spatial ALD cycle is in tens of milliseconds, i.e., 15 ms. Considering that the in-line spatial ALD is a continuous process without purging step, the ALD cycle time is greatly shortened, and the overall throughput is shown as high as 4 nm/s, compared to several nm/min in traditional ALD.

AF3-MoP5 Mechanistic Understanding of Dicholosilane Thermal Decomposition during Atomic Layer Deposition of Silicon Nitride, Gyeong Hwang, G. Hartmann, University of Texas at Austin; P. Ventzek, Tokyo Electron America Inc.; T. Hwie, K. Ishibashi, Tokyo Electron Ltd.

Silicon nitride (SiN) thin films have been widely employed for various applications including microelectronics, but their deposition presents a challenge especially when highly conformal layers are necessary on wafer edge regions or at high temperatures. Alkylamine-enhanced atomic layer deposition (REALD) has been demonstrated to be a promising technique for controlled growth of SiN thin films at relatively low temperatures (<400 °C), in which thermal decomposition of Si-containing precursors on a N-rich surface is a critical step. In this talk, we will present our recent findings regarding potential underlying mechanisms leading to facile thermal decomposition of dicholosilane (DCS, SiH₂Cl₂) on the N-rich SiN surface, based on periodic density functional theory calculations. Our study highlights the importance of high hydrogen content on the N-rich surface, rendering primary and secondary amine groups. When the N-rich SiN surface is fully hydrogenated, the molecular adsorption of DCS is predicted to be exothermic by 0.6 eV. In this case, DCS decomposition appears to be initiated by nucleophilic attack by an amino lone-pair on the electrophilic Si, leading to the formation of a DCS amine adduct intermediate followed by release of a Cl₂ anion and a proton. The predicted activation barrier for the DCS decomposition reaction is only 0.3 eV or less, depending on its adsorption configuration. We will also discuss the formation and role of HCl, the subsequent formation and nature of Si-H bonds, and the interaction between adsorbed DCS molecules. While clearly demonstrating advantageous features of DCS as a Si precursor, this work suggests that thermal decomposition of Si precursors, and in turn the ALD kinetics and resulting film quality, can be strongly influenced by surface functional groups, in addition to product accumulation and precursor coverage.

AF3-MoP6 New Challenges of the Channeled Spectroscopic Ellipsometry for ALD Applications, Gai Chin, ULVAC Inc., Japan

The channeled spectroscopic ellipsometry is a snapshot method for the spectrally resolved polarization analysis. Two high-order retarders are utilized to generate a channeled spectrum carrying information about the wavelength-dependent multiple parameters of polarization of light. This method does not requires mechanical or active components for polarization-control, such as a rotating compensator and electro-optic modulator. It can measure the thickness and optical constants of thin films at an ultra-high speed. Its data acquisition time is as short as 10 ms per measurement.

This innovative technology created great opportunities for new applications of spectroscopic ellipsometry in which the compactness, the simplicity and the rapid response are extremely important. It can be integrated into many kind of deposition tools and successfully measured thin films in-situ and ex-situ. Obviously, ALD is one of the promising applications for this novel spectroscopic ellipsometry. This paper describes the principle, system configuration and new challenges on developing this compact high-speed spectroscopic ellipsometry to satisfy daily increasing in-situ monitoring requirements from the ALD industrial and R&D users.

Some of the successful ALD applications will be introduced, such as measurement data obtained on Al₂O₃, HfO₂, TiO₂, Ta₂O₅ and TiN thin films etc. By acquiring thickness and optical constants data from this spectroscopic ellipsometry, the layer by layer growth and material properties of the films can be studied in detail. The growth rate per cycle was determined directly, and an automatic process control can be realized by feedback and feed-forward approach on the ALD tools.

AF3-MoP7 In-situ Ellipsometric Analysis of the Plasma Influence on Atomic Layer Deposited AlIn Thin Films, Necmi Bayikli, S. Ilhom, D. Shukla, A. Mohammad, B. Willis, University of Connecticut

In this report we have carried out real-time process monitoring to understand the impact of RF-plasma power and plasma exposure time on aluminum nitride (AlN) growth and film properties via in-situellipsometry. AlIn thin films were grown on Si(100) substrates with plasma-enhanced aluminum atomic layer deposition (PE-ALD) using trimethyl-aluminum (TMA) as metal precursor and Ar/N₂/H₂ plasma as co-reactant. Saturation experiments have been performed in the range of 25-200 W plasma power and 30-120 s plasma exposure time within 100 - 250 °C substrate temperature. In-situmultiwavelength ellipsometry provided the necessary sensitivity to identify single chemical adsorption (chemisorption) and plasma-assisted ligand removal events, as well as changes in growth-per-cycle (GPC) with respect to plasma power. Our real-time dynamic in-situ monitoring study
revealed mainly the following insights about the plasma power influence on AlN growth: GPC and TMA chemisorption amount exhibited plasma-power dependent saturation behavior at 30 seconds of plasma duration. The amount of chemisorption saturated at ~2.25 Å for higher RF-power levels, while for 25 and 50 W it went to below 1 Å, which was attributed to insufficient ligand removal. Besides in-situ-characterization, ex-situ measurements to identify optical, structural, and chemical properties were also carried out on single-cycle AlN films as a function of plasma power. Two samples displayed single-phase hexagonal crystal structure with (002) preferred orientation for 150 and 200 W, while the dominant orientation shifted towards (100) at 100 W. On the other hand, 50 and 25 W resulted in films with amorphous character with no apparent crystal signature. Furthermore, it was found that when the plasma exposure time was increased from 30 to 120 s for 25 and 50 W, the amount of chemisorption exceeded the thickness gain values recorded for 150-200 W: ~2.4 Å. However, such a recovery in chemisorption did not reveal crystalline material as the AlN films grown at sub-50 W both showed amorphous character.

**AF3-MoP8 Reaction Mechanisms of Thermal and Plasma-Modified ALD Growth Studied by In-Situ Mass Spectrometry, Thomas J. Larrabee, L.B. Ruppert, U.S. Naval Research Laboratory**

Mechanisms of gas-surface chemical reactions, and reactions caused by plasma-surface interactions, have been studied to understand different aspects of the atomic layer deposition (ALD) of zinc oxide (ZnO) and niobium oxide (Nb2O5) using a differentially-pumped, highly-sensitive in-situ quadrupole mass spectrometer to detect reactant and product gas species. Examination and comparison of the gaseous reaction products of these two ALD processes aid our understanding of how to use plasmas to modify ALD oxide growth.

In some of these cases, the ALD process was modified by inserting argon/hydrogen plasma steps, which has been shown to alter the stoichiometry of ZnO and NbO2. In particular, the driving metal-enriched films and lower oxidation states. To date, it has been unclear what the mechanism of the plasma-surface reactions is in these processes or precisely how the thermal ALD growth has been altered by the insertion of argon/hydrogen plasma steps. By examining the reactant and product gas species detected by the in-situ quadrupole mass spectrometer, we are able to investigate the chemical reactions that occur during the ALD process, uncovering information not only about the impact of the plasma step, but also the underlying mechanism of the thermal growth process itself.

**AF3-MoP10 In-situ Quartz Microbalance Study of Poly(3,4-ethylenedioxythiophene) (PEDOT) by Oxidative Molecular Layer Deposition (o-MLD), Jungik Kim, A. Volk, North Carolina State University**

Molecular Layer Deposition (MLD) has emerged as a promising vapor-phase deposition technique due to its self-limiting reactions and conformal film growth. This work investigates oxidative MLD (o-MLD) of poly(3,4-ethylenedioxythiophene) (PEDOT) by using a volatile liquid oxidant agent and 3,4-ethylenedioxythiophene monomer (EDOT). Traditionally, PEDOT growth has been synthesized through solution-based processes involving oxidation and deprotonation steps. Despite its simplicity, poor solubility of PEDOT requires a water-soluble polyanion, poly(styrenesulfonate) (PSS), often increasing the film resistivity. Alternative vapor-phase methods such as oxidative chemical vapor deposition (o-CVD) have been reported, but chemical additives/post treatments are necessary to obtain high conductivity. Previously, Atanasov et al. has reported an o-MLD process of PEDOT using molybdnum(V) chloride oxidant (MoCl5) and EDOT [1]. However, the low vapor pressure of MoCl5 limits deposition temperature and facile dosing. Moreover, few basic growth analyses such as in-situ quartz crystal microbalance (QCM) have been carried out to understand PEDOT growth by o-MLD.

In this work, in-depth PEDOT growth behavior during o-MLD has been studied. The relationship between the film growth and various deposition conditions such as precursor dose/purge time, working pressure, and chamber/precursor temperature was investigated. The mass change per cycle is linear with the number of cycles for two different oxidant dose times. However, much longer purge times are required for the longer oxidant dose to remove the byproducts. QCM, X-ray photoelectron spectroscopy (XPS), spectroscopic ellipsometry (SE), and scanning electron microscopy (SEM) show that PEDOT film has been uniformly deposited at 100 °C, with a growth rate of ~1.5 Å/cycle. At higher chamber temperature, the growth rate decreases; above 150 °C, PEDOT growth is hindered by decomposition of precursors and monomer limited adsorption, resulting in rapid decrease of film growth. These QCM studies will play a pivotal role for understanding nucleation and growth mechanism of PEDOT via o-MLD and developing area selective MLD processes.


**ALD Fundamentals**

**Evergreen Ballroom & Foyer - Session AF4-MoP**

**Plasma Enhanced ALD Poster Session**

**AF4-MoP1 Low-temperature Atomic Layer Deposition of Yttrium Oxide using tris(butylcyclopentadienyl)yttrium and a Plasma-Excited Humidified Argon, Kentaro Saito, K. Yosida, K. Kanamato, M. Miura, B. Ahmmad, K. Shigeru, F. Hirose, Yamagata University, Japan**

Yttria (Y2O3) is attracting much attention since it has a high dielectric constant and it is expected to be used as an oxide insulator in the field of large scale integration. Conventionally Y2O3 film has been deposited by chemical vapor deposition (CVD) and atomic layer deposition (ALD). These require heating at 200 °C or higher. This high temperature process is not suitable for the fabrication of flexible electronics. To decrease the process temperature, we developed a low-temperature ALD of Y2O3 using tris(butylcyclopentadienyl)yttrium ([BuCp]3Y) as the Y precursor and a plasma-excited humidified argon as an oxidizer.

We used a double-sided polished p-type Si (100) with a size of 20 x 20 mm2 as a sample. Y2O3 ALD was performed by introducing a precursor from the heated container at 140 °C and the oxidizer alternately into a chamber at 80 °C. We designed the process condition of ALD as follows, ([BuCp]3Y) injection of 300 sec and plasma excited humidified argon of 600 sec. The evacuation times after the ([BuCp]3Y) and plasma excited humidified argon are 30 sec and 90 sec respectively. We measured chemical status of Y2O3 films by X-ray photoelectron spectroscopy (XPS) to confirm the presence of Y2O3. We extracted a growth per cycle of ALD by spectroscopic ellipsometry. In Fig. 1, we show a wide scan XPS spectrum obtained from the 80 °C grown Y2O3 film. Fig. 2 shows Y2O3 thicknesses as a function of ALD growth cycles. We estimated the growth per cycle of 0.084 nm/cycle.

In this work, we succeeded in 80 °C ALD of Y2O3. It must be possible to form Y2O3 films on most of flexible substrates by this process, because the process temperature was limited below 80 °C in this ALD process. In the conference, we showed the related results and discuss the reaction mechanism.

**AF4-MoP2 Plasma Enhanced Atomic Layer Deposition of Silicon Nitride Thin Film by Organosilane Precursor and Process Engineering, Se-Won Lee, C. Lee, M.-S. Kim, Versum Materials Korea, Republic of Korea; S. Yi, X. Lei, Versum Materials, Inc.**

In this study, we demonstrated that a multi chloride ligand organosilane precursor with no oxygen content, designated as Precursor T to deposit SiN film at the identical deposition temperature for a possible low thermal budget and reliable device operating in industrial applications. Precursor T was used as a Si precursor, and NH3 and N2 were used as the reactants. Ar gas was used as a main and a carrier gas. Plasma enhanced ALD (PEALD) method was conducted to obtain SiN film at 300 °C wafer temperature. SiN PEALD deposition conditions with two different reactants are as follows: Precursor T/purge/NH3*/purge (process A, * denotes plasma use), Precursor T/purge/N2*/purge (process B).

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purge/N2*/purge (process C, applied additional N2 plasma after NH3 plasma) and Precursor T/purge/N2*/purge/NH3*/purge (process D, applied additional NH3 plasma after N2 plasma).

Deposited SiN film with process A and process C exhibited good stoichiometric film compositions at about Si : N ratio of 3 : 4 with low oxygen and carbon contents and excellent SC of more than 95 %. SiN film with process D also showed good stoichiometric characteristic but, SC was ~ 65 % which is not good property than the above two methods. SiN film with process B showed a higher level of impurities over 3 % carbon and chlorine and 20 % oxygen contents, and a poor SC less than 20 % was found. Consistent with the above results, the XRR results also differed significantly from the other three process in SiN film with process B. The film density from process A to D were 2.65, 2.44, 2.73, and 2.73 g/cm³, respectively, which show that the density of process B are not perfect in SiN film.

For the WER performance with 0.1% HF solution, SiN with process C shows the lowest WER of 10 A/min among the four conditions. (WERs of process A, process B and process D SiN films were 88, 187 and 15 A/min, respectively.) It is demonstrated that WER is improved with combinatorial deposition with NH3*/N2*/SiN* compared to the deposition with NH3* or N2* alone.

In summary, we have deposited SiN film by using a multi chloride ligand organosilane precursor and ALD process design. SiN film was deposited with NH3 and N2 reactant gases by PEALD. Excellent SC and WER results were obtained for SiN film deposited with Precursor T/NH3*/N2*/ SiN* PEALD process. These results would be able to be applied to spacers or passivation layers via hollow-cathode plasma-assisted atomic layer deposition (HCPA-ALD) using trimethyl-aluminum (TMA) and Ar/N2/H2 plasma as metal precursors or organosilane precursor and ALD process design. SiN film was deposited in an ALD reactor pressure. Towards this aim, AlN films were grown on Si(100) substrates via hollow-cathode plasma-assisted atomic layer deposition (HCPA-ALD) using trimethylaluminum (TMA) and Ar/N2/H2 plasma as metal precursors and co-reactant, respectively. Growth saturation experiments have been carried out within 0-1000 sccm range for each co-reactant gas, at 100W RF-plasma power and 200°C substrate temperature. In-situ ellipsometry was utilized to monitor the growth-per-cycle (GPC) characteristics and real-time surface reactions including chemisorption and plasma-assisted ligand removal and nitrogen incorporation events. GPC values showed a fairly constant behavior at lower pressures followed by a considerable decrease at ~1 Torr. Our real-time dynamic in-situ monitoring suggests that the decline in GPC at higher pressures, and thus higher co-reactant gas flow rates, is mainly due to incomplete removal of surface ligand groups. Each of the plasma gas content was decoupled by keeping two of the co-reactants at an optimal flow rate and changing one over the range of 5-100 sccm in order to observe the GPC behaviour. In general, decoupling of N2 and H2 showed that the GPC is reduced at lowest and highest flow rates with rather a higher and fairly constant value in between. On the other hand, for Ar the GPC increased under low flow rates followed by a decay at higher flow rates. Moreover, N2 and H2 plasma gas mixture were also decoupled in time domain to investigate the GPC behavior in such a regime. We have observed that GPC was reduced for shorter H2 plasma exposure times of 5 and 10 seconds followed with higher and constant value for longer durations, which was correlated to the incorporation of ligand removal at the shorter H2 plasma exposures that was supported by the single-cycle real-time in-situ measurements data. Also, extended 500-cycle long runs of AlN growth were carried out as a function of different plasma gas content and pressure. All AlN samples displayed single-phase wurzite polycrystalline character, which exhibited preferred (002) crystalline orientation with peak intensity values changing as a function of Ar flow rate.

AF4-MoP3 Understanding the Effect of Plasma Gas Chemistry and Reactor Pressure on the Crystallinity of ALD Films Grown via Plasma-Assisted Atomic Layer Deposition, Saidjafarzoda Ilhom, D. Shukla, A. Mohammad, N. Biyikli, B. Willis, University of Connecticut

In this study we investigate the correlation between the structural properties of ALD thin films and the plasma gas composition as well as the ALD reactor pressure. Towards this aim, AlN films were grown on Si(100) substrates via hollow-cathode plasma-assisted atomic layer deposition (HCPA-ALD) using trimethylaluminum (TMA) and Ar/N2/H2 plasma as metal precursors and co-reactant, respectively. Growth saturation experiments have been carried out within 0-1000 sccm range for each co-reactant gas, at 100W RF-plasma power and 200°C substrate temperature. In-situ ellipsometry was utilized to monitor the growth-per-cycle (GPC) characteristics and real-time surface reactions including chemisorption and plasma-assisted ligand removal and nitrogen incorporation events. GPC values showed a fairly constant behavior at lower pressures followed by a considerable decrease at ~1 Torr. Our real-time dynamic in-situ monitoring suggests that the decline in GPC at higher pressures, and thus higher co-reactant gas flow rates, is mainly due to incomplete removal of surface ligand groups. Each of the plasma gas content was decoupled by keeping two of the co-reactants at an optimal flow rate and changing one over the range of 5-100 sccm in order to observe the GPC behaviour. In general, decoupling of N2 and H2 showed that the GPC is reduced at lowest and highest flow rates with rather a higher and fairly constant value in between. On the other hand, for Ar the GPC increased under low flow rates followed by a decay at higher flow rates. Moreover, N2 and H2 plasma gas mixture were also decoupled in time domain to investigate the GPC behavior in such a regime. We have observed that GPC was reduced for shorter H2 plasma exposure times of 5 and 10 seconds followed with higher and constant value for longer durations, which was correlated to the incorporation of ligand removal at the shorter H2 plasma exposures that was supported by the single-cycle real-time in-situ measurements data. Also, extended 500-cycle long runs of AlN growth were carried out as a function of different plasma gas content and pressure. All AlN samples displayed single-phase wurzite polycrystalline character, which exhibited preferred (002) crystalline orientation with peak intensity values changing as a function of Ar flow rate.


Plasma enhanced atomic layer deposition (PEALD) is an emerging energy enhanced ALD technique that utilizes plasma radicals to drive surface reactions rather than thermal energy, as in traditional ALD. PEALD allows for lower impurities, increased growth rates, improved stoichiometry, and lower deposition temperatures, which are essential for the development of high reflectivity UV structures and multilayer Fabry-Perot bandpass filters. The goal of this project is to develop an oxygen and nitrogen free ALD process to grow both aluminum and AlF₃ in the same chamber to enable UV optical filters that can be operated at <120 nm. The system is designed to deposit aluminum on a hydrogen terminated Si substrate, by sequential exposures of trimethylaluminum (TMA), an Ar purge, and a hydrogen plasma. The deposition of metal fluorides has been limited by difficulty in handling, storing, and anhydrous HF. The use of Pyridine-HF as the fluoride source reduces the risk for deposition of UV fluoride layers including AlF₃ and MgF₂. The process designed for the growth of AlF₃ layers proceeds by exposing the fresh PEALD Al to HF followed by an Ar purge. The process is designed for growth of Al and AlF₃ at 100-300°C. The PEALD system is connected to an X-ray photoelectron spectroscopy (XPS) system for elemental analysis and a UV spectrometer for far UV optical properties. Ex-situ characterization was conducted using atomic force microscopy (AFM), Rutherford backscattering (RBS), UV-VIS ellipsometry, and X-ray topography (XRT).

Research supported by NASA through grant NNX16AC30G.

AF4-MoP5 High-temperature Hollow Cathode Plasma Enhanced Atomic Layer Deposition of Silicon Nitride (SiN₃) Thin Films using Hexachlorodisilane (HCDS), Su Min Hwang, A.L.N. Kondusamy, Q. Zhiffany, H.S. Kim, J. Kim, University of Texas at Dallas; X. Zhou, B.K. Hwang, Dow Chemicals

Recently, plasma enhanced aluminum layer deposition (PEALD) is expected to overcome the limitation of conventional LPCVD and PECVD processes and could be used to deposit conformal thin films in convoluted high aspect ratio structures with thickness scalability. A number of studies on PEALD SiN₃ process have been reported and mostly capacitively coupled plasma (CCP), inductively coupled plasma (ICP) or microwave (MW) plasma source was employed. The characteristics of the process, such as low plasma density in CCP, high plasma damage in ICP and high oxygen contamination in MW, etc., can be problematic for film properties, especially wet etch resistance. On the other hand, hollow cathode plasma (HCP) can be applied for high-quality silicon nitride films due to its lower oxygen contamination, higher plasma density and lower plasma damage. Inspired by the unique characteristics of HCP, we proposed to explore the feasibility of high-quality PEALD-SiN₃ films by improving the films properties with HCP. Additionally, the relationship between plasma source and PEALD-SiN₃ films properties has rarely been studied.

In this work, we not only clarified the effect of plasma source on the oxygen contamination of PEALD SiN₃ films, but also achieved high-quality SiN₃ films using hollow cathode PEALD. PEALD system with ICP or HCP source was employed to study SiN₃ films comprehensively. Hexachlorodisilane (HCDS, Si₂Cl₆) was used as the silicon precursor due to its higher reactivity than SiCl₄ and SiH₂Cl₂ while exhibiting a distinct self-limiting growth behavior. We explored the effect of process temperature (310–570 °C), precursor exposure, and plasma gas composition (NH₃/N₂ or NH₃/Ar) on the film properties. Within a range of process temperature window (310–480 °C), the combination of SiCl₄ and NH₃ plasma showed the distinct self-limiting growth behavior at a low precursor exposure (5×10⁻¹ L). In plasma source comparison, the SiN₃ films deposited with ICP source showed higher oxygen contamination (> 7.0 at%) than the HCP-PEALD SiN₃ films (> 3.5 at%). Particularly, the HCP-PEALD SiN₃ film deposited at 480 °C had the wet etch resistance in HF acid (> 0.4 nm/min, 200:1 HF) and film density (2.9 g/cm³) comparable to the LPCVD SiN₃ films. These results could pave the way for achieving high-quality SiN₃ films using the unique HCP source.

AF4-MoP6 Effects of Ion Bombardment in Plasma Enhanced Atomic Layer Deposition Processes, Hu Li, Tokyo Electron Technology Solutions Ltd., Japan; T. Ito, Osaka University, Japan; M. Kayaga, T. Moriya, Tokyo Electron Technology Solutions Ltd., Japan; K. Karahashi, S. Hamaguchi, Osaka University, Japan; M. Matsukuma, Tokyo Electron Technology Solutions Ltd., Japan

Plasma enhanced technology has been widely used in the fabrication of thin films. In an atomic layer process, for example in a plasma enhanced atomic layer deposition (PEALD) process, chemically reactive plasma is expected to achieve high growth per cycle (GPC) at relatively low process pressure.
temperature. A typical PEALD process may also be used in multiple patterning. In such patterning processes, much more precise resolution of film patterning is highly required for the nanoscale patterning. However, the film surfaces suffer the bombardment of energetic ion species, which are generated in the plasma. In such processes, film properties are affected. Therefore, the goal of this study is to clarify the effects of ions or radicals in the plasma enhanced atomic layer processes and gain a further understanding of deposition mechanisms.

In this study, we have estimated the sputtering yields of a SiO₂ film deposited by a PEALD process, by an oxygen ion (O⁺) beam as well as inert gas species with the use of a mass-selected ion beam system. We have also examined the effects of low-energy ion bombardment on a precursor-absorbed SiO₂ or Si surface. After precursor exposure, the surface was exposed to energetic argon ions (Ar⁺). The surface chemical compositions after ion bombardment were analyzed by in-situ X-ray Photoelectron Spectroscopy (XPS). From the XPS observations, it has been found that impurities, such as nitrogen (N) and carbon (C) originating from the organic precursor molecules, remain in the surface region even after Ar⁺ ion bombardment. We have also examined the effects of oxygen, which will be discussed in the presentation.

AF4-MoP8 - Microwave-Generated Plasma-Enhanced Atomic Layer Deposition of Oxides, J.Hye Kim, Y.D. Tok, Y.B. Lee, ISAC Research Inc., Republic of Korea; A. Puraba, I. Dolak, SVCS Process Innovation s.r.o., Czech Republic; H.S. Park, ISAC Research Inc., Republic of Korea

With the continued down-scaling of devices and structure changed to 3-dimensional, new ALD processes are in great demand. Microwave surfatron plasma is considered new plasma source because it enables very low-temperature deposition and good film quality due to its low electron temperature and higher plasma density.

In this work, surfatron plasma source was incorporated to ALD reactor. We studied the characteristics of oxide films grown by microwave plasma enhanced ALD in the reactor. The films had high growth rate and low impurities, and this is very useful conformally on 6-inch Si wafer. The successful incorporation of surfatron plasma source to ALD reactor encourages the study of challenging ALD processes.

AF4-MoP9 - Epitaxial Growth of GaN by Plasma-Enhanced Atomic Layer Deposition, Songjie Liu, X. Zhang, University of Science and Technology, Beijing, China

In this work, the epitaxial growth of single crystalline GaN films on sapphire substrates by plasma-enhanced atomic layer deposition (PEALD) at a growth temperature of 350 °C. The XRD patterns show that the GaN films are single crystalline and display a single hexagonal (002) phase. The high-resolution transmission electron microscopy reveals a nanoscale single-crystal GaN heteroepitaxy and a sharp interface. The full width at half-maximum of the X-ray rocking curve of the GaN epilayers is 700 arcsec. The hetero-epitaxial GaN thin films have broaden its application in photovoltaic area, such as improving the performance of the solar cells.


In our continuous evaluation of inorganic compounds as silicon source precursors for plasma enhanced atomic layer deposition of silicon nitride films (PEALD SiN), a halodisilane is found to give a superior film-forming performance and film properties. The halodisilane having 99% purity was evaluated with ammonia plasma on a PEALD tool with a remote hollow cathode plasma source. SiN films were deposited at about 1 Å/cycle growth rate within the ALD window up to about 450 °C. This growth rate represents a 20% improvement over the growth rate of hexachlorodisilane (HCDs). The wet etch rate (WER) of the PEALD SiN film of the halodisilane is 50% lower than that of HCDs in 200:1 HF. The step coverage is comparable to that of HCDs in high aspect ratio trenches. The PEALD SiN film results of this precursor including saturation behavior, ALD window, composition, refractive index, uniformity, density, wet etch rate and step coverage are summarized and compared with those of HCDs and pentachlorodisilane (PCDS) in this presentation.

AF4-MoP11 - Characteristics of Silicon Nitride Film Deposited by Multi-electrode VHF (162 MHz)-PEALD, K.Hyun Kim, K.S. Kim, Y.J. Ji, J.Y. Byun, Sungkyunkwan University, Republic of Korea; A.R. Ellingboe, Dublin City University; G.Y. Yeom, Sungkyunkwan University, Republic of Korea

Silicon nitride (SiN) thin films are used as passivation layers, diffusion barrier materials, and structural materials for various micro-electro-
Atomic Layer Deposition (ALD) is a materials growth technique that has been acknowledged until recently. The core activity of VPHA is to overview early days of ALD. Especially the ML path has remained poorly known and volunteer-based Open Science effort set up in 2013 [2] to clarify the early understanding of ALD has been discovered independently twice, under the names Molecular Vista, Chemical Vapor Deposition 20 (2014) 332–344, and Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES), trace metals, Gallium Nitride (GaN). 

Keywords: Direct film stripping (DFS), Inductively Coupled Plasma Mass Spectrometry (ICP-MS), Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES), trace metals, Gallium Nitride (GaN)

AF5-MoP2 Overview of Doctoral Theses on Atomic Layer Deposition Worldwide - Outcome of the Virtual Project on the History of ALD. J. Aarik, University of Tartu, Estonia; J. Aav, E. Ahvenniemi, Aalto University, Finland; A.R. Akhachev, Stanford University; S. Ali, Aalto University, Finland; M. Bechelany, Institut Européen des Membranes, France; M. Berdova, Aalto University, Finland; I. Bodalyov, St. Petersburg State Institute of Technology, Russian Federation; S. Boyadjiev, Bulgarian Academy of Sciences, Bulgaria; D. Cameron, Masaryk University, Czech Republic; N. Chekurov, Oxford Instruments Analytical Oy, Finland; R. Cheng, Huazhong University of Science and Technology, China; M. Chubarov, The Pennsylvania State University; V. Cremer, Ghent University, Belgium; A. Devi, Ruhr University Bochum, Germany; V.E. Drodz, St. Petersburg State Institute of Technology, Russian Federation; L. Elkinova, Institute for Theoretical and Experimental Physics, Russian Federation; G. Gottardi, Fondazione Bruno Kessler, Center for Materials and Microsystems, Italy; J. Ruud van Oommen, Delft University of Technology, Netherlands; R. Puurunen, Aalto University, Finland

Atomic Layer Deposition (ALD) is a materials growth technique that has become globally important during the past decades. In 2018 the Finnish inventor of ALD, Tuomo Suntola, received the Millennium Technology Prize. ALD has been discovered independently twice, under the names Molecular Layering (ML) in the 1960s in the USSR and Atomic Layer Epitaxy (ALE) in 1974 in Finland. The Virtual Project on the History of ALD (VPHA) is an open-access database of ALD theses, started in 2013 to document the origins and early days of ALD and to identify the key contributors to the development of the technique. The VPHA is a volunteer-based Open Science effort set up in 2013 to clarify the early development of ALD.

The poster will overview doctoral theses worldwide related to ALD up to year 2018. The doctoral thesis list has been built by combining the lists of J. Niinistö, M. Putkonen, L Niinstö. Chem. Matter, 16 (2004) 2953-2958, and allowing volunteers to enter missing information (open list in http://vph-ald.com/VPHAopenfiles.html). At the time of writing the abstract, the doctoral thesis collection contains close to 500 entries. The list is likely not yet complete and more entries are welcome. More volunteers are still welcome to join and contribute in the VPHA.

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References:

Monday Evening Poster Sessions, July 22, 2019


Chemical analysis of ultrathin films with nanometer scale lateral spatial resolution remains a challenge for the nanotechnology community. In this poster, we introduce a new nanoscale and non-destructive chemical imaging technique called photo-induced force microscopy (PiFM) where the dipole-dipole force due to optical response of the sample is measured by an atomic force microscope (AFM) along the standard AFM topography [1]. This dipole-dipole optical force interaction between the AFM tip and the sample is strongly enhanced at the apex of the metal-coated tip due to the antenna effect and leads to a routine spatial resolution better than 10 nm. Since both the optical excitation and detection are accomplished in near-field, the optical information can be acquired without the far-field background interference, making the technique easy-to-use compared to other near-field techniques. PiFM can be coupled with a tunable infrared (IR) light sources to probe the IR absorption of various organic and inorganic materials for identification of molecular materials and their relationship to local topography. PiFM is surface sensitive due to the short interaction range of the measured dipole-dipole force and can detect monolayer of materials with good sensitivity, making it an ideal tool for characterizing ultrathin films.

PiFM works equally well with both organic and inorganic materials and lends itself as an excellent analytical to characterize ALD, molecular layer deposition, and organic-inorganic hybrid materials.


AF5-MoP4 The Effect of Impurities on Film Properties in the Y(MeCp)/O3 Process, J. Kalliomäki, T. Lehto, M. Kääriä, T. Sarnet, Jani Kivijärvi, Picosun Oy, Finland

Y2O3 thin films are utilized as insulating materials in electronic devices, hydrophobic layers and corrosion inhibiting coatings. Several different yttrium ALD precursors have been demonstrated in the literature, from β-diketonates to heteroleptic cyclcopentadienyls. When the deposition temperature is below 300 °C, authors usually report deterioration of film properties, such as crystallinity and density, with increasing impurity levels. [1,2] Nevertheless, further studies on the impurities are often outside the scope of the research found in literature. The cyclcopentadienyl-based ligands are commonly used in rare earth metal precursors, and the reaction mechanisms for them are proposed in literature. [3] However, the effect of deposition temperature over the full available range is not as widely researched.

This work focuses on the effects the reaction mechanism of the Y(MeCp)/O3 process has on the type of carbon-based impurity species that result and deposition temperature range 150-425 °C. The change in coordination/bonding of the impurities, and associated effect on film properties, is considered.

The experiments were made with a Picosun® R-200 Advanced hot-wall ALD system. Si wafers with native oxide layers were used as substrates. According to the results, the deposition temperature range can be divided into three regions that produce films with notably different materials properties (Figures 1-2). Each region is categorized by its distinct type of carbon-based impurity content, and the effect on optical, structural and electrical film properties will be discussed.

Understanding the underlying mechanism of growth, and how it can change and shape the process and the properties of the resulting films, is one key factor to widen the effective deposition temperature range of known oxide processes. Knowing the impact of the reaction mechanisms on the film properties allows more accurate process controls for specific applications and ultimately will help to create more high-quality end products.


Growth and film deposition characteristic in a downstream ICP PEALD reactor where uniform variable density O₂ and N₂ or H₂ plasmas are used. This process is implemented in a Birol Kuyel reactor and has been studied in a comprehensive fashion.

While there have been examinations of any ALD films, we studied down to room temperature depositions. Results are compared to thermal deposition in the same reactor and others’ reported findings. Representative (IPE yield) 1/2 vs. photon energy (2-5 eV) plots (Fig. 1) under negative and positive polarity allow extraction of voltage dependent spectral thresholds for the (a) Ru/Al₂O₃ interface and (b) TaN/Al₂O₃ interface, respectively. Scotkky plots of spectral thresholds vs. field reveals the spectral thresholds of the interface.

ALD Ru and RuO₂ films with Al₂O₃ and HfO₂ in MIM devices were also measured. Some devices were annealed at 500 °C for 60 min in H₂/N₂.

Table 2 shows near zero nucleation, low roughness, and low resistivity. The ALD Ru and RuO₂ films exhibit low roughness, low resistivity, and after annealing in H₂/N₂ will be reported and compared to ΦRu-eff extracted using C-V techniques as well as IPE results on amorphous materials.

References

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AF5-MoP10 Structural Aspects of Nanometer-Sized Amorphous Materials, Yael Etinger-Geller, A. Kotzman, & B. Pokroy, Technion - Israel Institute of Technology, Israel

Cristallization in the course of biomineralization, often occurs via an amorphous precursor phase, allowing additional control over the mineralization process. One of the main advantages of this method is that it enables organisms to exert control over the resulting polymorph, which is not necessarily the thermodynamically stable one, by manipulating the short-range order of the amorphous phase.

Although many aspects of science and technology rely on amorphous materials, considerably less research focuses on the structure of amorphous materials as compared to their crystalline counterparts. In this research, we draw inspiration from nature and study the ability to control the short-range ordering in amorphous materials via nanometer size effects. We chose atomic layer deposition (ALD) to deposit thin amorphous oxides since this technique can provide extremely precise, sub-nanometric, thickness control and can deposit conformal and pinhole-free films of various materials.

We report on the characterization of the etch rates of 9 oxide ALD films in 20 different wet and vapor etchants, which include many commonly used silicon etchants, oxide etchants and metal etchants, as well as solvents, cleaning solutions and photoresist strippers. Each of the 180 etch rates is based on data from a minimum of 4 separate etches, with a total of over 1500 thickness measurements performed by ellipsometry. To allow efficient coverage of such a large scope, a high-throughput sample fabrication and measurement workflow was developed and successfully employed. Extension of the work to nitride ALD films is currently underway.

All oxide films were deposited at 200°C in Veeco / Cambridge Nanotech Fiji F202 ALD reactors, employing both thermal and plasma-enhanced ALD (PEALD), when available. To achieve representative results, standard deposition recipes were used, which are not optimized for low etch rates or any other specific metric, but have been developed for general purpose use. Chemicals were freshly poured for all wet etching. Film compositions as deposited were characterized using X-ray photoelectron spectroscopy (XPS).

References

AFS-MoP7 Growth and Characterization: Low Temperature ALD, Birol Kuyel, A. Alphonse, K.P. Hong, J. Marshall, Nano-Master, Inc.

Growth and film deposition characteristic in a downstream ICP PEALD reactor are studied using a unique new process called Continuous Flow Process that cuts the cycle time in half. This process is implemented in a PEALD reactor where uniform variable density O₂ and N₂ or H₂ plasmas are produced but any contact of the plasma with the substrate is prevented. Precursors are not allowed to enter the plasma production region making it possible to obtain repeatable operation free of deposits or plasma instabilities. This Continuous Flow Process is used for Depositing PEALD GaN, Al₂O₃, and AlN films on Si substrates. It is shown that with this process ultra-smooth and uniform films with thickness linearly proportional to the number of cycles are deposited. Then it is applied to low temperature deposition of SiNₓ and SiOₓ films on Si wafers. The film surface roughness, thickness, uniformity, index of refraction, composition, and stress are studied down to room temperature depositions. Results are compared to thermal deposition in the same reactor and others’ reported findings.

*US Patent # 9,972,501 B1 May 15, 2018


For designing any kind of nanofabrication process, knowing the etch rates of available thin films, as well as their compatibility with commonly used processing chemicals is crucially important. Previous work by Williams et al. [1][2] tabulating rates for large numbers of film-etchant combinations has gained great popularity in the nanofabrication community, but does not include any ALD films. While there have been examinations [3] for select ALD processes and etchants since, the etch rates of ALD films have not yet been studied in comprehensive fashion.

We report on the characterization of the etch rates of 9 oxide ALD films in 20 different wet and vapor etchants, which include many commonly used silicon etchants, oxide etchants and metal etchants, as well as solvents, cleaning solutions and photoresist strippers. Each of the 180 etch rates is based on data from a minimum of 4 separate etches, with a total of over 1500 thickness measurements performed by ellipsometry. To allow efficient coverage of such a large scope, a high-throughput sample fabrication and measurement workflow was developed and successfully employed. Extension of the work to nitride ALD films is currently underway.

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References
layer. Additionally deposited cobalt (and longer term ruthenium) metal will displace copper and tungsten because of lower resistivity and these materials require no liner or barrier when used as an interconnect.

Unfortunately, there are significant uncertainties in the supply chain.

Ethical sourcing of Cobalt: While Cobalt is not yet listed as a conflict material like gold, tantalum, tungsten and others, articles published by Amnesty International in Jan 2016 (https://www.amnesty.org/en/latest/news/2016/01/child-labour-behind-smart-phone-and-electric-car-batteries/) and Nov. 2017 (https://www.amnesty.org/en/latest/news/2017/11/industry-giants-fail-to-tackle-child-labour-allegations-in-cobalt-battery-supply-chains/) alerted end users and Semiconductor companies alike about child labor and artisanal mining being used to produce cobalt minerals. Umicore is worldwide one of the largest users of cobalt and has taken significant measures to ensure that cobalt sourced and downstream products supplied by Umicore don’t come from unethical sources. This has been audited and certified by an independent firm. Our poster contains more details on these issues.

The manufacture of cobalt precursors requires access to an intermediate called dicobaltoctacarbonyl. This material is currently only manufactured by two minor companies with limited production resources, one of these companies is even located in a geographical area, which may add to the supply complexity. The poster details how Umicore plans to overcome this bottleneck and ensure sufficient supply for future growth of the industry.

Cobalt is also a raw material for Lithium batteries. This application is forecasted to grow significantly in future because of the electrification of the automobile. This raises questions about future price development and availability of cobalt raw materials. Our poster reviews the impact on the electronics industry, the impact on the electronics industry and possible solutions.

In addition, we will introduce the latest Co metal precursors as potential candidates for ALD and MOCVD applications.

**AM-MoP2 Homogeneous and Stress Controlled PEALD Films for Large Optics, Hassan Gargouri, F. Naumann, S. Goika, SENTECH Instruments GmbH, Germany; K. Pfeiffer, Fraunhofer Institute for Applied Optics and Precision Engineering IOF, Germany; V. Beladlya, Friedrich Schiller University, Germany; A. Szezhalmi, Fraunhofer Institute for Applied Optics and Precision Engineering IOF, Germany**

The deposition of homogenous conformal films with a precise thickness control on structured surfaces is essential for numerous applications for semiconductors, sensors and optics. Atomic Layer Deposition (ALD) is the key technology to fulfill the high requirements of such devices e.g. DRAM, MEMS, gratings. Plasma Enhanced Atomic Layer Deposition (PEALD) is an extension of ALD that opens up new possibilities such as an increased choice in materials and precursors, extended process region, and processing at reduced substrate temperatures. The new SILAYO ALD system of SENTECH Instruments GmbH with Planar Triple Spiral Antenna (PTSA) as large planar inductively coupled (IC) plasma source promises highly uniform and conformal ICPEALD deposition. Furthermore, the SILAYO system is equipped with substrate bias to control film stress during the deposition process.

**ICEPEALD Al2O3, SiO2 and TiO2 films were deposited on 8-inch silicon (Si) substrates. Trimethylaluminium (TMA), bis(diethylamino) silane (SAM24) and tetrakis(dimethylamino) titan (TDMAT) were used as metal organic precursors and oxygen plasma was applied as oxygen source for the ICEPEALD processes. Due to the low vapor pressure of the Si- and Ti-precursor, the material containers were heated to 70 °C. During the deposition process the substrate temperature of 250 °C was kept constant. Nitrogen (N2) was used as carrier gas for the precursors and a constant flow of oxygen was applied through the plasma source. The Al2O3 process exhibits a growth rate of 1.4 Å/cycle and an excellent non-uniformity of ± 0.3 % over the 8-inch Si wafer. The 66 nm Al2O3 film shows a refractive index of 1.64 with also an excellent non-uniformity of ± 0.08 %. The SiO2 and TiO2 processes show a growth rate of 1.1 Å/cycle and 0.6 Å/cycle, respectively. The two processes reveal an excellent non-uniformity of ± 0.7 % or ± 0.8 % over the 8-inch Si wafer. Furthermore, ICEPEALD Al2O3 films were deposited with substrate bias. Standard Al2O3 film shows 97 MPa tensile stress. Applying a bias voltage during the deposition process, the Al2O3 film shows compressive film stress between -109 MPa and -144 MPa, depending on the set bias voltage.**
AM-MoP5 Design and Manufacturing of ICP-Type Remote Plasma ALD, Dohyun Go, J.W. Shin, B.C. Yang, H.J. Kim, Seoul National University of Science and Technology, Republic of Korea

Plasma-enhanced ALD (PEALD) is a type of ALD, which utilizes ions and radicals in plasma as oxidants which have higher reactivity than conventional oxidants. Plasma can not only effectively eliminate ligand of precursors but also possibly reduce deposition temperature. While the system of commercial PEALD usually adopts capacitively coupled plasma (CCP) inductively coupled plasma (ICP), it is usually complicated regardless of plasma generating method; such complexity of system may increase the system cost and hamper the process flexibility.

In this presentation, we show the design and manufacturing of fully functioning compact size PEALD station using ICP plasma chamber. Systematic mechanical design process was applied including quality function deployment (QFD), fluid/thermal analysis, and 3D modeling. In the system manufacturing process, gate valve and stop valve have been modified to increase the versatility of the process conditions as well as the possible deposition of many more materials. In addition, the electrical biasing table was added to the system to control the characteristics of the plasma such as the density and flux of ions, and therefore the crystallinity of the film. Furthermore, the biasing table can be further applied for selectively functionalizing the 2-dimensional materials, e.g., graphene, on metal or silicon substrate, and accordingly selectively depositing ALD films on them. As a result, PEALD station that we have designed and manufactured can provide economic options for researchers who want to explore PEALD processes for novel applications.

AM-MoP6 ACS™ (Atmosically Clean Surface™) Cleaning and Analytical Validation of Recycled ALD Chamber Parts for the Semiconductor Industry, Russell Parise, I. Iordanov, B. Quinn, UCT - QuantumClean; P. Sun, UCT - ChemTrace

ALD deposition has enabled the semiconductor industry to deposit thin, highly conformal films. Foundational to delivering the consistent film quality is managing the quality of the parts within the chamber, especially the recycled parts sent offsite for cleaning. It is an under-recognized challenge to reliably produce “certifiably” clean chamber parts. The highly conformal, high step coverage nature of ALD process results in surface deposits on the parts that are tightly adhered. Additional considerations include: parts fragility, part size, high number of ALD film chemistries, and maintaining tight dimensional tolerances.

To address these challenges, recycled part cleaning processes and metrology validation methods have been developed. The processes are non-destructive and provide for an Atmosically Clean Surface™ (ACS™) that meets the micro contamination requirements of the most stringent processes. The validation scope spans impurities identification (e.g. trace metals, particles, and trace impurities) and dimensional measurements (e.g. surface roughness, defects, flatness) via use of equipment such as ICP-MS and CMM. Handling systems to provide for employee ergonomics and to protect the parts will also be discussed with regard to the multi-wafer equipment.

In addition, there is smaller demand to refurbish of valves, fittings, and other parts external to the process chamber that may become coated or damaged. Processes have been adapted to address these components as well as ensuring critical dimensions and surface roughness of mating surfaces is maintained.

This paper will review the technologies developed to clean, rinse, dry, and validate that the recycled parts meet performance requirements for various ALD processes.

Keywords: ACS™, ICP-MS, surface cleanliness, micro contamination, non-destructive, CMM

AM-MoP8 Process Control and Mass Delivery Optimization from Low Vapor Pressure Precursors, Jeffrey Spiegelman, C. Ramos, D. Alvarez, Z. Shamsi, RASIRC

Continual device shrinkage and incorporation of new alloy materials has led to difficult thermal constraints for ALD in microelectronic applications. Process temperatures are now required to be to less than 350° C where sub-300° C is desired. PEALD has successfully been used in some applications, but it is usually unsatisfied for 3D structures and aspect ratios greater than 50.

Therefore more reactive oxidant precursors for thermal ALD have been sought where water and ammonia no longer have sufficient reactivity at reduced temperatures. Examples include anhydrous Hydrogen Peroxide and Hydrazine, which exist as low vapor pressure liquids at room temperature. Delivery of a controlled and stable vapor from a liquid source is more challenging than delivering compressed gases with a mass flow controller. Due to the complex nature of chemical liquid-vapor equilibrium, it is difficult to accurately predict the vapor mass output of a liquid precursor for the wide range of ALD operating conditions when solely relying on theoretical models. The liquid phase is in constant equilibrium with its vapor phase counterpart. Slight changes in one, strongly affect the other. Transformation of a liquid to a vapor depends on:

- Ampoule headspace pressure
- Carrier gas flow rate
- Liquid precursor temperature
- ALD precursor pulsing recipe
- Saturation efficiency of the carrier gas with the precursor vapor

Intermolecular forces and binary interactions for multicomponent liquids
- System heat transfer
- Ampoule design

A liquid precursor ALD simulation manifold was built to re-create typical ALD conditions. The system is composed of mass flow and pressure flow controllers, pressure sensors, metering valves, vapor mass flow sensors, and several pneumatic valves. Automated test programs control the valves and sensors to simulate custom ALD process recipes. Data collected from the test fixture can quantify liquid precursor/ampoule vapor mass flow rates at different process pressures, carrier gas flow rates, precursor liquid temperatures, and different pulsing recipes. Mass delivery parameters can thus be optimized for process control and material utilization.

Anhydrous hydrogen peroxide gas can be precisely delivered in the range of 20-300 mg/min at moderate temperatures and pressures. Optimized delivery for several recipes will be presented as a function of pressure and liquid temperature. Conclusions pertinent to several low vapor pressure materials will be discussed.

AM-MoP9 Scaling Low-temperature Thermal ALD of SiO₂ to Batch, J. Kalliomäki, M. Mäntymäki, T. Lehto, S. Shukla, M. Kääriä, T. Sarnet, Juhana Kostamo, Picosun Oy, Finland

Silicon dioxide has become an integral part of the microelectronics industry, due to the abundance of silicon, and the convenient electrical properties of the thermally formed native oxide. As a thin film, SiO₂ can also be used to tailor the mechanical properties of film stacks, act as an etch stop layer or prevent gas diffusion. In industrial manufacturing, the rate of thin film deposition is crucial. Additionally, a low temperature SiO₂ process is desirable to minimize any effect the deposition process will have on other device materials or the substrate itself.

In ALD, SiO₂ has many available chemistries, each with its own pros and cons. The chlorides and chlorosilanes require a deposition temperature of >300°C and can cause particles and chloride impurities in the films. Since these are unacceptable in industrial applications, many amine chemistries have become available. They can fulfill the growth rate, if not always the temperature requirements, required for industrial production.

In general, lower temperature processes is needed as interlayer diffusion must be avoided and the substrates are becoming more sensitive – e.g. organic or polymer substrates might require <200°C thermal budget. The simplest solution, PEALD [1], can however result in sacrificing the higher throughput possibilities that thermal batch ALD can provide. Plasma processes also exhibit limited applicability on higher aspect ratio samples, due to the short lifetime of radical species.

Achieving industrially feasible growth rates at low temperatures with thermal processes is challenging. For example, with a commonly used process such as bis(diethylamino) silane and ozone, the growth rate at 100°C is only <0.1Å per cycle [2]. Most results in literature are also only on single wafers.

We present a reliable low temperature SiO₂ process with growth rates in excess of 1Å per cycle from 60 to 350°C, on single wafers (Figure 1) and in batches, using a precursor with 3 Si atoms and an amine group. While the film thickness increases linearly with the number of cycles, other properties will need to be a compromise between film quality and deposition temperature -- a feature common to many ALD processes. In our example, the impurity content was lower at higher deposition temperatures.

The experiments were made with Picosun™ R-200 Adv, P-300B and P-1000 hot-wall ALD systems. Si wafers with native oxide layers were used as substrates. The ALD process, its scalability to larger batches, and various properties of the resulting thin films were evaluated in this study.

Amongst this class of polymers, Poly(ethylene terephthalate) (PET) is of particular interest due to its widespread industrial usage, thermal stability, and gas and moisture barrier properties stemming from the terephthalate group. The use of conventional deposition reactors operating at high vacuum on flat substrates, but MLD also holds significant promise for a range of substrates. To date, most MLD studies have focused on coating La-Zara.

M. J. Quayle, G. Petersson, S. Folesad, J.R. van Ommen, H. Raza, N. Pinna, F. Pantò, Saveria Santangelo; Tecnologie Molecolari, Italy; S. Patanè, Università di Messina, Italy; A. Dino, Humboldt-Universität zu Berlin, Germany; Saverio Santangelo, Università Mediterranea, Italy

In the last years, thanks to its appealing properties (high abundance, low cost, environmental friendliness, good chemical stability, small energy band gap), hematite has attracted considerable attention as a photocatalyst for the energy production. Electropun -Fe2O3 nanofibers (NFs) have been evaluated in other energy related applications potentially benefiting from their high porosity and large surface area and could also be utilized in less common ones, e.g., as a theranostic agent [1]. Besides, magnetism of nanohematite is a current topic in fundamental research. [2] A study focused on the magnetic properties of electropun -Fe2O3 NFs has shown that the fiber diameter strongly controls the magnetic behaviour [3]. Coating elongated -Fe2O3 nanoparticles (NPs) by silica via sol-gel chemistry allows controlling the saturation magnetisation, remanent magnetisation and coercivity through the thickness of the coating layer [4]. ALD offers the possibility to coat NPs with well-calibrated and conformal thin films, thus facilitating the principle enabling the fine-tuning of the magnetic properties. This contribution focuses on SiO2-coated electropun -Fe2O3 NFs and their nanostructure. The changes of the magnetic properties, with respect to pristine hematite, due to the SiO2-coating are discussed as a function of the number of ALD cycles (10-100) and of the sequence of the production steps (i.e. calcination of the electropun NFs followed by SiO2-ALD or vice versa). SiO2-ALD prior to calcination results in fibers formed by smaller -Fe2O3 grains and by a higher structural disorder. Regardless of the sequence of production steps, ALD coating brings about a local rearrangement process in the oxide lattice with gradual surface defect suppression. These structural changes reflect on the magnetic NF properties, especially coercivity and remanence (Morin temperature).


Molecular layer deposition (MLD) is a vapour phase technique allowing the controlled, layer by layer growth of purely organic thin films on a wide range of substrates. To date, most MLD studies have focused on coating flat substrates, but MLD also holds significant promise for application to particles. In particular, the inherent biocompatibility of organic coatings is of interest to passivate the surface of pigment particles and to tailor the dissolution profile of drug particles. Of the organic coatings produced thus far, polyimide and polyurea coatings predominates, whereas polyester polymerisation chemistry has received considerably less attention. Amongst this class of polymers, Poly(ethylene terephthalate) (PET) is of particular interest due to its widespread industrial usage, thermal stability, and gas and moisture barrier properties stemming from the terephthalate group. The use of conventional deposition reactors operating at vacuum conditions, reported in nearly the entirety of MLD literature, hinders facile and low cost up-scaling. Therefore, the development of processes with better scale-up potential is crucial when aiming for commercial applications, especially when it concerns high-surface area powders.

In this work, we deposit ultrathin PET films on gram-scale batches of TiO2 P25 nanoparticles (NPs) using terephthaloyl chloride and ethylene glycol as precursors. The MLD process is carried out in an atmospheric-pressure fluidized bed reactor at 150-160 °C for a broad range of growth cycles (i.e., from 5 to 50). Ex-situ diffuse reflectance infrared fourier transform spectroscopy (DRIFTS-FTIR) shows the presence of the characteristic C=O stretch of ester groups in the range 1730-1750 cm⁻¹, thus demonstrating the successful MLD reaction. DRIFTS-FTIR and thermogravimetric analysis (TGA) confirm the self-saturating behaviour of the precursors, and the linear increase in mass with the number of cycles. Moreover, TGA highlights the good thermal stability of the PET films, which are stable up to ~225 °C. Transmission electron microscopy (TEM) enables the visualization of uniform PET films on the surface of TiO2-NPs. Preliminary TEM observations suggest a low PET growth per cycle (GPC), around 0.03-0.04 nm. This value seems also in agreement with the GPC estimated by the amount of deposited material on TiO2-NPs measured by TGA as well as with the GPC of PET on SiO2 wafers measured by spectroscopic ellipsometry. Finally, ultrathin PET films are effective in suppressing the photocatalytic activity of the TiO2 P25 NPs, without affecting its absorptive properties in the UV-vis spectrum.

EM-MoP3 Fabrication and Characterization of Organic-Inorganic Hybrid Thin Films, Chu Huang, Hanyang University, Republic of Korea

Currently, the next generation of electronic devices requires new materials that have great properties. The straight way to fabricate new materials is the hybridization of existing materials having different properties. The hybrid materials mixed by organic and inorganic components are expected to have combined properties both of inorganic parts, such as stability and high electrical or optical performance and organic parts with great flexibility and functionality. Furthermore, the hybrid materials are expected to have synergistic effects which are not shown in just one component. In this report, we fabricated new types of organic-inorganic hybrid thin films by molecular layer deposition. The hybrid thin films were made by sequential surface reactions of metal alkyls and bifunctional monomers. Diethylzinc and 2,4-hexadiyne 1,6-diol are used as an inorganic precursor and an organic precursor, respectively, in order to fabricate poly(amin diacetylene). Some methods are used to characterize the microstructure and composition of the hybrid films such as Raman and TEM analysis. And, the electric and optical properties were analyzed by a TET fabrication and photoluminescence spectroscopy, respectively. The high performance of TETs on/off ratio of over 10⁴ and saturation electron mobility of over 10 cm²/V·s. The molecular layer deposition process can proceed under low-temperature condition that indicates the possible use of hybrid films to flexible devices.

EM-MoP4 High Performance Encapsulation Polymer-Al2O3 Hybrid Thin Layer by Atomic Layer Infiltration, Hong Rho Yoon, J. Park, N.V. Long, C. Huang, Hanyang University, Republic of Korea

Encapsulation is an important technology for isolating and protecting air-sensitive materials and is key in the development of new generation flexible electronic devices. Here we report an extremely high performance encapsulation hybrid thin layer prepared by filling the free volume of the polymer with Al2O3 using gas-phase atomic layer infiltration. The high density polymer-inorganic hybrid thin layer shows extremely low gas transmission rate, below the detection limit of the Ca corrosion test (water vapor transmission rate <10⁻² g/m²·2 day⁻¹). Furthermore, because of the remarkable nanometer-scale thickness of the complete polymer-inorganic hybrid, it is highly flexible, which makes it useful for encapsulation technology of new generation flexible devices.

EM-MoP5 ALD of Metal Oxides Fabricated by using La(NO3)3·6H2O Oxidant and their Applications, In-Sung Park, S.Y. Kim, T. Lee, S. Seong, Y.C. Jung, J. Ahn, Hanyang University, Republic of Korea

The oxide films with high-k including Al2O3, HfO2, and ZrO2 have been widely applied to dielectric of capacitor devices in fabrication of semiconductor memory. Recently, ALD method has been widely spreading to make the ultra-thin, conformal, and wide-uniform deposition areas in spite of its very low productivity. In ALD process, the selection of oxidant is very important because of the variability of film characteristics such as growth rate, ALD temperature window, crystalline structure, contamination, and dielectric/electrical properties. In this work, the using of La(NO3)3·6H2O catalytic oxidant will be focused to fabricate HfO2 films for insulator of resistor and dielectric of capacitor. The H2O oxidant was used to make above films for the comparison. The devices with metal-insulator-metal structure were prepared and their electrical properties were also compared.

HfO2 films were synthesized by ALD method using Hf(NCH3C2H5)4 precursor and La(NO3)3·6H2O:6H2O solution, which is catalyst and oxidant. The growth rate of HfO2 film made with La(NO3)3·6H2O solution is approximately three times faster than that with H2O oxidant. The La(NO3)3·6H2O solution effectively altered the surface roughness, crystalline state, and resistive switching properties of HfO2 films. In spite of the same crystalline structure of both HfO2 films made with La(NO3)3·6H2O and H2O, the surface roughness of
Although literature shows that TMA readily coordinates onto carbonyl groups of the acrylonitrile unit, the density of the resulting aluminum derivatives in PMMA is eliminated to the density of carbonyl groups. By increasing the carbonyl density in the monomer unit of the polymer, we can expect to have higher aluminum content in the polymer after the infiltration process which could result in higher etch-resistance.

Recently we have synthesized a polymer having two or more carbonyl groups branched on the main-chain to increase carbonyl density compared to PMMA. Evidences show that TMA was infiltrated into the polymer at a higher density compared to that of PMMA and the etch-resistance increased as the aluminum content increased. Our novel strategy shows further pathways for future applications.


Infiltration synthesis is an emerging technology that enables to realize organic-inorganic hybrid materials. The gaseous metal precursors penetrate into polymers followed by oxidation process, which stabilizes the metal derivatives into the polymer-matrix. Up to date, many fundamental studies have been carried out on the infiltration of trimethylaluminum (TMA) into poly(methylmethacrylate) (PMMA) thin films[1][2]. There has also been reported that TMA is selectively infiltrated to PMMA phase of the phase-separated block copolymer of PMMA and polystyrene, where etch-resistance of infiltrated PMMA is remarkably increased[3].

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Multiferroic materials of simple stoichiometry may have prospective applications in memory and sensor technologies, especially if they could be produced at low temperatures over large area substrates by ALD. Tetragonal or cubic zirconic ZrO2 has found to be ferromagnetic [1], and, when combined with HfO2 by ALD, behaved as a ferroelectric material[2]. Therefore, it is of interest to investigate if ZrO2 coupled with another metal oxide would exhibit both ferromagnetic and ferroelectric hysteresis behavior in the same material sample.

We have studied, for instance, ZrO2–Fe3O4, ZrO2–Co3O4, ZrO2–HfO2, ZrO2–Co3O4 and ZrO2–Co3O4–Fe3O4 mixed layers or nanolaminates grown by ALD from ZrCl4, Fe(OAc)3, HfCl4, Co(acac)3, H2O and/or O2 mostly at 300 °C. The composition of the films could be controlled by varying the ratio of constituent metal oxide cycles. Structural evaluation revealed dominantly tetragonal or cubic ZrO2. All oxides, as deposited, exhibited magnetization field behavior characteristic of that in ferromagnetic materials. Most of the films in as-deposited state also showed certain remnant charge polarization in their charge field dependences. The behavior could be strongly influenced by the charge transport and interface charge trapping. Certain ferroelectric component contributions to the polarization could not be neglected, although the charging was probably overwhelmed by leakage currents. Nonetheless, in some films, in particular ZrO2–HfO2, hysteresis loops implying both ferromagnetic and ferroelectric components in the materials could be observed. In this presentation, performance of different oxides as potential multiferroic host materials will be comparatively discussed.


EM-MoP8: Vapor Phase Infiltration as a New Approach in the Fabrication of Advanced Hybrid Thermoelectric Materials, Jaime DuMont, M. Knez, CIC-nanoGUNE, Spain
Hybrid organic-inorganic materials are rising stars in the field of thermoelectrics (TE), whose principal aim is to salvage the rejected heat of energy conversion processes by directly converting waste heat into electrical energy. With two birds, one stone. TMA, required for global power consumption lost to the environment each year, the development of flexible, non-toxic, inexpensive and scalable TE materials would be of great economic and environmental interest. Realizing this ambition will require a new approach that can break away from the rare, toxic and expensive materials that have dominated the field until now.

This next generation of hybrid TE materials will require a synthesis strategy which 1) functions at temperatures low enough to not destructively act on the polymer 2) can tune the electrical and thermal conductivity of the hybrid material for optimal TE performance 3) maintain a strong chemical binding between the organic and inorganic components for long term stability and operational efficiency and 4) can be easily scaled for large area applications. Vapor phase infiltration (VPI) is a technique primed to meet these requirements. In this work we will survey VPI processes of various transition metal compounds for the top-down fabrication of metal-poly(3-hexyl)thiophene (P3HT) hybrids as promising candidates for advanced TE materials. By monitoring the electrical conductivity and thermopower of these novel hybrid materials, we will show how the VPI process can be used to generate and optimize a new set of thermoelectric materials.

EM-MoP9: Low-temperature Atomic Layer Deposition of Aluminum Oxide on Polymeric Powder Feedstocks for Improved Powder Rheology, John Miller, C. Gillespie, J. Chesser, Lawrence Livermore National Laboratory; A. Schepp, United States Air Force Academy; A. Nelson, N. Teslich, A. Lange, S. Elhadji, R. Reeves, Lawrence Livermore National Lab
Some organic materials of interest in the additive manufacturing industry require inkjet/colloid based processes to avoid degrading the properties of the material of interest. Some of these organic feedstocks are cohesive in nature and tend to form agglomerates in suspensions, making them undesirable for use in additive manufacturing printing processes. Atomic Layer Deposition (ALD) can be used as a technique to change the surface property of the material without changing the properties of the bulk material of interest. ALD sequentially pumps reactive precursors into and out of a reactor vessel, which react on the surface of a desired substrate to form films with sub-nm level control. This paper studies the reduced temperature ALD deposition of aluminum oxide on polystyrene/Si reference flats and melamine and nylon organic powder feedstocks for coating quality and its effect on the powder rheology and cohesivity. The result is a mixed amorphous phase aluminum oxide-hydroxide coating that is both highly uniform and conformal on the powder’s surface. Alumina coatings on the nylon powders did not produce a significant change in the flow properties of the powder, due to the initial low cohesivity of nylon. The melamine however experienced significant improvements to flowability due to a reduction in cohesivity of the melamine feedstocks from the surface coating. Results show that thin coatings of 20 mm or less on these feedstocks can remarkably improve their surface chemistry for use in additive manufacturing processes.

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The atomic layer deposition (ALD) of MoO(x)C and MoC films is described using MoCl5 and the co-reactants oxalic acid or formic acid. Self-limited ALD growth was demonstrated at 350 °C for MoCl5 and oxalic acid, however, the growth rate decreased at long MoCl5 doses, consistent with etching. The growth rate of the MoCl5 and oxalic acid process was 0.18 Å/cycle within an ALD window of 325-400 °C. The resistivities of the films decreased with increasing deposition temperature and was 366 μΩ cm for an 18 nm thick film grown at 400 °C. A plot of thickness versus number of cycles was linear with no nucleation delay. X-ray diffraction of the as-deposited films was consistent with nanocrystalline MoO(x)C. Atomic force microscopy of 18 nm thick films grown with MoCl5 and oxalic acid in the ALD window gave RMS roughnesses of 0.49-0.56 nm, indicating very smooth surfaces. X-ray photoelectron spectroscopy (XPS)
showed Mo, O, and C in the films, with low levels of other elements. The films obtained using MoCl₅ and oxalic acid are thus Mo(O,C). Formic acid was also used with MoO₃ as a co-reactant, since oxalic acid decomposes thermally at high temperatures to formic acid and CO₂. A plot of growth rate versus pulse length showed self-limited growth at 400 °C, but a plot of growth rate versus deposition temperature did not show an ALD window between 400–450 °C. Films grown with formic acid at 400 and 450 °C with thicknesses of 28.5 and 48.1 nm, respectively, showed RMS roughnesses between 0.55 and 0.59 nm. XPS of a film grown using MoCl₅ and formic acid at 450 °C showed a composition of MoC, with low oxygen and chlorine levels. The resistivity of a 48 nm thick Mo film grown at 450 °C with 1000 cycles was 177 μΩ·cm.


An atomic layer deposition (ALD) process is reported for the growth of PrAlO₃ thin films using tris(isopropylcyclopentadienyl)praseodymium (Pr(C₅H₄iPr)₃), trimethylaluminum (AlMe₃), and water. Pr(C₅H₄iPr)₃ was chosen as a precursor because of its good volatility, high thermal stability, and high reactivity with water. Pr(C₅H₄iPr)₃ was first evaluated as a precursor for the formation of Pr₂O₃ films using water as the co-reactant. Self-limited growth was demonstrated for pulse lengths of ≥3 s, with a growth rate of ~0.85 Å/cycle. An ALD window was observed between 275 and 350 °C, and the as-deposited Pr₂O₃ films were crystalline. The ALD growth PrAlO₃ films was examined next on Si(100) and SiO₂ substrates. Self-limited growth was demonstrated for Pr(C₅H₄iPr)₃, AlMe₃, and water at 300 °C using a 1:1 ratio of Pr(C₅H₄iPr)₃ and AlMe₃ pulses. An ALD window was observed from 275 to 325 °C with a growth rate of ~1.7 Å/cycle. The increase in film thickness as a function of the number of cycles at 300 °C was linear and showed a small nucleation delay. The as-deposited PrAlO₃ films were amorphous, had smooth surfaces, and contained <0.5% carbon and chlorine, as analyzed by grazing incidence wide-angle X-ray scattering, X-ray reflectivity and atomic force microscopy, and X-ray photoelectron spectroscopy, respectively. The films grown with a 1:1 ratio of Pr(C₅H₄iPr)₃ and AlMe₃ pulses were slightly aluminum-rich (PrAlO₃.12-1.4) by electron probe microanalysis. As deposited PrAlO₃ films grown on single crystal (100) SrTiO₃ substrates at 300 °C were amorphous and annealing at 800 °C for 3 h resulted in fully crystallized PrAlO₃ films. The crystallized PrAlO₃ films were highly (001)-oriented with a small population of polycrystalline grains with other orientations. The PrAlO₃ 00L and SrTiO₃ 00L reflections appeared on the same rod of reciprocal space, further indicating that the amorphous PrAlO₃ film transforms into an epitaxial layer. The rocking curve width of the PrAlO₃ (001) reflection was 9°. By contrast, PrAlO₃ films deposited on Si(100) substrates with native SiO₂ remained amorphous after annealing at 1000 °C for 8 h. The difference in the crystallization between PrAlO₃ layers deposited on crystalline SrTiO₃ and amorphous native SiO₂ substrates indicates that PrAlO₃ on SrTiO₃ crystallized by solid phase epitaxy, in which the nucleation and orientation of the crystallized layer is set by the substrate.

**EM-MoP12 Homogeneous Distribution of Dopants in ALD Films: Tin-Doped Zinc Oxide (ZTO) Case Study, Tiratrina Muneshwar, D. Barlage, K. Cadien, University of Alberta, Canada**

ALD is a well-established thin film deposition technique where the material growth stems from the stacking of partial atomic monolayer in each surface reaction step. Being a bottom-up approach, doping of ALD could be readily achieved from introduction of dopant species during growth. For example, the well-known ALD reaction scheme for deposition of tin-doped AlOₓ is periodically deposit oxides AO with n₁ cycles and BO with n₂ cycles (super-cycle: n₁ AO + n₂ BO). Although the relative A/B content is precisely controlled by changing the ratio of the sub-cycles, the resulting multilayered structure would have a non-homogeneous dopant-B distribution (hence may require additional processing steps like annealing, ion bombardment, etc.). To overcome this limitation we demonstrate a method for homogeneously doped ALD films with BAOBAO... pulsing sequence. We show that the choice of dopant precursor, process parameter and also the sequence (ABO... or BOA...) are critical in controlling dopant concentration. As example we report our early results on tin-doped zinc oxide (ZTO) ALD films grown at 50 °C substrate temperature using tetraethylzinc (TAEZn), diethyl zinc (DEZ), and remote ICP O₂ plasma. We show that the pulsing sequence Sn/ZnO gives a better control over Sn-content in ZTO films. With increasing Sn-content, measured room temperature electrical resistivity (p=θ) of as-grown ZTO films (each ~24 nm thick) was found to systematically decrease from 450 Ω-cm for ZnO, to 19.72 Ω-cm, 5.7×10⁴ Ω-cm, and 2.8×10⁵ Ω-cm for samples ZTO#1, ZTO#2 and ZTO#3 respectively.

**EM-MoP13 Uniform, Thermal ALD of Al₂O₃ and ZnO on Zirconia Particles, Drhuv Shah, D. Patel, J. O’Tani, M. Linford, Brigham Young University**

The technical literature contains relatively little on the topic of atomic layer deposition (ALD) on particles. Here we report thermal ALD of thin films of alumina and zinc oxide on zirconia powder substrates from trimethylaluminum and water, and diethylzinc and water, respectively. Very similar growth was obtained when oxygen was substituted for water in these depositions. Depositions were optimized by varying the dose and purge times for the precursors with an aim to obtain uniform film thickness and growth per cycle (GPC). X-ray photoelectron spectroscopy (XPS) clearly showed an increase in surface aluminum and zinc with increasing numbers of ALD cycles. Transmission electron microscopy (TEM) showed uniform film growth and particle coverage. Film thicknesses were also measured on planar witness shards by spectroscopic ellipsometry (SE). Ultimately, up to 10 nm films of alumina and zinc oxide were grown on zirconia particles via 100 ALD cycles.

**EM-MoP14 Composite Control of Ge-Sb-Te Film by Supercycles of ALD GeSb and ALD Sb Followed by Tellurization Annealing, Yewon Kim, J. Lee, Sejong University, Republic of Korea; S.J. Baik, Hankyong National University, Republic of Korea; W. Koh, UP Chemical Co., Ltd., Republic of Korea; W.-J. Lee, Sejong University, Republic of Korea**

Phase change random-access memory (PCRAM) is getting attention as storage class memory (SCM) which is can fill the performance and cost gap between DRAM and NAND flash. Ge-Sb-Te (GST) compounds have been extensively studied due to their fast switching speed and high data retention. The GST thin films were prepared by physical vapor deposition, chemical vapor deposition and atomic layer deposition (ALD) techniques. As the mushroom structure changes to confined cell structure because of thermal interference, ALD technique is needed in order to deposit a thin film in a nano-size hole. Conventional ALD GST film was prepared with ALD GeTe and ALD Sb2Te3 supercycle. This method is complicated and deposited as amorphous during deposition, resulting in void formation during repeated PCRAM operation. In previous work, we prepared GST film by tellurization of ALD Ge-Sb. This process simplifies the supercycle ALD GST process and can form a crystalline GST thin film. Also, the incorporation of Te improves the gap fill characteristic by expanding the volume. Tellurization of the ALD Ge-Sb film could control the composition of Te by the tellurization temperature or the number of cycles, however it cannot control the composition ratio of Ge to Sb. Since the switching speed and durability of the phase change memory cell depend on the composition of the GST film, a method of controlling the composition ratio of Ge and Sb in the GST film is also required. In the present work, GST films with different compositions were prepared by ALD super-cycle process consisting of ALD Ge-Sb and ALD Sb. The composition ratio of Ge to Sb was controlled by changing the ratio of the sub-cycles. The temperature and growth rate of ALD Ge-Sb and ALD Sb were investigated to determine the temperature and sub-cycle ratios of the super-cycle process. Ge-Sb films of different compositions were prepared by ALD super-cycle processes and then annealed in a tellurium atmosphere. The composition and phase transition temperature of the GST thin films were examined before and after the tellurium annealing. The phase transition temperature was tunable by controlling the subcycle ratio or tellurization conditions. Step coverage and gap filling characteristics were also investigated.

**EM-MoP15 Study on The Crystallinity and The Dielectric Constant of ZrₓGeₓO_{3+x} Films using Mixed Zr - Ge Precursor by Atomic Layer Deposition, Ju Young Jeong, Y. Han, H. Sohn, Yonsei University, Korea; H. Noh, H. Park, SK Hynix Inc**

Scaling of Dynamic Random Access Memory (DRAM) requires high k dielectric materials for data storage capacitor. ZrO₂ is favorite material for storage capacitors because of large band gap, low leakage current, good thermal stability. Dielectric constant of ZrO₂ depends on the crystal structure (monoclinic =19.7, cubic = 36.8, tetragonal=46.6). It was reported that doping of ZrO₂ with elements such as Mg, Ca, Y, La, and Ge enhances tetragonal phase of ZrO₂. In general, such elements are incorporated in ZrO₂ using laminated growth structure.

In this study, Ge-doped ZrO₂ films were fabricated using mixed Zr-Ge precursor (Cp₂Zr(NC₅H₅)₂).
8:00am AA1-TuM1 ALD for Solar Fuels: Rendering Halide Perovskites Acid- Compatible + Precision Cluster Electrocatalysts. Alex Martinez, J. S. Kim, M. Bello, Argonne National Laboratory — INVITED

Although solution-processable halide perovskite semiconductors exhibit optoelectronic performance comparable to the best photovoltaics for solar fuel production, halide perovskites rapidly decompose in the presence of water or even humid air. We show that a hybrid electron transport layer, a β-C$_2$H$_5$MnO$_3$ film (18±40 nm thickness) grown over the solar cell absorber layer, provides a stable post-deposition, low-cost, passivation layer that increases proton reduction without further encapsulation. These semitransparent photocathodes, when paired with a Pt catalyst, display continuous reduction of H$^+$ to H$_2$, hours under illumination, even while in direct contact with a strongly acidic aqueous electrolyte (0.5 M H$_2$SO$_4$). More affordable and active catalysts for more challenging solar-to-fuels reactions (e.g. N$_2$ or CO$_2$ reduction) will require catalysts with exquisite precision. The bottom-up, selective ALD synthesis of controlled-atom-number clusters will also be discussed as a potentially powerful route to designer solar fuels cathode catalysts.


Water splitting is a viable approach to enable storage of renewable energy in the form of fuels. Major issues hampering the development and implementation of this technology are the high cost associated with the use of noble-metal-based electro-catalysts; the sluggish kinetics of the oxygen evolution reaction (OER). Cost-effective, transition metal-based electro-catalysts [1], e.g. cobalt phosphate (CoPi), show promising results in terms of performance towards OER. So far, CoPi has been synthesized by electro-deposition with severe limits in the control of layer thickness and chemical composition, the latter being highly influenced by the choice of precursors, electrolyte and pH. Instead, a higher level of control in terms of layer thickness and tunable stoichiometry is expected when adopting ALD.

In the present work we synthesize CoPi thin films by plasma-assisted ALD [2]. The process is based on an ABCD scheme, where A and C are the cobaltocene (CoCp) and trimethylphosphate (TMP) exposure steps. B and D correspond to O$_2$ plasma steps. CoPi layers, characterized by a stoichiometry of Co$_{2x}$(PO$_4$)$_2$($x$), are deposited at 300°C with a growth per cycle of 1.1 Å, as determined by in-situ spectroscopic ellipsometry. Cyclic voltammetry shows that the ALD CoPi layer exhibits a current density peak of 1.8 mA/cm$^2$ at 1.8 V vs. Reversible Hydrogen Electrode (RHE). This value is comparable to those reported in literature for electro-deposited CoPi. Since cobalt is recognized in literature as reactive center governing the electrocatalytic activity [3], we also investigate the effect of Co-to-P concentration ratio on the OER. The deposition process is then based on a (AB)$_n$CD$_n$ supercycle. For just 1 extra AB cycle, accompanied by 11 cycles of CoPi (x = 12; y = 11), a Co-rich stoichiometry ($\text{Co}_4\text{PO}_{12}$$^{12}$) is achieved. The later leads a higher current density peak (2.9 mA/cm$^2$ at 1.8 V vs RHE) than the earlier addressed CoPi sample. When comparing the performance of the ALD Co-rich CoPi layer with electro-deposited CoPi [4] in terms of current density, the former exhibits superior OER performance. These results highlight the role that stoichiometry of cobalt phosphate has on its OER activity, suggesting that tuning the Co-to-P ratio can be adopted as approach to design efficient Co-based electro-catalysts for OER.


8:45am AA1-TuM4 Improved Electrochemical Activity of Pt Catalyst Fabricated by Vertical Forced-Flow Atomic Layer Deposition. Tzu-Kang Chin, T.-P. Perng, National Tsing Hua University, Republic of China

Currently, carbon black is the most commonly used support material for depositing platinum (Pt) nanoparticle catalyst by wet chemical reduction of Pt salts in aqueous solution. However, oxidation of carbon black occurs under highly humid atmosphere and corrosive operating condition of proton exchange membrane fuel cell (PEMFC), which results in agglomeration of Pt nanoparticles, leading to degradation of catalytic performance. In addition, Pt nanoparticles fabricated by wet chemical reduction require additional steps to purify, such as removing the residual capping agent, and post-treatment to increase the crystallinity of Pt. Consequently, it is urgent to develop a novel support material with high electrical conductivity and electrochemical stability and a more facile fabrication method for Pt catalyst. Titanium oxyxidride (TiO$_n$N$_m$) is an intermediate phase which is regarded as a solid solution of titanium nitride (TiN) and the cubic titanium oxide (TiO). It has been reported that the Pt deposited on TiO$_n$N$_m$ results in significant enhancements of specific activity, mass activity, and corrosion resistance compared to that deposited onto carbonous support material. Atomic layer deposition (ALD) is a dry process that is able to deposit materials without contamination from capillary condensation and residual organic compounds. Pt catalyst prepared by ALD has advantages of high activity and precise particle size control. However, the uniformity and conformity of the coating by conventional ALD equipment on high aspect-ratio or porous substrate is still a great challenge to overcome. To solve this problem, a novel forced-flow configuration was designed recently by our group, i.e., vertical forced-flow ALD. In this study, conductive TiO$_n$N$_m$ nanoparticles were fabricated and investigated for the potential application in PEMFC as a catalyst support material. Vertical forced-flow ALD was utilized to deposit Pt nanoparticles with very small particle size uniformly on TiO$_n$N$_m$. The electrochemical activities were examined by cyclic voltammetry and oxygen reduction reaction. The Pt nanoparticles deposited on TiO$_n$N$_m$ with 30 cycles show 2-3 times higher electrochemical surface area and also larger half-wave potential of oxygen reduction reaction than those of Pt prepared by conventional wet chemical reduction and commercial E-tek electrolyt catalyst.

9:00am AA1-TuM5 Improved Catalyst Selectivity and Longevity using Atomic Layer Deposition. A. Dameron, R. Tracy, Forge Nano; C. Nicholas, L. Abrams, B. Barger, Honeywell UOP; T. Li, Lu Zheng, Argonne National Laboratory

Introduction

Many important industrial scale chemical reactions rely on catalysts and require high temperatures to achieve commercially viable product yields. However, catalysts deactivate over time and lose surface area due to thermal degradation (sintering) and poisoning. Decreasing catalytic activity results in lower selectivity and higher yields of unwanted byproducts. In many cases, the remedy for sintering of metals is to raise the reactor temperature and thus increase energy consumption, or to remove and replace the spent catalyst, which is expensive and leads to loss in productivity.

This project is overcoming catalyst degradation issues via an ALD overcoating technology that deposits protective layers around the active metal, preserving catalyst integrity under reaction conditions. The ALD overcoating technique applies one or more protective layers to the catalyst to inhibit metal sintering. Channels introduced into the ALD layers provide reactants with access to the catalyst’s active metal and improve reaction selectivity. This project is applying the overcoating technology to extruded platinum-based catalysts used in the propane dehydrogenation (PDH) to propylene. Improvements in both the efficiency and selectivity reduce the energy required for the process.

Materials and Methods

Alumina extrudates were synthesized by peptizing Versal-251 and extruding it into 1/16” cylinders. The dried extrudates are calcined at temperatures ranging from 500°C to 1185°C to generate Al$_2$O$_3$ bases with varying surface area and porosity. Pt is impregnated via standard incipient wetness techniques.

ALD is performed in fixed bed reactors typically at 200 °C during all depositions. Precursors for Al$_2$O$_3$ were TMA and H$_2$O, while for TiO$_2$ they were TiCl$_4$ and H$_2$O. Depositions are monitored in situ by measuring the reaction composition downstream of the reactor with a quadrupole mass spectrometer.
Results and Discussion

The project team applied overcoatings with different shell thicknesses and compositions. Initial investigations were carried out with TiCl₄ to distinguish overcoated layers from the catalyst base. The growth rate of TiO₂ measured by ellipsometry is 0.4Å/cycle, which is similar to previously reported studies. The TiCl₄ dose and soak time were then increased to investigate whether Co/Co₂C activity towards higher oxygenates could be increased, and its bands are favorably positioned for water oxidation. BVO has demonstrated potential for high anodic photocurrents, but it is limited by electron-hole separation, charge transport, and water oxidation kinetics. The development of an ALD process for BVO enables core-shell architectures that help address the charge transport and carrier separation challenges by decoupling carrier diffusion and light absorption lengths.

In this study we demonstrate the deposition of ALD BVO using B(OCMe₃)₃/Pt as the bismuth source, vanadium(V) oxytrispropanoxide as the vanadium source, and water as the oxidant [1]. The choice of this Bi precursor provides full control of Bi²⁺ stoichiometry. The BVO films were deposited as a nanolaminate of binary bismuth and vanadium oxides and then post-annealed to achieve the photoactive monoclinic BiVO₃ phase. Film composition and photocurrent were investigated as a function of deposition pulse ratio and film thickness. Additionally, we demonstrate 3D nanostructured BVO photoanodes by depositing the BVO on ZnO nanowires with an ALD SnO₂ interlayer.

The photocactivity of the ALD BVO photoanodes was measured in a three-electrode cell under simulated AM1.5G illumination. A planar photoanode of 42 nm thick BVO produced a photocurrent density of 2.24 mA/cm² at 1.23 V vs. RHE (reversible hydrogen electrode) and the application of a ZnO nanowire substrate provided a 54% increase in photocurrent to 3.45 mA/cm² at 1.23 V vs. RHE. These values are the highest reported to date for any photoanode using an ALD film as the primary light absorber.


9:45am AA1-TuM8 Improved Photocatalytic Efficiency by Depositing Pt and SiO₂ on TiO₂ (P25) using Atomic Layer Deposition in a Fluidized Bed, Dominik Benz, H. Nugteren, H. Hintzen, M. Kreutzer, R. van Ommen, Delft University of Technology, Netherlands

Photocatalysts for water cleaning typically lack efficiency for practical and economical applications. Here we present a new material that was developed using knowledge of working mechanisms of catalysts and the capabilities of Atomic Layer Deposition (ALD). The deposition of ultrathin SiO₂ layers on TiO₂ nanoparticles, applying ALD in a fluidized bed reactor, showed in earlier studies in our group their beneficial effects for the photocatalytic degradation of organic pollutants. There we assumed that due to the surface modification with SiO₂ the surface becomes more acidic which benefits the hydroxyl radical generation. Furthermore, we have investigated the role of Pt on P25 as an improved photocatalyst. There we found the main reason for the catalytic improvement is adsorbed oxygen on the Pt particles, which is an important reactant in the photocatalytic degradation process of organic pollutants. Having recognized, that the two independent materials, SiO₂:P25 and Pt:P25, have different mechanisms improving the photocatalytic activity gave us the opportunity to combine these two materials into a new material, where we deposited SiO₂ onto P25 followed by deposition of nanoclusters of Pt. Indeed, this new material exceeded the performance of the individual SiO₂:P25 and Pt:P25 catalysts. This unconventional approach shows that by understanding the individual materials’ behavior and using ALD as an appropriate deposition technique, new materials can be developed, further improving the (photo-)catalytic activity and moving one step closer to implementation. We will demonstrate that ALD is an attractive technology to produce the catalysts developed by this approach in a precise and scalable way.

ALD Applications

Grand Ballroom E-G - Session AA2-TuM

ALD for Batteries I

Moderators: Neil P. Dasgupta, University of Michigan, Noemi Leick, National Renewable Energy Laboratory


Solid electrolytes could enable significant improvements in the energy density, cycle life, and safety of next-generation battery chemistries. The ability to fabricate thin electrolyte films with high ionic conductivity and electrochemical stability on complex architectures has been a bottleneck to realizing a wide range of 3D structured thin-film and bulk batteries. Recent progress in ALD for solid electrolytes has shown great promise, and there is significant interest in realizing materials with even higher conductivities and stability with Li metal anodes in order to dramatically enhance the energy density of ALD-based batteries. High ionic conductivity and good stability could be used for interfacing engineering of bulk-type solid and liquid based batteries to improve stability and safety.

This work demonstrates a novel ALD process for glassy lithium borate-carbonate thin films with ionic conductivities above 10⁻⁶ S/cm at 298K [1]. This is the highest reported value to date for any ALD-deposited solid electrolyte. The composition, structure, and stability of the films are characterized with X-ray photoelectron spectroscopy and a range of electrochemical measurements. These experiments are compared with
those calculated with Density Functional Theory and Molecular Dynamics to elucidate the origins of the high ionic conductivity and excellent stability. The film properties are studied as a function of ALD deposition temperature, showing tradeoffs between process conditions and performance, and demonstrating the precise control afforded by the ALD process. The optimized film materials remain an ionic conductor when in contact with metallic Li, with no measurable changes after several weeks, and displays stable cycling when paired with a thin-film cathode and Li metal anode. This new ALD film material and process represents a pathway towards interfacial engineering of both thin-film and bulk solid-state batteries, enabling stable cycling against Li metal anodes.


11:00am AA2-TuM13 ALD Interlayers for Stabilization of Li+GeP3S12 Solid Electrolytes Against Li Metal Anodes, Andrew Davis, University of Michigan; K. W. Weis, Interface Science Research Institute, National Renewable Energy Laboratory; R. Garcia-Mendez, E. Kazyak, K.-H. Chen, J. Sakamoto, University of Michigan; G. Teeter, National Renewable Energy Laboratory; N.P. Dasgupta, University of Michigan

Solid-state batteries based on high-ionic-conductivity solid electrolytes are a promising technology to increase battery lifetime and capacity, and reduce safety concerns associated with flammability. In recent years, sulfide solid electrolytes such as Li10GeP2S12 (LGPS) have achieved ionic conductivities comparable to or higher than that of traditional liquid electrolytes. Despite these promising breakthroughs, realization of sulfide solid-state batteries with high capacities and energy densities has proved elusive. This can be attributed to the narrow electrochemical stability window of sulfide electrolytes, which leads to undesirable reactions at the electrolyte-electrode interface against both high voltage cathode materials and Li metal anodes. This forms an unstable solid electrolyte interphase (SEI), which dramatically degrades battery performance. Artificial SEIs made of ALD interlayers have recently been explored as a method of increasing stability of the Li metal/solid electrolyte interface. ALD allows for conformal, pinhole free coating of the LGPS which protects the surface from direct contact with lithium metal while facilitating Li-ion transport across the interface.

In this study, we explore the impact of ALD interlayers at the LGPS-Li metal interface, in order to gain a deeper fundamental understanding of the dynamic evolution of the SEI. A multi-modal characterization approach was performed that combined electrochemical measurements, operando X-ray photoelectron spectroscopy (XPS), in-situ auger spectroscopy, scanning electron microscopy (SEM), and optical microscopy. This allowed for quantitative evaluation of the time-dependent degradation of the interface, which occurs due to the evolution of a variety of decomposition by-products. ALD coated samples exhibited significantly less decomposition of the LGPS interface. Operando XPS was used to correlate the distinct decomposition products that correspond to increases in overpotential [1]. Auger, SEM and optical mapping of the surface shows spatial inhomogeneities that lead to preferential Li plating and corresponding Li2GeP2S5 breakdown. These observations were rationalized in the context of bulk solid-state batteries employing Li metal anodes, demonstrating the advantages and challenges associated with ALD modification of solid-state battery interfaces.


11:15am AA2-TuM14 ALD and MLD on Lithium Metal – A Practical Approach Toward Enabling Safe, Long Lasting, High Energy Density Batteries, Andrew Lushington, Arradance; Y. Zhao, L. Goncharova, Q. Sun, R. Li, X. Sun, University of Western Ontario, Canada

Global warming and rising levels of atmospheric CO2 have resulted in a rapid search for alternative energy sources. Among the possible portable energy storage systems available, lithium-based batteries have the highest theoretical energy density. Unfortunately, current battery technology is approaching its limits and research toward alternative battery chemistries with higher energy density, such as Li-S, Li-O2 and all solid-state batteries, is required to meet future energy storage demands. However, these next-generation batteries require the use of a pure Li-metal anode. Li metal has a high specific capacity of 3860 mAh g−1, a value 10X greater than the standard graphite anode (370 mAh g−1) used today. Unfortunately, Li-metal is highly reactive and forms a high surface area mossy-like reaction product with the electrolyte, known as the solid electrolyte interface (SEI). The uncontrolled growth of this SEI rapidly consumes liquid electrolyte, drying up the battery and causing it to quickly fail. This problem is further exacerbated by dendrite growth which can short circuit the battery, posing a significant safety threat. One effective strategy for mitigating these problems is to use Atomic layer deposition (ALD) and molecular layer deposition (MLD) to coat the surface of electrolytes. This strategy has been shown to help form a stable SEI layer and improve battery longevity.

Herein we compare the stripping and plating behavior of Li-metal coated using 3 different ALD and MLD films. Galvanostatic cycling revealed that MLD coated electrodes vastly outperform ALD coated ones. We use Gravimetric Intermersion Titration Technique (GIT) to carefully analyze the voltage behavior of coated electrodes and disseminate the key MLD film properties that enable the formation of a stable SEI layer. Additionally, electrode morphology was examined using scanning electron microscopy along with Rutherford backscattering spectroscopy to reveal the composition of the SEI. To further demonstrate the practicality of MLD coated Li-metal, full cell batteries using lithium iron phosphate and carbon-sulfur as a cathode was performed. This presentation provides the necessary fundamental understanding of the hurdles that face the commercialization of lithium metal anodes and how ALD/MLD can be used to address these challenges.


11:30am AA2-TuM15 Synergistic Effect of 3D Current Collectors and ALD Surface Modification for High Coulombic Efficiency Lithium Metal Anodes, Kuan-Hung Chen, A. Sanchez, E. Kazyak, A. Davis, N.P. Dasgupta, University of Michigan

Improving the performance of Li metal anodes is a critical bottleneck to enable next-generation battery systems beyond Li-ion. However, stability issues originating from undesirable electrode/electrolyte interactions and Li dendrite formation have impaired long-term cycling of Li metal anodes. In this work, we demonstrate a bottom-up fabrication process using templated electrodeposition of vertically aligned Cu pillars, which are subsequently coated by an ultrathin layer of ZnO by atomic layer deposition (ALD) to form a 3D core-shell geometry with precise thickness control [1]. Transmission electron microscopy (TEM) analysis was performed to show the uniform thickness and core-shell geometry on the pillar surface. We demonstrate the application of these core-shell 3-D architectures as an efficient current collector for Li metal electrodeposition and dissolution. By rationally tuning geometric parameters of the 3D current collector architecture, including pillar diameter, spacing, length, and ALD shell thickness, the morphology of Li plating/stripping upon cycling can be controlled.

We further demonstrate the mechanistic role of the ZnO shell on current collector surface, which facilitates the initial Li nucleation, and influences the morphology and reversibility of subsequent cycling. The improved nucleation is correlated with increased wettability of molten Li metal, which is quantitively evaluated using a sessile drop test inside of an argon glovebox. The resulting core-shell pillar architecture allows for the geometry and surface chemistry to be decoupled and individually controlled to optimize the electrode performance. Leveraging the synergistic effects of the optimized 3D geometry and ALD surface modification, we have demonstrated cycling of Li metal anodes with Coulombic efficiency of 99.5%, which is among the highest reported values to date for any Li metal anode. The results from this work thus provide a pathway toward high-efficiency and long-cycle life Li metal batteries with reduced excess Li loading.


11:45am AA2-TuM16 Atomic Layer Deposition FeS@CNT from Elemental Sulfur as an Electrode for Lithium-Ion batteries, Hongzheng Zhu, J. Liu, University of British Columbia, Canada

Iron sulfide (FeS) is regarded as an attractive anode material for high-performance LIBs because of its high lithium storage capability, natural abundance, and ecofriendly. However, FeS suffers from low reversible capacity and large volume change (200%) during charging and discharging process, resulting in mechanical degradation of cracking and loss of electrical connection with current collectors and then rapid capacity loss [1]. In order to overcome these problems, we choose ALD Atomic Layer
is already possible to deposit such films with high quality. However, cobalt metal film growth by atomic layer deposition (ALD) is required to satisfy conformity and thickness requirements in nanoscale devices.

In this report we will present experiments and results on the deposition of cobalt films with various plasma enhanced ALD (PEALD) processes using different standard cobalt precursors (e.g., cyclopentadienylcobalt dicarbonyl (CpCo(CO)$_2$), cobaltocene (CoCp)$_2$), and tricarbonylnitrosylcobalt (Co(CO)$_2$NO)) combined with hydrogen, nitrogen, ammonia and argon based plasma gases. All our experiments were performed in a cross-flow ALD reactor, which is equipped with a capacitively coupled hallow-cathode plasma source, specially designed for the deposition of cobalt films. In situ and in real-time highly sensitive quartz crystal microbalances (QCM) measurements allowed a rapid and low-cost process development. The utilized ALD reactor was clustered to an ultra-high vacuum analytic system for direct surface analysis like X-ray photoelectron spectroscopy (XPS) and scanning probe microscopy (SPM). The combination with a non-destructive analytic system enabled a sample transfer without vacuum break and thereby a direct qualification and quantification of the chemical surface composition under quasi in situ conditions. The high sensitivity of these measurements allowed investigations of interface reactions for a single PEALD pulse as well as initial film growth mechanism on different substrate materials. Furthermore we studied the impact of various cobalt precursors combined with different plasma gas compositions on the resulting film properties. The influence of process parameters (e.g., pulse times, plasma power, pressure and substrate temperature) on the film composition and film properties was also investigated. Cobalt films grown using the precursor CpCo(CO)$_2$ and H$_2$/N$_2$ plasma as coreactant showed a stable film composition of 75 at.% cobalt, 4 at.% carbon and 21 at.% nitrogen. Using scanning electron microscopy and four point probe measurements a moderate electrical resistivity of about 80 µΩcm is calculated for a 14 nm thick film.

Beyond those results in our publication we will discuss the suitability of the precursors for the deposition of high-quality cobalt films as well as the occurrence of sputtering and temperature effects due to high plasma powers.
The atmospheric pressure plasma-assisted atomic layer deposition (AP-SALD) technique offers several advantages over traditional ALD processes. In this work, we employed optical emission spectroscopy (OES) and infrared spectroscopy on effluent plasma gasses as diagnostic tools to study the underlying chemistry of the AP-SALD process of AlO\(_2\) films prepared using Al(CH\(_3\))\(_3\) and Ar-O\(_2\) plasma. We identified the main reaction products and studied their trend as a function of the exposure time to the precursor to verify the ALD layer-by-layer growth characteristic. Findings show that the spatial separation of the ALD half-reactions and the use of an atmospheric pressure plasma as the reactant give rise to a complex underlying chemistry. Infrared absorbance spectra show CO, CO\(_2\), H\(_2\)O and CH\(_2\) as the main ALD reaction byproducts originating from 1) combustion-like reactions of the metalated surface with oxygen plasma radicals and ozone, and 2) a concurrent latent thermal component due to surrounding substrate. In addition, CH\(_2\)O and CH\(_2\)OH are identified as ALD reaction byproducts either formed at the surface or in the plasma by electron-induced dissociation. Furthermore, the investigated trends in CO\(_2\) and CH\(_2\) formed as a function of the exposure time confirmed self-limiting ALD behavior. Finally, OES results corroborated that, as soon as the plasma-enhanced SALD process takes place, emission from OH and CH arises while excited oxygen species are consumed.

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activity, selectivity and stability. In this regard, there is an increasing interest in ALD to conformally deposit noble metal NPs with atomic-scale control over the metal loading (atoms per cm²) and NP size. Here, we aim to demonstrate that in situ X-ray fluorescence (XRF) and grazing incidence small angle X-ray scattering (GISAXS) can offer unique insights in the ALD growth and thermal stability of metal NPs, offering approaches towards superior size and coverage control, and improved stability.

In a first study, the Me(II)(MeCp)Pt precursor is combined with either O₂ gas or N₂ plasma to grow Pt NPs on planar SiO₂ surfaces, and in situ XRF and GISAXS measurements provide the evolution of Pt loading, NP dimensions and spacing. It is found that O₂ induces atomic and cluster surface diffusion and promotes the ripening of the Pt NPs, while diffusion phenomena seem to be suppressed during N₂ plasma-based ALD. This insight inspired a tuning strategy that combines both processes and offers independent control over NP size and coverage [Nat. Comm. 8, 1074 (2017)]. Next, in situ GISAXS is used to investigate the coarsening behavior of the Pt NPs [Nanoscale 9, 13159 (2017)] and probe the influence of stabilizing Al₂O₃ and promotes the ripening of the Pt NPs, while diffusion phenomena seem to be suppressed during N₂ plasma-based ALD. This insight inspired a tuning strategy that combines both processes and offers independent control over NP size and coverage [Nat. Comm. 8, 1074 (2017)]. Next, in situ GISAXS is used to investigate the coarsening behavior of the Pt NPs [Nanoscale 9, 13159 (2017)] and probe the influence of stabilizing Al₂O₃ tuning strategy that combines both processes and offers independent control over NP size and coverage [Nat. Comm. 8, 1074 (2017)]. Next, in situ GISAXS is used to investigate the coarsening behavior of the Pt NPs [Nanoscale 9, 13159 (2017)] and probe the influence of stabilizing Al₂O₃ and promotes the ripening of the Pt NPs, while diffusion phenomena seem to be suppressed during N₂ plasma-based ALD. This insight inspired a tuning strategy that combines both processes and offers independent control over NP size and coverage [Nat. Comm. 8, 1074 (2017)]. Next, in situ GISAXS is used to investigate the coarsening behavior of the Pt NPs [Nanoscale 9, 13159 (2017)] and probe the influence of stabilizing Al₂O₃ tuning strategy that combines both processes and offers independent control over NP size and coverage [Nat. Comm. 8, 1074 (2017)]. Next, in situ GISAXS is used to investigate the coarsening behavior of the Pt NPs [Nanoscale 9, 13159 (2017)] and probe the influence of stabilizing Al₂O₃ tuning strategy that combines both processes and offers independent control over NP size and coverage [Nat. Comm. 8, 1074 (2017)]. Next, in situ GISAXS is used to investigate the coarsening behavior of the Pt NPs [Nanoscale 9, 13159 (2017)] and probe the influence of stabilizing Al₂O₃ tuning strategy that combines both processes and offers independent control over NP size and coverage [Nat. Comm. 8, 1074 (2017)]. Next, in situ GISAXS is used to investigate the coarsening behavior of the Pt NPs [Nanoscale 9, 13159 (2017)] and probe the influence of stabilizing Al₂O₃ tuning strategy that combines both processes and offers independent control over NP size and coverage [Nat. Comm. 8, 1074 (2017)]. Next, in situ GISAXS is used to investigate the coarsening behavior of the Pt NPs [Nanoscale 9, 13159 (2017)] and probe the influence of stabilizing Al₂O₃ tuning strategy that combines both processes and offers independent control over NP size and coverage [Nat. Comm. 8, 1074 (2017)]. Next, in situ GISAXS is used to investigate the coarsening behavior of the Pt NPs [Nanoscale 9, 13159 (2017)] and probe the influence of stabilizing Al₂O₃ tuning strategy that combines both processes and offers independent control over NP size and coverage [Nat. Comm. 8, 1074 (2017)]. Next, in situ GISAXS is used to investigate the coarsening behavior of the Pt NPs [Nanoscale 9, 13159 (2017)] and probe the influence of stabilizing Al₂O₃ tuning strategy that combines both processes and offers independent control over NP size and coverage [Nat. Comm. 8, 1074 (2017)].

The metal precursor and tertiary amine compound, irreproducible water delivery can result in undesired film properties. The goal of this work is to obtain a better understanding of the factors influencing water delivery from bubblers and vapor draw ampoules. To achieve this goal, both the amount of water delivered from an ampoule and the temperature distribution of the water in the ampoule were measured under a range of process conditions, in bubblers and vapor draw ampoules. The amount of water delivered and the water temperature vertical distribution in the ampoule were measured using a tunable diode laser spectroscopy system and a five-element temperature sensor array, respectively. These data were used determine the degree to which the amount of water delivered was correlated to evaporative cooling in the ampoule. For bubblers, this determination was relatively straightforward as bubbling tended to homogenize the water temperature. For vapor draw ampoules, however, this determination was complicated by a temperature gradient that existed during flow. The focus of this investigation was on commercial 1.5 L ampoules (with a maximum fill of 1.2 L), although different ampoule designs were examined. The results from this work could facilitate development of ALD process recipes, delivery control methods, and improved ampoule designs.
unsuitable ALD candidates using these ligands, will also be discussed in this presentation.


8:45am AF2-TuM4 Atomic Layer Deposition of Lead(II) Sulfide at Temperatures Below 100 °C. Georigi Popov, University of Helsinki, Finland; G. Bačić, Carleton University, Canada; M. Mattinen, M. Vehkamäki, K. Mizohta, M. Kemell, University of Helsinki, Finland; S. Barry, Carleton University, Canada; J. Rääsänen, M. Keskelä, M. Ritala, University of Helsinki, Finland

Lead(II) sulfide (PbS) is one of the oldest known semiconductors. It has a narrow band-gap of 0.4 eV that can be widened by quantum confinement effects. Owing to these properties, PbS is a recognized material in IR detection and quantum dot (QD) based devices such as light emitting diodes (LEDs) and photovoltaics. Photovoltaics are also central to our study. The aim is to develop an ALD PbS process that can be applied in halide perovskite solar cells.

ALD processes for PbS exist at least since 1990,[1] however we discovered that known ALD PbS processes are incompatible with halide perovskites such as CH3NH3PbI3 due to their extremely low thermal budget.[2] To our knowledge the lowest temperature at which PbS can be deposited with existing ALD processes is 130 °C.[3] CH3NH3PbI3 film degrades completely at this temperature in our ALD reactors. Thus, we set out for a new PbS process that would work at even lower temperatures. From our previous studies on ALD of PbS we already knew one lead precursor suitable for low temperature ALD: lead(II) bis[bis(trimethylsilyl)amide] or Pb(btsa)2.[4] Recently Bačić et al. reported another suitable candidate: lead(II) rac-N,N-di-tert-butylbutane-2,3-diamide or Pb(dbda).[5] With these lead precursors and H2S as a co-reactant we developed two new processes capable of depositing PbS even below 100 °C.

Pb(btsa)2:H2S process produces uniform, high-quality, crystalline PbS films in the 65 – 155 °C range. TOF-ERDA composition analysis revealed exceptionally high purity for such low deposition temperatures. The process exhibits two regions with temperature independent growth per cycle values (GPC) of 0.50 Å and 0.15 Å at 65 – 80 °C and 115 – 155 °C, respectively. The GPC saturates rapidly with respect to both precursor pulses and is independent of the purge duration and number of deposition cycles. CH3NH3PbI3 films survive the PbS deposition at the lowest deposition temperatures and studies of perovskite stability after PbS deposition are ongoing.

With Pb(dbda) film deposition occurs in an even wider temperature range of 45 – 155 °C. However, XRD measurements show that at 95 °C and above, the films contain crystalline impurities. Nevertheless, high-quality polycrystalline PbS films can be deposited at temperatures as low as 45 – 75 °C. We are currently conducting studies on the influence of process parameters on the PbS film properties.


9:00am AF2-TuM5 Development and Characterization of a Novel Atomic Layer Deposition Process for Transparent p-Type Semiconducting Nickel Oxide using Ni(Ni(II)DAD) and Ozone, Konner Holder, Oregon State University; C.L. Dezelah, EMD Performance Materials; J.F. Conley, Jr., Oregon State University

Nickel oxide (NiO), a wide band gap p-type semiconductor, is of interest for applications in solar energy conversion,[6] electrocatalysis,[7] and as a tunnel barrier for metal/insulator/metal (MIM) diodes for infrared energy harvesting.[8] ALD is an ideal technique for the highly conformal, uniform thin films needed for these applications. We develop a new process for ALD of NiO using Ni(Ni(II)DAD) and O3.

ALD growth of metallic Ni was demonstrated recently using Ni(Ni(II)DAD) and tert-butylamine.[8] ALD of metallic Co and cobalt oxide have been reported using Co(Ni(II)DAD) with formic acid and O3, respectively.[9,8] Taking a similar approach, we deposit NiO in a Picosun Sunalet R-150 using N2-purge-separated cycles of Ni(Ni(II)DAD) held at 150°C and an O3/O2 mixture of ~10% nickel films were characterized using grazing-incidence x-ray diffraction (GIXRD), x-ray photoelectron spectroscopy (XPS), atomic force microscopy (AFM), variable angle spectroscopic ellipsometry (VASE), and p-NiO/n-Si heterojunction diodes. A plot of GPC vs. temperature for depositions using a 5/30/40/30 s Ni(Ni(II)DAD)/Ni3O4/O2/N2 pulse sequence shows a clear ALD “window” of constant GPC = 0.12 nm/cycle from 185-200 °C (Fig. 1) in which Ni(Ni(II)DAD) and O2 pulses saturate after ~5 s and ~4 s, respectively (Fig. 2). Below the temperature window, condensation of Ni(Ni(II)DAD) occurs resulting in uncontrolled growth with 1.2% C and 0.7% Ni impurities (XPS) at 150 °C. Above the window, from 200-230 °C, desorption of Ni(Ni(II)DAD) occurs, followed by decomposition of NiN(NO3)3 above 230 °C on the chamber walls. To achieve both contributing to decreased GPC. Inside the temperature window, for saturating films deposited at 200 °C, GIXRD shows randomness-oriented polycrystalline cubic NiO (Fig. 3), consistent with XPS elemental analysis showing a Ni/O ratio near unity, without any detectable C or Ni impurities. VASE reveals that refractive index (~2.4) and band-gap (~3.8 eV) are close to bulk values while AFM RMS roughness was 0.6 nm for an 18 nm thick film (Fig. 4). p-NiO/n-Si diodes show highly asymmetric (i/I,lim = 10^7) behavior. All results point towards an as-deposited transparent p-type semiconducting NiO. Further growth studies, characterization, and electrical measurements will be discussed at the meeting.

The deposition and the properties of rare earth oxide thin films have been extensively studied for applications as protective coatings, optics and microelectronics. Sc$_2$O$_3$ thin films have recently attracted a strong interest for application as gate dielectrics for metal-oxide-semiconductor field-effect transistors (MOSFET) because they have a dielectric constant of 14, a band gap of 6.3 eV and excellent thermal stability. Despite its advantages, very few studies have investigated Sc$_2$O$_3$ on Si. We therefore investigated growth characteristics of Sc$_2$O$_3$ films deposited by atomic layer deposition (ALD) from Sc(cp)$_3$ and a novel liquid heteroleptic cyclopentadienyl containing Sc precursor, which are thermally stable (>300 °C), volatile, with a good reactivity to H$_2$O. The depositions were done in a hot-wall cross-flow-type ASM Pulstar® 3000 reactor connected to a Polygon 8300 platform.

The film growth properties, such as growth per cycle, impurity concentrations, and thickness uniformity on 300 mm Si (100) wafers were studied. A growth rate per cycle of 0.46 Å/cycle and 0.52 Å/cycle was obtained at 225 °C with novel Sc based precursor and Sc(cp)$_3$, respectively. The Sc$_2$O$_3$ film non-uniformity was about 1% and 5% with novel Sc heteroleptic precursor and Sc(cp)$_3$, respectively. Sc$_2$O$_3$ films based on the novel Sc precursor were stoichiometric, with a low C impurity content of <1%, while films based on Sc(cp)$_3$ precursor exhibited ~4.5% of residual carbon impurity level under similar processing conditions.

Electrical measurements were done on planar TiN gated MOS capacitor (MOSCAP) with high k thickness ~8 nm. Sc(cp)$_3$ based Sc$_2$O$_3$ exhibited a leakage current density of 1.5 x 10$^{-4}$ A/cm$^2$ and an effective work function (eWF) of 4.05 eV for an equivalent oxide thickness (EOT) of 3.43 nm at 1.0 V, which is significantly lower than TiN eWF (~4.8 eV) indicating considerable positive fixed charges incorporated in deposited Sc$_2$O$_3$ film. While novel heteroleptic Sc based Sc$_2$O$_3$ films exhibited much lower leakage current density of 1.0 x 10$^{-5}$ A/cm$^2$ and close to TiN eWF of 4.77 eV for an EOT of 3.15 nm at 1.0 V. It was shown that good quality and low defects Sc$_2$O$_3$ films can be obtained by using the novel heteroleptic Sc precursor.

A novel self-limiting chemical approach for the deposition of WS$_2$ by atomic layer deposition based on chemisorption of bis(t-butylimidido)bis(dimethylamino) Complexes, Nicola Pinna, Humboldt-Universität zu Berlin, Germany

A novel self-terminating chemical approach for the deposition of WS$_2$ by atomic layer deposition based on chemisorption of bis(t-butylimidido)bis(dimethylamino) tungsten(VI) followed by sulfurization by H$_2$S is reported. A broad spectrum of reaction parameters including temperatures of the reaction chamber and the precursor and durations of every ALD step are investigated and optimized to reach a high growth per cycle of 1.7 Å and a high quality of the deposited thin films. The self-terminating behaviour of this reaction is determined by the variation of the dose of the precursors. The physical, chemical and morphological properties are characterized by a combination of analytical techniques. XRD, XPS and Raman prove that highly pure and well-defined WS$_2$ layers can be synthesized by ALD. TEM and AFM images show that WS$_2$ grows as platelets with a thickness of 6-10 nm and diameter of 30 nm, which do not vary dramatically with the number of ALD cycles. A low deposition temperature process followed by a post annealing under H$_2$S is also investigated in order to produce a conformal WS$_2$ film. Finally, a reaction mechanism could be proposed by studying the chemisorption of bis(t-butylimidido)bis(dimethylamino)tungsten(VI) onto silica, and the thermal and chemical reactivity of chemisorbed species by 'H NMR, GC-MS and FT-IR.
Silicon nitride is a widely used material in semiconductor applications, such as gate dielectrics, III/V surface passivation and etch stop layer. PEALD SiNx films have been previously grown using aminosilanes like BTBAS with N2 plasma at 250–350 °C [2]. NH3 plasma at 50–400 °C [3] and N2 plasma at 250 – 350 °C [4] to grow PEALD SiNx films. However, in these works the low temperature range has remained either inaccessible or uncharted.

In this work we explored the PEALD TSA-N2 plasma process with a wide deposition temperature range from 50 to 350 °C. Focus was given to the electrical and optical properties of the films. A Beneq TFS 200 capacitatively coupled hot wall plasma ALD reactor was used at direct plasma mode. It was found that reactor temperature, plasma power and time had the highest impact on the film properties. Film deposition was observed at temperatures as low as 50 °C. Metal catalyst semiconductor (MIS) structures were used to determine the breakdown field and leakage current at different temperatures. Films were doped in 1 % HF solution for etch rate determination.

Films deposited by remote plasma atomic layer deposition. physica sta tus solidi (a), 2014, 211.9: 2166-2171.

\[1\] KNOOPS, Harm CM, et al. Atomic layer deposition of silicon nitride from Bis (tert-butylamino) silane and N2 plasma. ACS applied materials & interfaces, 2015, 7.35: 19857-19862.


\[3\] JANG, Woohool, et al. Temperature dependence of silicon nitride deposited by remote plasma atomic layer deposition. physica status solidi (a), 2014, 211.9: 2166-2171.


Films deposited using the quartz source consist of small (a few nm size) columnar grains. Deposition using the sapphire ICP source results in films with large (120nm size) columnar grains (Fig.4). The most technologically important parameter of conductive nitrides is film resistivity. At thicknesses significantly higher than the electron mean free path film resistivity is increased due to scattering at grain boundaries and point defects. Therefore, the main parameters determining film resistivity of the deposited 30nm thick TiN films are the grain size and the oxygen contamination. For all examined nitrides, the lowest film resistivity and the highest film density was obtained for the H2 plasma-grown films deposited using the sapphire based ICP source (Fig.5,6). Sapphire source enabled higher deposition rates, better crystallization, lower film resistivity, and lower oxygen contamination. This indicates a superior chemical resistivity of sapphire to etching by hydrogen radicals compared to that of quartz. The advantage of the sapphire based ICP source is pronounced when a H2 plasma and/or at high reactive gas flow are used for nitride deposition. The influence of ICP source material choice on the nitride film quality may be minimized if nitrogen based reactive gases and low flow conditions are used for nitride deposition. Optimal deposition conditions for both ICP source materials are determined.

Tuesday Morning, July 23, 2019 96 8:00 AM

Atomic Layer Etching

Regency Ballroom A-C - Session ALE1-TuM

ALE: Gas-phase and/or Thermal ALE

Moderators: Steven M. George, University of Colorado - Boulder, Venkateswaran Paliyam, American Air Liquid

8:00am ALE1-TuM1 Analyses of Hexafluoroacetylacetonate (Hfac) Adsorbed on Transition Metal Surfaces, Tomoko Ito, K. Karahashi, S. Hamaguchi, Osaka University, Japan

Invited Transition metals are known as hard-to-etch materials for reactive ion etching (RIE) processes. Although Ar milling processes are now widely used for such metal etching, physical sputtering processes with high energy ions have problems of low selectivity and poorly controlled etched profiles. Surface damages induced by energetic ion bombardment may also cause degradation of the material surface properties. Therefore alternative transition-metal etching processes with high selectivity and low damage, rather than physical sputtering, have been sought after in the industry. In recent years, atomic layer etching (ALE) by the formations of volatile organic metal complexes has attracted much attention as a means to achieve atomically controlled and low damage etching. ALE reactions may be considered as reverse reactions of atomic layer deposition (ALD). For example, metal beta-ketoenolate complexes are often used as precursors for ALD, so stable adsorption of beta-ketones on a metal surface and the
formation of metal beta-ketoenolates thereon are crucial steps for the development of corresponding ALE processes. In this study, we have examined surface reactions of transition metals or their oxides with hexafluoroacetylacetone (hfac) [1] and demonstrated that such reactions can be used to develop ALE processes for some transition metals. Experiments were performed in what we call the “Atomic-Layer-Process (ALP) Surface Analysis System,” which consists of ALP reaction chambers and an in-situ high-resolution X-ray photoelectron spectroscopy (XPS) system. In the reaction chamber, the substrate temperature can be controlled by a ceramic heater, which is installed on the back side of the sample. After exposure to reactive gases, the sample can be transferred from the reaction chamber to the XPS chamber without being exposed to ambient air for in-situ surface chemical analysis. Ion irradiation effects on an hfac adsorbed metal surface may be studied with the use of low energy Ar+ ion beam of the XPS system. We used Ni and Cu substrates in this study. It has been found that hfac molecules adsorbed on a metal oxide surface are less likely to be decomposed at room temperature than those on a metal surface and, at an elevated temperature, a metal oxide surface is preferentially etched by hfac than a metal surface.


8:30am ALE1-TuM3 Thermal Atomic Layer Etching of Silicon Nitride using an Oxidation and “Conversion-Etch” Mechanism, Aziz Abdulagatov, S.M. George, University of Colorado - Boulder

The thermal atomic layer etching (ALE) of silicon nitride was demonstrated using an oxidation and “conversion-etch” mechanism (see Supplemental Figure 1). In this process, the silicon nitride surface was oxidized to a silicon oxide layer using O2 or ozone. The silicon oxide layer was converted to an Al2O3 layer using trimethylaluminum (TMA). The Al2O3 layer was fluorinated by HF to an AlF3 layer prior to the removal of the AlF3 layer by ligand-exchange using TMA. Silicon nitride ALE was studied using Si3N4 films deposited using low pressure chemical vapor deposition (LPCVD). In situ spectroscopic ellipsometry was employed to monitor the thickness of both the Si3N4 and the silicon oxide layer during ALE. These studies observed that the silicon nitride film thickness decreased linearly with number of reaction cycles while the silicon oxide thickness remained constant.

Using an O2-HF-TMA reaction sequence, the Si3N4 ALE etch rate was 0.26 Å/cycle at 290°C. This etch rate was obtained using static reactive pressures of 250, 0.65 and 1.0 Torr, and exposure times of 10, 5 and 5 s, for O2, HF, and TMA, respectively. Employing similar dosing conditions, the etch rate remained the same for O2 pressures from 30-250 Torr. The order of the reactant sequence affected the Si3N4 etch etch rate from 0.26 Å/cycle at 290°C. The Si3N4 ALE etch etch rate was also reduced at lower temperatures. Using the O2-HF-TMA reaction sequence, the Si3N4 etch rate was reduced from 0.47 Å/cycle at 290°C to 0.07 Å/cycle at 210°C.

Si3N4 ALE also decreased the roughness of the Si3N4 surface. The RMS roughness of the initial Si3N4 films was 4.7 Å measured using atomic force microscopy (AFM). The RMS roughness decreased to 3.1 Å after 80 ALE cycles. An SiO2 oxide thickness of 100-150 Å remained after Si3N4 ALE at 290°C. This oxide could be removed by 15 sequential TMA and HF exposures after the Si3N4 ALE. Thermal Si3N4 ALE should be useful in advanced semiconductor fabrication. Thermal Si3N4 ALE could also find applications in optoelectronics, photonics and MEMS fabrication.

8:45am ALE1-TuM4 Thermal Dry Atomic Layer Etching of Cobalt with Sequential Exposure to Molecular Chlorine and Diketones, M. Konh, C. He, X. Lin, University of Delaware; X. Guo, V. Pallem, American Air Liquide; R. Opila, Andrew Tepljakov, Z. Wang, B. Yuan, University of Delaware

The mechanism of thermal dry etching of cobalt films is discussed for a thermal process and a sequential exposure to chlorine gas and a diketone (either 1,1,1,5,5,5-hexafluoro-2,4-pentanedione (hexafluoroacetylacetone, hfach) or 2,4-pentanone (acetylacetone, acach)). The process can be optimized experimentally to approach atomic layer etching (ALE), and a sequential exposure to Cl2 and hfach dry etchants at 140°C is shown to proceed efficiently. The use of acach as a diketone does not result in ALE with chlorine even at 180°C; however, the decrease of surface chlorine concentration and chemical reduction of cobalt is noted. Thermal desorption analysis suggests that the reaction of chlorinated cobalt surface exposed to the ambient conditions (oxidized) with hfach does produce volatile Co-containing products within the desired temperature range and the products contain Co2+. The effect of ligands on the energy required to remove surface cobalt atoms is evaluated using density functional theory and the findings are consistent with the experimental observation of surface smoothing during atomic layer etching.

9:00am ALE1-TuM5 Spontaneous Etching of B2O3 and TiO2 by HF: Removal Reaction in WO3, ALE and TiN ALE, Austin Cono, University of Colorado - Boulder; S.K. Natarajan, Tyndall National Institute, Ireland; J. Clancy, University of Colorado - Boulder; S. Elliot, Schrödinger Inc; S.M. George, University of Colorado - Boulder

Thermal atomic layer etching is typically based on two sequential surface reactions. The first reaction activates the surface layer and the second reaction leads to material removal by the desorption of volatile etch products. The surface activation can be halogenation, conversion to a different material, or oxidation of the initial material. For example, BCl3 is able to convert the WO3 surface to a B2O3 surface layer during WO3 ALE. The B2O3 surface layer is then spontaneously removed by etching using HF. In another example, O2 is able to oxidize the TiN surface to a TiO2 surface layer during TiN ALE. The TiO2 surface layer is then spontaneously removed by etching using HF.

This study explored the spontaneous etching of B2O3 and TiO2 with HF using Fourier Transform Infrared (FTIR) spectroscopy and quadrupole mass spectrometry (QMS) analysis. The initial B2O3 films were grown using B2O3 ALD with BCl3 and H2O as the reactants. The initial TiO2 films were grown using TiO2 ALD with TiCl4 and H2O as the reactants. FTIR measurements observed the growth of the B2O3 films and TiO2 films by monitoring the absorbance of the B-O and Ti-O stretching vibrations, respectively, versus number of ALE cycles. FTIR experiments also observed the spontaneous etching of B2O3 and TiO2 with HF by measuring the loss of the absorbance of the B-O and Ti-O stretching vibrations, respectively (See Supplemental Figure 1).

QMS studies were also able to monitor the volatile etch products during the spontaneous etching of B2O3 nanopowder with HF. The expected reaction products are BF3 and H2O based on the reaction B2O3 + 6HF → 2BF3 + 3H2O. In comparison, the QMS detected BOH, BF3 and H2O as the main etch products (See Supplemental Figure 2). In addition, the QMS also revealed species at higher masses that were consistent with six-member ring species, such as BO2F2.

The reaction of HF with B2O3 and TiO2 was also examined using a density functional theory (DFT) based computational approach. By comparing the thermodynamic free energy profiles of competing self-limiting surface and bulk reactions, the DFT calculations predicted the spontaneous etching of B2O3 by HF above ~160°C and of TiO2 (but not TiN) above 90°C, in agreement with the experimental findings.

9:15am ALE1-TuM6 Thermal Based Atomic Layer Etching of Aluminum Oxide and Titanium Nitride, Varun Sharma, Ashok Sharma, ASM, Finland; T. Blomberg, Picusson Oy/ASM, Finland; M. Tuominen, S. Haukka, ASM, Finland

Thermal based Atomic Layer Etching (th-ALEt) has opened a new horizon and triggered an increased interest in the Semiconductor Industry for the fabrication of sub-10 nm as well as complex 3D nano-devices. In the th-ALEt technique, a material is chemically etched from thermally activated surface by sequence of one or more reactants each separated by purge steps. Unlike the conventional anisotropic plasma etching, th-ALEt is isotropic, selective and its slow etch rate may possess excellent atomic-scale control. Most of the reported th-ALEt chemistries utilize hydrogen fluoride (HF from HF-pyridine) as one of the reactants. However, due to some safety concerns associated with the use and handling of HF, we have considered other fluoride donating compounds. In this work, we report niobium pentfluoride (NbF5) as an alternative to HF. Carbon tetrachloride (CCl4) is used as a co-reactant with NbF5 to etch aluminum oxide (Al2O3) as well as titanium nitride (TiN). The various attributes of the etching process like etch rates, selectivity and post-etch surface roughness were studied. It was found that NbF5 promotes the fluorination of Al2O3 and the fluorinated Al2O3 surface can be etched away by a subsequent exposure of CCl4 gas. TiN can be etched in continuous pulsed mode just by CCl4, while adding NbF5 to the process enables etch-rate control. The etch results and proposed reaction pathway for the etching of Al2O3 and TiN will be discussed in the presentation.

9:30am ALE1-TuM7 Thermal Atomic Layer Etching of Amorphous and Crystalline Hafnium Oxide, Zirconium Oxide and Hafnium Zirconium Oxide, Jessica A. Murdzek, S.M. George, University of Colorado - Boulder

Thermal atomic layer etching (ALE) can be achieved with sequential surface reactions using the fluorination and ligand-exchange mechanism. For metal oxide ALE, fluorination converts the metal oxide to a metal fluoride. The ligand-exchange reaction then removes the metal fluoride by forming...
volatile products. Previous studies have demonstrated the thermal ALE of amorphous HfO2 and ZrO2 ALD films. No previous investigations have explored the differences between the thermal ALE of amorphous and crystalline films. The thermal ALE of crystalline films is important because amorphous films may not crystallize easily when they are too thin. Consequently, amorphous films may have to be grown thicker, crystallized, and then etched back to obtain the desired ultrathin crystalline film thickness.

This study explored the thermal ALE of amorphous and polycrystalline films of hafnium oxide, zirconium oxide, and hafnium zirconium oxide. HF was used as the fluorination reactant. Dimethylaluminum chloride (DMAC) or titanium tetrachloride was employed as the metal precursor for ligand-exchange. The amorphous films had a much higher etch rate per cycle than the crystalline films. The differences were most pronounced for hafnium oxide. At 250 °C with HF and DMAC as the reactants, the etch rate was 0.03-0.08 Å/cycle for crystalline HfO2 and 0.68 Å/cycle for amorphous HfO2. (See Supplemental Figure 1).

Under the same conditions at 250 °C with HF and DMAC as the reactants, the etch rate was 0.60-0.82 Å/cycle for crystalline ZrO2 and 1.11 Å/cycle for amorphous ZrO2. In comparison, the etch rate was 0.16-0.26 Å/cycle for crystalline HfZrO2 and 0.69 Å/cycle for amorphous HfZrO2. The etch rates for HfZrO2 were between HfO2 and ZrO2 for both the amorphous and crystalline films. When HF and TiCl4 were used as the reactants at 250 °C, the etch rates were smaller than the etch rates with HF and DMAC as the reactants for every material. The etch rates also increased with temperature for both the amorphous and crystalline films. The differences between amorphous and crystalline HfO2 are sufficient to obtain selective thermal ALE of amorphous HfO2.

9:45am ALE1-TuM8 Isotropic Atomic Layer Etching of Cobalt with Smooth Etched Surfaces by using Cyclic Repetition of Plasma Oxidation and Organometallic Formation, Sumiko Fujisaki, Hitachi R&D Group, Japan

Isotropic atomic layer etching (ALE), which produces atomically precise, conformal removal, will have an important role in semiconductor manufacturing. This is because highly selective ALE has become necessary to deal with processing of new materials with the advances in miniutilization of devices such as 3D structures. In the past several years, isotropic ALE of various materials has been reported which includes thermal ALE for metal oxides and thermal-cyclic ALE for nitride films [1]. To meet the requirements concerning the variety of materials to be etched, isotropic ALE of cobalt must be developed. In 2018, thermal ALE of cobalt has been reported by using treatment with formic acid and ligands to produce volatile cobalt complexes [2]. In this paper, the authors successfully demonstrate isotropic ALE of cobalt film with smooth etched surfaces, which is important issue in the development of ALE of cobalt.

The experimental apparatus used in this study is 30-nm ALE tool equipped with inductively-coupled plasma source and infrared lamps. The cyclic ALE process is composed of three step repetitions: oxidation of cobalt surface with oxygen plasma, organometallic formation of the cobalt oxide with a low acidity ligand vapor, and sublimation of the organo-metallic volatile by thermal annealing.

The etching depth of cobalt increased with increasing the number of repetitions of the cycle. For one cycle of etching, it was 1 nm high. The root-mean-square (RMS) roughness of etched cobalt surface was estimated to be 0.8 nm. It was found that formation of homogeneous CoO (I) was important because compound oxide such as CoOx (I & II) resulted in rough etched surfaces with columnar morphology. Furthermore, controllability of etching amount was substantially improved by using low reactivity ligands compared to high-reactivity ligands. These results implied that the combination of homogenous CoO formation, low-reactivity ligands, and sublimation was essential for achieving smooth etched surfaces and excellent controllability of etching amount.

In conclusion, we have obtained well-controlled etch front roughness and etching depth of cobalt, which can be applied to semiconductor process, by controlling reactions of both oxidation and metal complex formation using the 300-nm ALE apparatus.

selectivity a new process was proposed recently, that contains SiCl in addition to fluorocarbon in the etching chemistry. XPS analyses showed that this specific gas composition leads to the deposition of SiOxFy, which acts as a passivation layer on silicon, instead of the usual carbon-rich organic film deposited with CHxFyOz chemistries. Ellipsometry measurements highlighted that SiOxFy passivation grows preferentially on silicon than on silicon nitride, which allows etching to carry on this material while silicon is passivated. Less than 1nm of silicon consumption is consistently measured even for long process times while at the same time silicon nitride is etched linearly providing a selectivity up to 40:1 between nitride and silicon.

To further improve process performance this SiCl-containing process was combined in a cyclic mode with a non-selective CHFx step. The SiClx step function is to etch silicon nitride while depositing passivation on silicon. During the CHFx step both silicon nitride and passivation on silicon are etched and respective step times were set up in such way that silicon nitride is linearly etched at a rate of 7.3nm/cycle while the silicon surface is permanently covered by the SiOxFy layer. This ALE-inspired process was demonstrated on a stacked nanowires integration: a 12.5nm thick SiN IRAD spacer was etched with very limited CD bias on the gate while parasitic spacers formed on 36nm high active area sidewalls were thoroughly removed without inducing more than 1.5nm silicon consumption.

11:30am ALE2-TuM15 Atomic Layer Etching of Transition Metals with Gas Cluster Ion Beam Irradiation and Acetylacetonate, Noriaki Toyota, K. Uematsu, University of Hyogo, Japan

Atomic layer etchings (ALE) of transition metals with gas cluster ion beam (GCIB) and acetylacetonate were investigated. In general, the ion energy in the removal step in ALE is several tens of eV, which is higher than the sublimation energy of the surface layer (several eV). These excess energies might be the origin of the damages on the target materials. We have investigated the feasibility of GCIB as energetic ions in the removal steps of ALE process. Since GCIBs are aggregates of thousands of gas atoms or molecules, the energy/atoms or energy/molecules can be easily reduced to several eV even though the total energy of GCIB is several keV. In additions, since GCIB induce dense energy deposition without severe damage, the bombarded area experiences transient high-temperature and high-pressure conditions. As a result, chemical reactions are enhanced at low-temperature. In the previous study, ALE of Cu films was demonstrated successfully using O2-GCIB and acetic acid.

In this study, we have investigated ALE process for transition metals (Cu and Ni) using acetylacetonate. We separated each etching step as following: (1) adsorption of acetylacetonate on metal oxide, (2) evacuation of residual acetylacetone vapor, (3) irradiation of O2-GCIB to remove metal oxide. Effects of the following etching parameters on ALE were investigated from real-time thickness on a quartz crystal monitor; acceleration voltage of oxygen GCIB, irradiation time of GCIB, exposure time of acetylacetonate.

When the acceleration voltage of O2-GCIB is 20 kV, very thin layer of nickel oxygen GCIB, irradiation time of GCIB, exposure time of acetylacetone. are physically sputtered. Consequently, the etching process with 20 kV oxygen GCIB is not self-limiting. On the contrary, surface nickel oxide with adsorbed acetylacetone are removed by 5 kV O2-GCIB and there is no physical sputtering. Since the average cluster size of O2-GCIB is 3000 molecules/ion, the energy/molecules is below 2 eV. By using 5 kV O2-GCIB, self-limiting removal step is realized.

11:45am ALE2-Tum16 Atomic Layer Etching at Atmospheric Pressure, Eugen Shkura, D. Theirich, K. Brinkmann, T. Haeger, University of Wuppertal, Germany; J. Schneidewind, M. Siebert, SENTECH Instruments GmbH, Germany; T. Riedl, University of Wuppertal, Germany

Atomic Layer Etching (ALE) is a cyclic process which is based on sequential surface reaction of two or more reactants and ideally provides control on the monolayer level. In the last decade the main focus was on two types of ALE. The first approach relies on the chlorination and sometimes fluorination to initially create metal-halide species at the surface which are subsequently removed by a plasma [1,2]. Another approach is thermally driven ALE, e.g. by using HF and Sn(acac)2 to etch metal oxides [3]. More recent reports indicated isotropic etching by using radicals driven, plasma enhanced ALE [4]. In all these examples, the ALE process is vacuum based and as such provides some limitations towards high throughput and low manufacturing costs. Here, we introduce a novel process for Atomic Layer Etching at atmospheric pressure (AP-ALE). As a case study, we investigate the etching of ZnO by AP-ALE and spatial AP plasma enhanced-ALE by using Hacac at substrate temperatures in the range of 80-140 °C. Ozone as well as an atmospheric pressure dielectric Ar/O2 barrier discharge is used for AP-ALE and spatial AP Plasma Enhanced-ALE, respectively. In-situ quartz crystal microbalance as well as ex-situ spectroscopic ellipsometry were used to characterize the etching process. Depending on the processing conditions, an etch per cycle of 0.5 to 5 Å is found. Ex-situ AFM measurements before and after ALE show a modification of ZnO-Surface and a decrease in film thickness. Furthermore, growth characteristics in dependence of process parameters like substrate velocity and substrate temperature were investigated. We discuss the prospects to use spatial AP-ALE for materials other than metal oxides, such as III-V semiconductors like GaN or AlGaN.


Area Selective ALD

Grand Ballroom H-K - Session AS1-TuM

Tuesday Morning, July 23, 2019 9:00 AM

10:45am AS1-TuM12 Overview of Wet And Dry Selective Processes Driven by Area Activation or Deactivation Down to Below 20nm Critical Dimensions, Silvia Armini, IMEC, Belgium

Area selective deposition (ASD) is proposed as a method for preferentially depositing a material on a specific area on the surface while the remainder is left uncoated, providing spatial control over a deposited thin film. In the context of downscaling microelectronics components below 1x nm of critical dimension, ASD by Atomic Layer Deposition (ALD), Chemical Vapor Deposition (CVD) or Electroless Deposition (ELD) offers the potential to relax downstream processing steps by enabling self-aligned patterning processes, such as self-aligned vias and tone reversal, or bottom-up metallization schemes, such as supervia or via prefill. Due to the limitations of inherent ALD selectivity, we focus our work on material surface functionalization by selective grafting thin organic films both in ALD activation and passivation mode or by plasma exposure.

For ASD ALD processes which relies on delayed nucleation on a non-growth area, defectivity and the lack of a wide portfolio of application-relevant materials are two of the main concerns for the adoption of this technology in nanofabrication. Among the strategies addressing the selectivity issue, repetitive refreshment of the non-growth surface and selective etching of undesired nuclei are particularly promising.

In this study, we review our current understanding of the relationship between structure and properties of the inhibiting/activating materials and the correspondent surface dependence of different ALD processes. Nucleation and growth behaviour of ALD on different surfaces functionalized by organic films deposited from the liquid and vapor phase on 300nm wafers or by plasma will be analyzed and wet depassivation processes will be investigated in the attempt of removing the defects formed on top of the inhibition films.

In an attempt to understand the interaction between the ALD conditions (i.e. temperature, coreactants...) to the decomposition and modification of the organic films, in-situ XPS is exploited such as high sensitivity characterization techniques such as Secondary Ion Mass Spectrometry (SIMS).

Finally, the selectivity of the passivation and subsequent ASD process will be evaluated as a function of the patterned pitch size down to 16nm half-pitch structures. We aim at building some understanding about the relationship between the changes in surface composition due to the patterning, pitch variation and/or due to diffusion (in case of mobile species such as metals) and the ASD performance.

11:15am AS1-TuM14 Electron-Enhanced Atomic Layer Deposition (EE-ALD) of Cobalt Metal Films at Room Temperature, Zach Sobell, A. Cavanagh, S.M. George, University of Colorado - Boulder

Electron-enhanced atomic layer deposition (EE-ALD) is possible at room temperature by using electrons to stimulate the desorption of surface species. The electron stimulated desorption (ESD) process opens up free surface sites that enable the adsorption of reactants. ALD can be achieved by sequential application of electron and reactant exposures. A variety of materials have been deposited using EE-ALD at room temperature.
including GaN, Si and BN. Because EE-ALD is dependent on the electron flux, EE-ALD films are deposited only on surface areas illuminated by the electron beam.

In this study, Co EE-ALD was performed using sequential, self-limiting cobalt tricarbonyl nitrosyl [Co(CO)3NO (CTN)] and low energy electrons exposures at room temperature. The electron energies were varied from 75 to 175 eV. In the Co EE-ALD process, the CTN molecules first adsorb on the substrate. The electrons then induce ESD of the carbonyl (CO) and nitrosyl (NO) ligands from the adsorbed CTN. The ESD produces reactive surface sites. Subsequent CTN exposures react with the reactive surface sites and add Co to the substrate. The consumption of the reactive surface sites produces self-limiting Co EE-ALD.

In situ ellipsometry measurements observed a maximum growth rate of 0.5 Å per cycle at an electron energy of 125 eV. The in situ ellipsometry measurements also could monitor the CTN adsorption and the desorption of CO and NO ligands (see supplemental Figure 1). Quadrupole mass spectrometer (QMS) measurements confirmed the desorption of CO and NO during electron exposures. The spatial profile of the Co EE-ALD film resulting from the finite surface area illuminated by electrons was mapped by ex situ ellipsometry. This spatial profile was used to calculate an ESD cross section of $\sigma = 1 \times 10^{-15}$ cm$^2$. This ESD cross section is close to the electron dissociation cross section for CTN observed in the gas phase.

There are many applications for EE-ALD because the ESD process is topographically selective. This area selectivity comes from the directionality of the electron flux. Surfaces normal to the incident electrons receive the full electron flux, whereas surfaces parallel to the incident electron path receive no electron flux. EE-ALD should be useful for the bottom-up fill of high aspect ratio structures like trenches and vias. EE-ALD may also be important for depositing ALD films on thermally-sensitive substrates. In addition, EE-ALD could be valuable for enhancing the nucleation of ALD films by creating reactive surface species on the initial substrate.

In this study, we have carried out the investigation on the effect of surface selectivity using several types of Co ALD precursors, and found that selectivity was affected by high steric hindrance structure, chemical surface characteristics and so on. Based on the results, new Co ALD precursors having a good selectivity have been developed. At an example, Bis(N,N,N-trimethylaminoethylacetamidinato)cobalt (III) (CBPA-1) has high selectivity and is liquid at room temperature. CBPA-1 showed a very clean TG curve without decomposition and residue at 10 Torr. Additionally, thermal ALD of thin Co film was demonstrated using CBPA-1 and hydrogen as the co-reactant on Ru and SiO$_2$ substrates, and succeeded in making shiny metallic Co films at 150-300 °C only on the Ru substrate. Regarding film quality, X-ray photoelectron spectroscopy (XPS) shows that high purity Co film was deposited. As a comparison, we also carried out thermal ALD using reference precursor Bis(N,N,N-di-tert-butylacetamidinato)cobalt (III). However, Co was detected on both Ru and SiO$_2$ substrates over 275 °C by X-ray fluorescence (XRF) measurement. As a conclusion, CBPA-1 is better suited for Co AS-ALD process compared to conventional precursors such as diethylhexacarbonyl tert-butylacetylene (DEHCTBA) and Co amidinate complex. On top of that, a reducing method of isolated particles growth on SiO$_2$ substrates by using aminoisobutane was found out so it will be reported likewise.

First, we compare the inherent selectivity for a range of thermal ALD processes for oxides, nitrides and metals by investigating the surface dependence on blanket substrates. OH-terminated SiO$_2$ is the growth surface as all ALD processes considered here show linear growth on this surface, while CH$_2$-terminated SiO$_2$ is the non-growth surface. Both precursor and co-reactent affect selectivity (figure 1a). The selectivity for H$_2$O based ALD depends on the precursor in the order TiCl$_4$ > HfCl$_4$ > Al(CH$_3$)$_3$. The selectivity is higher for TiCl$_4$/NH$_3$ ALD than for TiCl$_4$/H$_2$O ALD in spite of the higher deposition temperature.

In view of the high inherent selectivity of TiCl$_4$/NH$_3$ ALD, we investigate TiN ASD in nanoscale patterns consisting of SiN$_x$ spaces and amorphous carbon (aC) lines with a critical dimension (CD) of 45nm. This material system is relevant for a tone inversion application of ASD for line-space patterning [2]. A H$_2$ plasma pretreatment enables ASD by passivating the aC surface by formation of methyl groups [2,3]. The selectivity for SiN$_x$ versus aC is 0.94 for 6.4 nm TiN, even higher than for OH- versus CH$_3$-terminated SiO$_2$ (blanks). The selectivity is maintained for ALD temperatures between 250 and 390 °C. However, in nanoscale patterns, the selectivity is affected by impurities due to patterning. By considering surface cleans before ASD, we demonstrate ASD of 7.5nm TiN on the 45nm CD line-space patterns, with little to no TiN detected on the aC top surface and sidewalls by transmission electron microscopy (Figure 1b).

References:
mass-production of OLED TVs because it showed remarkable performance, the surface roughness of the Sb$_2$Te$_3$ buried layer, proving their conformal properties. Scanning Electron Microscopy (SEM) and Transmission Electron Microscopy (TEM) were employed to study the heterostructures. The results demonstrated the possibility to synthesize Co thin films and demonstrating their device properties. However, ALD IGZO systems are quite difficult to understand their electrical and chemical properties because each precursor is affected to growth mechanism, crystallinity, and electrical performance. In this talk, I will show key properties (growth behavior, electrical/chemical properties, and device performances) of indium gallium oxide (IGO) and indium gallium zinc oxide (IGZO) thin films depending on a few In and Ga precursor species. There films are deposited using the concept of “super-cycle” – IGO (n cycle InO$_x$ – m cycle Ga$_2$O$_3$) and IGZO (n cycle of InO$_x$ – m cycle of GaO$_x$ – k cycle of ZnO). Then, the bottom gate-top contact (inverted staggered structure) thin film transistors were fabricated by ALD processes. The devices with IGO and IGZO active layers are named Device A (IGO TFT using Indium A precursor), Device B (IGZO TFT using Indium B precursor), Device C (IGZO TFT using Indium B precursor), Device D (IGZO TFT using Indium B precursor). The representative transfer curves and performance parameters are shown in Figure 1 and Table 1. The IGZO device D exhibited better mobility of 0.75 cm$^2$/V·sec, but the IGZO device B and C with different Indium precursors showed different mobilities of devices. It may result from a different growth rate and film composition. Thus, it is believed that ALD IGZO TFT will be very promising for the next generation switching transistor beyond the low-temperature poly-silicon (LTPS) thin film.

2:00pm AA1-TuA3 ALD Growth of Ultra-thin Co Layers on the Topological Insulator Sb$_2$Te$_3$, Emanuele Longo, R. Mantovani, R. Cecchini, CNR-IMM Unit of Agrate Brianza, Italy; M.D. Overbeek, Wayne State University; M. Longo, CNR-IMM Unit of Agrate Brianza, Italy; L. Lazzarini, CNR-IMEM, Italy; M. Fanciulli, Università degli Studi di Milano-Bicocca, Italy; C.H. Winter, Wayne State University; C. Wiemer, CNR-IMM Unit of Agrate Brianza, Italy

The coupling between ferromagnetic thin films (FMs) and topological insulators (TIs) is nowadays one of the hottest topics in the context of spintronics. The presence of Dirac-like dispersed surface states in the TI, jointly with the presence of a large spin-orbit coupling, is expected to favor a super-efficient (i.e. low-power) FM’s magnetization manipulation through a large spin orbit torque (SOT). The role of the interface between Co and TI is fundamental in driving SOT functionalities, making the choice of the deposition technique crucial and itself often responsible of low-quality interfaces formation. The high conformality, excellent low thickness control and its energetic character make atomic layer deposition (ALD) an appealing technique for spintronic applications. We present here a pure ALD process to grow few nm-thick Co metal films in direct contact with a granular-TI Sb$_2$Te$_3$ thin film grown by Metal Organic Chemical Vapor Deposition (MOCVD). The ALD of Co metal films was performed by alternating a saturative pulsing sequence of bis(1,4-di-tet-butyl-1,3-diazadienyl)cobalt (Co[1,4-DAD]J$_4$) (4 s), Ni$_2$ purge (10 s), tert- butylamine (tBuNH$_2$) (0.1 s) and Ni$_2$ purge (10 s) at 180°C. In order to compare the Co growth on the Sb$_2$Te$_3$ substrate, we performed simultaneous Co deposition on a spin-coated Pt substrate (conventionally used as Co deposition material), maintaining the same number of cycles. We conducted a thorough chemical-structural characterization of the Co/Sb$_2$Te$_3$ and Co/Pt heterostructures by employing X-Ray Diffraction (XRD), X-Ray Reflectivity, Scanning Electron Microscopy (SEM) and Transmission Electron Microscopy (TEM). The results demonstrated the possibility to synthesize Co thin films from several tens, down to 4 nm, forming uniform and high-quality Co thin films characterized by a stable and sharp interface with the Sb$_2$Te$_3$ substrate. Indeed, XRR showed that the thinner Co films replicate the surface roughness of the Sb$_2$Te$_3$ buried layer, proving their conformal growth. The growth rate was found to be higher on Sb$_2$Te$_3$ than on Pt. XRD evidenced the substrate selectivity of this growth process, showing the structural continuity of the grown Co layer on the underlying substrate. On Pt, the Co grains were found to adapt to the [111] textured substrate by developing a strained cubic structure. On Sb$_2$Te$_3$, Co was shown to grow with hexagonal structure, with out-of-plane grains oriented along the [001] direction, as the rhombohedral Sb$_2$Te$_3$ layer. The distinct magnetic ordering of cubic and hexagonal Co polymorphs, with the possibility to selectively grow Co with different magnetic properties, pave the way towards novel applications in spintronics.

2:15pm AA1-TuA4 Modifying Interfacial Chemistry of Cellulose-Reinforced Epoxy Resin Composites using Atomic Layer Deposition (ALD). Jamie Wooding, Y. Li, K. Kalantzisou, M. Losego, Georgia Institute of Tech Automotive and aerospace industries require new lightweight materials that can be easily processable and cost-effective via vehicle weight reduction. Employing composites, such as fiber-reinforced polymer resins, is a common approach to light-weighting these vehicles. In this talk, we will examine the use of ALD to modify the surface chemistry of cellulose reinforcements to improve the interfacial adhesion in polymer resin composites. Cellulosic reinforcements offer advantages in sustainable materials sourcing, lower density, and lower cost. However, raw cellulosics are hydrophilic and are immiscible with most non-polar thermosetting polymer resins. In this study, a variety of ALD-derived surface modification schemes are discussed as a means to improve resin permeation within the fibrous structure and to establish better adhesion at the cellulose – polymer matrix interface. Specifically, we consider surface modification with ALD-precurors trimethylcholium (TMA) and trimethyltetrachlore (TiCl$_4$), as well as with vapor-delivered carboxylic acids and silanes. Surface modification is confirmed with XPS studies and contact angle measurements. All are found to make the cellulose prepreg more hydrophobic, but the TiCl$_4$ – H$_2$O treatment demonstrates the best permeability for the polymer resin. Composites treated with low cycles of TiCl$_4$ – H$_2$O are found to have a 30% improvement in the modulus of elasticity and a 38% increase in the tensile strength compared to untreated cellulose – resin composites. Furthermore, the TiCl$_4$ – H$_2$O surface treatment results in a composite tensile strength equal to that of a 3-aminopropyliethoxysilane, a widely-used surface modifying agent, treatment while avoiding the disadvantages of using wet chemistry. The structural enhancements in the cellulose – resin composite, as demonstrated via wicking studies and scanning electron microscopy (SEM), inform these improvements in mechanical properties.

2:30pm AA1-TuA5 Atomic Layer Deposition of Au Nanoparticles on Titania, Fatemeh S.M. Hashemi, Delft University of Technology, Netherlands; F. Grillo, ETH Zurich, Switzerland; D. Benz, A. Shekhar, Delft University of Technology, Netherlands; M. Griffiths, S. Barry, Carleton University, Canada; J.R. van Ommen, Delft University of Technology, Netherlands

Nanoparticles of Au supported on TiO$_2$ have various applications in photocatalysis, plasmonics and photovoltaics. These supported materials are commonly synthesized using liquid-based techniques such as sol-gel and deposition-preparation. These methods, while being low-cost, result in high level of impurities and formation of Au particles with inhomogeneous size and composition. Here we present a vapor-based approach via atomic layer deposition (ALD) for controlled deposition of Au nanoparticles on TiO$_2$. We also use the designed structures for photocatalytic degradation of pollutants. We perform a low temperature (105 °C) thermal ALD process using Trimethylphosphino-trimethylgold (III) and two oxidizers (ozone and water) in a fluidized bed reactor under atmospheric pressure condition. While plasma-assisted ALD of Au using Trimethylphosphino-trimethylgold (III) has been previously reported (Griffiths et al., Chemistry of Materials 2016), no studies have looked into the thermal deposition process for this precursor. We investigate the effects of Au precursor saturation and oxidizing reagents on controlling the nucleation, particle size distribution and composition of the Au nanoparticles. Our studies suggest that ozone and water have an opposite effect on Au particle size distribution. While longer ozone pulse time results in the deposition of smaller Au particles, larger particles are formed when water pulse time is increased. TiO$_2$ nanoparticles have a high surface area of about 50 m$^2$/g, thus achieving precursor saturation on them requires long precursor dosage times. However, we show that the growth properties can also be controlled in the under-saturation regime. We also investigated the effects of Au loading and particle size on the photocatalytic activity of
Au/TiO2 nanoparticles. A 3 fold enhancement in the photocatalytic activity of TiO2 is achieved when Au/TiO2 nanoparticles are used for degradation of the model pollutants (Acid Blue 9 and Rhodamine B). This all vapor process provides a highly controlled and efficient method for producing Au/TiO2 particulates that meet the criteria for various applications.

In the work presented above, film stacks of pure silver (99.99%) can be coated with SiO2 and Al2O3 without a perceptible color difference (ΔE00 < 1) for a wide angle of incidence range across the visible spectrum. It is found that (a) optical properties of the coated substrate is compared to an uncoated substrate using the color ellipsometric data. The optical model of the substrates obtained by ellipsometry is used to obtain the reflection spectrum and color of the substrates when coated with various ALD films such as SiO2, Al2O3, and TiO2. The modeled color of the coated substrate is compared to an uncoated substrate using the color difference metric (ΔE00) [2]. Consistent with previous findings [2], we show that pure silver (99.99%) can be coated with SiO2 and Al2O3 without a perceptible color difference (Δ E00 < 1) for a wide angle of incidence range (AOI = 0-75°). However, for silver alloys (80-95% silver) there is no coating thicker than 10nm that results in ΔE00 < 1. [Figure-1]

The need to find a film stack that worked not just for pure silver but for silver alloys led to a multi-objective optimization problem – minimizing ΔE00 for silver substrates of different composition and AOI in 0-60°. A multi-layer film stack was found that showed Δ E00 < 1.25 for all substrates for AOI=0-70°.

In addition to the optical characterization, modelling and optimization work mentioned above, we will report on the deposition and color measurement of the ALD films stacks on the silver substrates.

References:

3:00pm AA1-TuA7 Nonlinear Optical Properties of TiO2-Based ALD Thin Films, Theodosia Gougoursi, R. Kuis, I. Basaldua, P. Burkins, J.A. Kropp, A. Johnson, University of Maryland, Baltimore County

Nonlinear materials in thin film form are highly desirable for the development of ultrafast all-optical system-on-a-chip platforms, optical frequency converters and optical limiting applications. Conventional nonlinear optical (NLO) materials are usually cut from bulk crystals or are liquids that are not suitable for integration with the contemporary semiconductor industry process flow. The third order nonlinear response of ALD TiO2-based films is investigated using thermally managed Z-scan technique. Some of the as-deposited films exhibit very high nonlinear response which is orders of magnitude higher than conventional nonlinear optical materials such as silica fibers and CS2. Thermal treatment of the films at 450°C for 3 hours in an oxygen rich atmosphere affects the films’ optical properties and results in the loss of the high nonlinear optical response. TiO2 films deposited by Physical Vapor Deposition (PVD) from a 99.9% TiO2 target at room temperature are used as control samples and their nonlinear optical response is found below the detection limit of the Z-scan setup. This extraordinary nonlinear optical behavior of the TiO2 ALD films is linked to the presence of a very small at. % of TiN bonding in the film. We will present detailed characterization of these films by x-ray photoelectron spectroscopy, x-ray diffraction and UV-Vis absorption. The high level of control of the nonlinear index of refraction, n2, using the deposition process coupled with the ability of ALD to coat non-planar geometries with atomic level precision and the fact that these processes are CMOS compatible have the potential to provide a breakthrough in optical device design and applications.


4:00pm AA1-TuA11 Tunable Electrical Properties of Lithium Fluoride Thin Films using Different Fluorine Sources, Devika Choudhury, A. Mane, J.W. Elam, Argonne National Laboratory

Considering that it has one of the largest optical bandgaps, lithium fluoride is probably the most popular material of choice for ultraviolet coatings today, as compared to other metal fluorides like MgF2 and AlF3. The low refractive index of 1.39 (at 580nm) also makes it useful as a window material in the UV-region of electromagnetic radiation. Other utilities of LiF include thermoluminescent detector layers for X-rays and extreme UV sensor applications, electron injection layers in LED or photovoltaics etc. Apart from optical applications, LiF may be used as a protective coating on the cathodes of Li-ion batteries due to its chemical stability and wide electrochemical window. In this regard, LiF can be mixed with other metal fluorides to improve the lithium-ion conductivity while maintaining the chemical stability. Lithium ion conductivities of order 10-4 S/cm at room temperature have been reported for Li1AlF6 and Li2NiF4.3

LiF thin films grown by atomic layer deposition have been reported earlier using lithium tert-butoxide and HF-pyridine resulting in a room temperature ionic conductivity of 10-14 S/cm. In this work we explore the possibility of growing LiF films with alternate sources of fluorine, WFs6, and MoFs6. In-situ quartz crystal microbalance and Fourier transform infrared spectroscopy studies are carried out to obtain the growth characteristics of the films. Compositional analysis is obtained from XPS measurements. Impedance spectroscopy measurements are performed to evaluate the effect of LiF concentration in mixed metal fluoride coatings.

References:
2. John Hennessy et al., Inorganics 2018, 6, 46.


4:45pm AA2-TuA14 The Role of Al2O3 ALD Precursor Chemistry on the Electrochemical Performance of Lithium Ion Battery Cathode Materials, Donghyeon Kang, D. Manne, I.W. Elam, Argonne National Laboratory; R.F. Warburton, J.P. Greeley, Purdue University

Al2O3 coatings prepared by atomic layer deposition (ALD) using trimethyl aluminum (TMA) and H2O on lithium metal oxide cathode surfaces have been shown to enhance the performance of lithium ion batteries. However, the effects depend on the choice of cathode material. For example, 1-2 TMA/H2O cycles on lithium cobalt oxide (LCO) dramatically improves cyclability and slightly decreases capacity [1]. In contrast, the same treatment on lithium manganese oxide (LMO) improves capacity but has little effect on cyclability [2]. Furthermore, the TMA surface reactions on LMO are unusual in that they do not involve hydroxyls, ethane is released, and the Mn undergoes redox chemistry. Density functional theory (DFT) calculations reveal that this unique mechanism is driven by the large free energy changes upon methyl loss from TMA [2]. This leads us to speculate that the surface reactions and subsequent electrochemistry might also depend on the choice of AI precursor. To evaluate this hypothesis, we are exploring a range of aluminum precursors including trimethyl aluminum (TMA), tris(dimethylamido) aluminum (AI-TDMA), aluminum trichloride (AlCl3), dimethyl aluminum isopropoxide (DMAI), and aluminum trisopropoxide (ATIP) on a variety of cathode materials such as LCO, LMO, and nickel manganese cobalt (NMC) materials. Our initial results suggest a correlation between cation reduction on the cathode surface and the relative Lewis acidity of the AI precursor ligands. We will elaborate on these findings using results from XPS measurements, DFT calculations, and coin cell cycling studies.


5:00pm AA2-TuA15 ALD Infiltration of LiCoO2 for High Rate Lithium Ion Batteries, Ian Povey, M. Modreanu, S. O’Brien, Tyndall National Institute, Ireland; T. Teranishi, Y. Yoshikawa, M. Yonedo, A. Kishimoto, Okayama University, Japan

The field of energy storage is constantly evolving and facing new challenges. The next-generation batteries should be cheap, constitute of abundant elements only, and show electrochemical performances at least on par with the current state-of-the-art lithium-ion batteries. One of the promising new material families is the organic electrode materials; they are composed of light elements and thus possess high gravimetric capacities. Organic electrode materials do however suffer from low electronic conductivity and solubility issues when applied with a liquid electrolyte. Coating the organic materials with a thin passivation or solid-electrolyte layer is an effective way to suppress the dissolution without dramatically affecting the electrochemical properties. An attractive way to deposit these layers in a controlled manner is the atomic/molecular layer deposition (ALD/MLD) method. When organic electrodes are deposited with ALD/MLD the redox mechanisms are easy to experiment on since the system works as such without any conducting carbon or binder making it a simple model system. The deposition of solid electrolytes or protective coatings is also a highly feasible application for ALD/MLD.

In this research, a new ALD/MLD processes were developed for promising organic electrode materials and novel Li-organic coatings. The experimented molecules are related on the known electrode material lithium terephthalate with additional functional groups which alter the electrochemical properties. Since the bulk electrode composition is not standard in literature the comparison of the materials is difficult and prone to error. When the thin films of lithium-2-amino-terephthalate and lithium-2,5-dihydroxyterephthalate (Li2HTP) are compared with lithium terephthalate (Li1TP) the direct comparison of electrochemical performance is possible. We find that both of the films do decrease the redox voltage as expected but also the flat discharge plateau of Li1TP is lost. In addition, the rate capability and the cycling life of the films were negatively affected. We propose that the functional groups that donate electron density to the π-conjugated system are causing π-π repulsion between adjacent molecules. In addition, it was found hydroxyl groups of Li2HTP are lithiated at low potentials vs. Li/Li. Also, a novel lithium ethylene glycyl ALD/MLD process was developed showing promising properties as a coating material for lithium-ion batteries. This and previous studies demonstrate the feasibility of this approach for developing better batteries and battery materials and highlights the potential of ALD/MLD technique for actual battery applications.
Recently, various coatings produced by Atomic Layer Deposition (ALD) on electrode materials have been explored extensively in LIBs. For example, Al₂O₃ and TiO₂ coatings act as a protective layer for the suppression of the solid electrolyte interphase (SEI) in various electrode materials. However, their influence on increasing the electronic conductivity of the electrode material has not been explored in details. In addition, it is also possible to synthesize using ALD the main electrode materials, such as oxides and material has not been explored in details. In addition, it is also possible to dope HfOₓ and ZrOₓ-based ferroelectric and anti-ferroelectric films will be demonstrated using lanthanum doping and is co-related to changes in unit expansion, short diffusion lengths for Li⁺ ion transport and good capacity retention even at faster kinetics.

In this presentation, we will show ALD synthesis of Al₂O₃ and MoS₂ coatings on TNTs as new electrode material for lithium-ion batteries. We show an influence of different coating thicknesses on the battery performance, in particular on the charging and discharging capacity.

References


ALD Applications

Grand Ballroom A-C - Session AA3-TuA

ALD for Memory Applications

Moderators: Scott B. Clendenning, Intel Corp., Adrien LaVoie, Lam Research Corp.

4:00pm AA3-TuA11 Doped Hi-K ALD Films of HfO₂ and ZrO₂ for Advanced Ferroelectric and Anti-Ferroelectric Memory Device Applications; Niloy Mukherjee, J. Mack, S. Rathi, Eugenius, Inc.; Z. Wang, A. Gaskell, N. Tasneem, A. Khan, Georgia Institute of Technology; M. Dopita, D. Krieger, Charles University

The discovery of ferroelectricity in doped hafnium oxide has generated excitement in the solid-state device community in recent years since hafnium oxide is a relatively simple oxide compared to traditional perovskite-based ferro-/anti-ferroelectric materials, and hafnium oxide is already used widely in the semiconductor industry. The discovery has inspired many researchers to study the system in further detail in the past few years. Recently, this group has discovered the ability to obtain anti-ferroelectric ZrOₓ in as-deposited ALD films alone, without the need for capping metallic electrodes or any post-deposition/post-metallization annealing. Tunability of the anti-ferroelectric behavior of ZrOₓ is also demonstrated using lanthanum doping and is related to changes in unit cell tetragonality with lanthanum doping. Process methods, including precursor delivery schemes and ALD deposition schemes, used to deposit doped HfO₂ and ZrO₂-based ferroelectric and anti-ferroelectric films will be described in detail. Structural and electrical properties of such films will be described in detail and co-related.

4:30pm AA3-TuA13 ALD of La-Doped HfO₂ Films for Ferroelectric Applications; Tatiana Ivanova, P. Sippola, M. Givens, ASM, Finland; H. Sprey, ASM, Belgium; T.M. Büttner, P. Polakowski, K. Seidel, Fraunhofer IPMS-CNT, Germany

Ferroelectric (FE) HfO₂ and its doped compounds [1] have received increasing interest for potential to harness these materials for non-volatile memory applications. ALD HfO₂-based ferroelectrics can provide smooth process integration to silicon based semiconductor technology in contrast to e.g. perovskite FE materials. Especially, La-doped HfO₂ films have been shown to exhibit superior ferroelectric responses with the so far highest reported remanent polarization for doped FE-HfO₂ [2]. Nevertheless, a comprehensive in depth study of this promising material system has not been done.

This research covers highlights of the growth and FE properties of La-doped HfO₂ ALD films. The 10 nm La-doped HfO₂ films were deposited on 300 mm Si wafers in an ASM Pulsar® 3000 ALD reactor over a temperature range of 200-300 °C. The La-doped HfO₂ ALD process utilized HfCl₄ and a novel lanthanum precursor with co-reactant oxidants. Spectroscopic ellipsometry and x-ray photoemission spectroscopy were used to study the film growth and composition properties, respectively. In addition, La-doped HfO₂ crystallization kinetics were studied with in situ x-ray diffractionmetry (IS-XRD). The FE properties were studied via fabrication and electrical characterization of planar metal-ferroelectric-metal capacitors (MFMCap).

Control of La-doped HfO₂ in the range of [La] ~ 1-10% (based on 100*[La]/([La] + [Hf])) was studied by varying the ratio of LaO₃:HfO₂ subcycles during the ALD process. The La-doped HfO₂ growth rate and residual C and Cl impurity concentrations were studied as a function of LaO₃:HfO₂ subcycle ratio and temperature for as-deposited films. IS-XRD analysis during high temperature annealing revealed the presence of the desired high symmetry phase of FE hafnium oxide for low [La] (1-5%) and lower temperature (200-250 °C) deposited samples, while samples with higher [La] showed an even stronger stabilization of the film which showed electrically no FE behavior. Crystallization temperatures increased with increasing La content, while it decreased with increasing deposition temperature: e.g. [La]~2% samples deposited at 200-300 °C crystallized at 615-470 °C, respectively. The MFMCap studies confirmed the presence of strong FE responses for the low La content films exhibiting maximum remanent polarization of 26.5 μC/cm² (post cycle conditioning) for [La]~2% films deposited at 250 °C.


4:45pm AA3-TuA14 Characterization of Multi-Domain Ferroelectric ZrO₂ Thin Films for Negative Capacitance and Inductive Responses; Yu-Tung Yin, P.-H. Cheng, Y.-S. Jiang, J. Shieh, M.J. Chen, National Taiwan University, Republic of China

By using a specific plasma-enhanced atomic layer deposition (PEALD) process, an as-deposited nanoscale ferroelectric ZrO₂ (nano-f-ZrO₂) thin film has been prepared. A unique periodically arranged crystalline has been observed under nano-beam electron diffraction (EBED) and dark field TEM images, indicating the presence of multi-domain structure in nano-f-ZrO₂. From the large-signal RLC oscillations in time domain analysis, the existence of positive imaginary part of the impedance, enhancement of small-signal capacitance of the series-connected capacitors, and the sub-60mV/dec subthreshold swing in nanoscale transistors, the multi-domain nano-f-ZrO₂ has provided the experimental observation for the inductive behavior and negative capacitance induced by the net polarization switching. According to the theoretical calculation, the net polarization switching of multi-domain nano-f-ZrO₂ produces an effective electromotive force which is similar in behavior with Lenz’s law, leading to the inductive responses and the negative capacitance effect. Since the as-deposited multi-domain nano-f-ZrO₂ thin film provides a significant inductance behavior compared to conventional inductors, the PEALD deposited nano-f-ZrO₂ would become a promising material in a variety of applications including nanoscale transistors, filters, oscillators, and radio-frequency integrated circuits.

5:00pm AA3-TuA15 Scaling Ferroelectric HfₓZr₁₋ₓO₂ on Metal-Ferroelectric-Metal (MFM) and Metal-Ferroelectric-Insulator-Semiconductor (MFIS) Structures; Jaidah Mohan, H. Hernandez-Arriaga, H.S. Kim, A. Khosravi, A. Sahota, The University of Texas at Dallas; R. Wolffe, University of Texas at Dallas; J. Kim, The University of Texas at Dallas

Ferroelectricity in Hafnium Zirconate (HZO) has recently garnered interest due to the possibility of achieving sub-60mV/decade Subthreshold swing...
In this study, the ferroelectric properties of HZO was studied on MIM and MFIS structures, scaling down to 3nm. HZO was deposited using TDMAB-hafnium (Hf[N(CH3)2]4), TDMAC-zirconium (Zr[N(CH3)2]4), and O3 as the Hf-precursor, Zr-precursor and oxygen source respectively at 250°C. Blanket TiN (90 nm thick) electrodes were deposited after the HZO deposition as the stress given by the TiN electrode helps in crystallizing HZO into the ferroelectric phase. Then, rapid thermal annealing was done at 450°C in an N2 atmosphere for 60s to crystallize the HZO films. A conventional photolithography/etching process was used to make capacitors of different diameters. Grazing incidence X-ray Diffraction (GIXRD) confirms that the ferroelectric orthorhombic phase is stable for HZO deposited on top of HF treated Silicon. The ferroelectric HZO film was scaled up to 5nm on top of Silicon and showed significant ferroelectric properties while 4nm and 3nm HZO showed very high leakage properties. Effects or reannealing to increase the grain size and hence the ferroelectric behavior was also studied. It was also observed that as the ferroelectric thickness decreases or the SiO2 thickness increases, there is an increase in the ferroelectric dipole relaxation, i.e. the ferroelectric domains are naturally tend to orient themselves in a particular direction.

REFERENCES:

5:15pm AA3-TuA16 Interface Characteristics of MIM Capacitors using Vanadium Nitride Electrode and ALD-grown ZrO2, High-k Dielectric Film, Jae Hyoung Choi, Y. Kim, H.I. Lee, H.-J. Lim, K. Hwang, S.W. Nam, H.-K. Yang, J. Nanoelectronics, Research Institute, Korea University of Technology, South Korea

ALD Fundamentals
Grand Ballroom A-C - Session AF-TuA

Plasma ALD: Growth and Characterization
Moderators: Hyeongtae Jeon, Hanyang University, Jiyoung Kim, The University of Texas at Dallas

1:30pm AF-TuA1 Low Temperature High Quality Silicon Dioxide by Neutral Beam Enhanced Atomic Layer Deposition, Hua-Hsuan Chen, D. Ohtori, T. Ozaki, Tohoku University, Japan; M. Utsuno, T. Kubota, T. Nozawa, ASM Japan K.K., Japan; S. Samukawa, Tohoku University, Japan

Atomic layer deposition (ALD) has shown to have high control of conformality on thin films in recent decades. Instead of conventional deposition technique, such as physical vapor deposition and plasma-enhanced chemical vapor deposition, it is usually used to deposit thin layers on complex structures due to its thickness control ability. Plasma-enhanced ALD (PEALD) and thermal ALD are the examples. However, there are some serious problems. For instance, plasma irradiation and charge accumulation existed in PEALD [1] can cause defects in thin films; high temperature is also needed in thermal ALD. In previous studies, neutral beam technology has shown advantages on depositing high quality films, such as low-k SIO2 film [2] and nitrogen doping diamond-like carbon film [3]. Here, we demonstrated the atomic layer growth of SiO2 film on Si using novel neutral beam-enhanced deposition (NBEALD) technique, which was deposited at room temperature, and serves as an important material in various applications.

Neutral beam enhanced atomic layer deposition system consists of a large-radius ALD process chamber and an inductively coupled plasma source. We used Aminosilane as the precursor and O2 as the neutral beam source to deposit films on the Si substrate. The substrate temperature was controlled at 305. After the ALD cycle which was composed of: precursor feed, precursor purge, O2 injection, neutral beam irradiation and O2 purge, the SiO2 film was grown on silicon wafers. We used spectroscopic ellipsometry to measure film thickness; the atomic force microscope was used to investigate the surface morphology; the X-ray photoelectron spectroscopy (XPS), X-ray reflectivity (XRR) and secondary ion mass spectrometry (SIMS) were used to analyze the chemical composition of the films for investigating the SiO2 film quality.

The ALD cycle shows the thickness is linearly dependent on the number of cycles with growth per cycle comparable to that of PEALD [4]. The uniformity of the film was obtained by measuring thickness on different places of 8 inch wafer, and the result shows the film has good uniformity. For the XPS, XRR and SIMS results, high quality and high density SiO2 film composition was confirmed. Furthermore, the excellent surface morphology could be seen on SiO2 films as no difference for thickness discrepancy. Therefore, we succeeded to make high quality SiO2 films using NBEALD technique under room temperature.

REFERENCES
reactive radicals through surface recombination. Using plasma ALD of SiO₂, TiO₂ and Al₂O₃ as case studies, we show that the AR up to which film growth is achieved gives quantitative insight into the recombination probability \( r \) of plasma radicals on given material surfaces. Such quantitative information on \( r \) is often not available in the literature and difficult to obtain by conventional methods, while it is essential for predicting and understanding the conformity achieved by plasma ALD. Applications of plasma ALD such as the conformal growth of SiO₂ spacers for self-aligned patterning can thus benefit from this work.

In this study we use microscopic lateral-high-aspect-ratio structures supplied by VTT (PillarHull® LHARA) to assess the conformity of plasma ALD processes. As these chips have extremely high AR trenches (AR=10000) deposition is typically limited up to a certain penetration depth. For the first time, we demonstrate that this penetration depth can be used to quantify \( r \) during plasma ALD.

By carrying out plasma ALD of SiO₂ using SiH₄(N(CH₃)₂)₂ and different O₂/Ar plasma exposure times, we have observed that the penetration depth increases logarithmically with the plasma time used in the ALD cycle. This relation is well described by a simple analytical model which can be used to calculate \( r \). For plasma ALD of SiO₂ this gives \( r=6(\text{e}^{-3})^{-1} \), which compares well to reported literature values. Using a long plasma exposure, deposition of SiO₂ is achieved up to an AR as high as 900. Similarly, growth of TiO₂ using Ti(N(CH₃)₂)₄ reaches AR=250. In contrast, plasma ALD of Al₂O₃ using Al(CH₃)₃ shows a surprisingly low penetration (AR=80) compared to the traditional ALD processes, even with long plasma exposure, which indicates the impact of a relatively high surface recombination probability. Estimations of the corresponding values of \( r \) and additional insights will be provided in this contribution. These results demonstrate that our method is a powerful and straightforward way to gain knowledge on surface recombination during plasma ALD and its strong effect on film conformity.


2:00pm AF-TuA3 A Robust Method for In-situ Gas Monitoring of ALD Processes using Optical Emission Spectroscopy of a Pulsed Remote Plasma, Joe Brindley, B. Daniel, V. Bellido-Gonzalez, Gencoa Limited, UK; R. Potter, B. Peek, University of Liverpool, UK

Effective and robust monitoring of individual gas concentrations during the ALD processes offer a unique insight into the process behavior as well as being an important step in the eventual wide-spread industrialization of the ALD technique.

Conventional quadrupole residual gas analyzers have difficulty monitoring ALD processes due to the high process pressures and the presence of contaminating hydrocarbons contained within many ALD precursors. For these reasons monitoring of precursor gas concentrations during the ALD process is not often undertaken, especially at the production stage.

An alternative gas sensing technique that operates directly at pressures above \( 1 \text{e}^{-1} \) mBar has been built around remote plasma emission monitoring. This technique involves the generation of a small, remote plasma using an inverted magnetron placed within the ALD vacuum system. Consequently, species that are present within the vacuum become excited in the sensor’s plasma, emitting a spectrum of light, which can then be used to identify and monitor the emitting species. Importantly, this plasma, generated inside the sensor, has a sole function as a gas detector and does not affect the ALD process itself.

This work will demonstrate that the sensing method is robust when exposed to the ALD processing environment. Previous work had demonstrated the usefulness of this technique but limitations were encountered when using a DC voltage to generate the sensor’s plasma as contamination and reduced sensitivity developed when used with certain precursors. This work will describe a novel method of generating the detector plasma using a high peak power, low duty cycle pulsed voltage. It will be demonstrated that the pulsed power technique is more effective than DC in preventing contamination of the sensor’s electrodes as well as improving the detection sensitivity of common ALD precursors and their reaction by-products.

Examples of this sensing technique’s practical uses for Al₂O₃ and TiO₂ ALD processes are discussed; this includes detection of contaminants, optimizing purge cycle length and monitoring the reaction dynamics in terms of precursor gas consumption and reaction by-products.

2:15pm AF-TuA4 Near Room Temperature Plasma Enhanced Atomic Layer Deposition of Gold Metal, Michiel Van Daele, Gent University, Belgium; M. Griffiths, Carleton University, Canada; A. Raza, Gent University - IMEC, Belgium; M. Minjaeuw, Ghent University, Belgium; S. Barry, Carleton University, Canada; R. Baets, Gent University - IMEC, Belgium; C. Detavernier, J. Dendooven, Gent University, Belgium

Currently only two Au ALD processes exist, using different precursors. The first Au ALD process, reported by Griffiths et al. [1], is a three step process using MeAuPMe₃ as the precursor in combination with an oxygen plasma and water vapour as the reactants. The deposition of metallic gold was reported at a deposition temperature of 120°C, with only some carbon and oxygen impurities present in the film (6.65% C and 1.83% O). A growth rate of 0.05 nm per cycle was achieved. The Au ALD process, reported by Mäkelä et al. [2], uses MeAu(SCN)Et₃ as the precursor and ozone as the reactant. Deposition between 120-180°C was reported with self-limiting growth at 180°C and a growth rate of 0.09 nm per cycle. The deposited films had low resistivity values (4-16µΩ cm) and were chemically pure with few impurities, O (2.9%), H (0.9%), C (0.2%), and N (0.2%).

A new plasma enhanced ALD process has been developed using Me₃AuPMe₃ and H₂ plasma as the precursor and reactant, respectively. Both precursor and reactant exhibit catalytic behaviour, with a growth per cycle of 0.03 nm per cycle. A temperature window between 50°C and 120°C has been achieved, with decomposition of the precursor above 120°C. The as-deposited gold films are polycrystalline and pure, with no phosphorus present in the film and very few carbon impurities (0.3%). Measured resistivity values (5.85µΩ cm) were close to the expected bulk value of gold (2.44 µΩ cm).

The surface chemistry and growth mechanism were investigated using in-situ RAIRS measurements, optical emission spectroscopy, and mass-spectrometry, pointing to an abbreviated growth cycle, instead of a complete one [3]. The initial growth starts off with the nucleation of gold particles on the surface. The formed gold nanoparticles grow and coalesce during the ALD process, as characterized using SEM measurements. The spacing of the gold particles makes this process interesting for surface enhanced Raman spectroscopy (SERS). Free space Raman measurements were performed on some of the samples and these showed excellent surface enhancement of the Raman signal. As far as we know this is the first report of an ALD gold film that shows SERS properties. In contrast to other SERS substrate fabrication methods, often involving lithography, this ALD process provides a direct way to fabricate SERS substrates without the need for a lot of process steps.


2:30pm AF-TuA5 Low-Temperature Deposition of Gallium Oxide and Aluminum Oxide with Arrays of Microcavity Plasma Enhanced Atomic Layer Deposition, Jinhong Kim, A. Mironov, S.-J. Park, J.G. Eden, University of Illinois at Urbana-Champaign

A new atomic layer deposition (ALD) technology has been developed with an array of microcavity plasma devices which enable to grow the atomic layers at low temperature and enhance the growth rate with less defects and contamination. Confining low temperature plasma to an array of microcavities yields uniform growth at low substrate temperature of 1 atmosphere and beyond. Not only are electron densities above \( 10^{18} \text{ cm}^{-3} \) now routine, but the plasma electron temperature (\( T_e \)) and the ratio of the local electric field strength to the gas number density (\( E/N \)) are also increased significantly relative to conventional (macroscopic) plasmas. All of these characteristics are ideal for plasma chemical processing to generate oxidants efficiently compared to conventional RF or others existing source technology. A compact ALD system of which volume reduced by at least a factor of five was realized thanks to the miniaturized microplasma source operating in lower frequency ac waveform. The uniform and conformal gallium oxide \((Ga_2O_3)\) and aluminum oxide \((Al_2O_3)\) thin films were deposited at low temperatures (< 50 °C) on silicon, quartz, and even polyethylene terephthalate (PET). Due to the complete reaction between precursors, the stoichiometric value of films presents ~ 1.5 in crystalline state, indicating the presence of negligible levels of impurities. MOSCAP was fabricated to analyze the electrical characterization of 30 nm thickness of Al₂O₃ film. This MOSCAP exhibits higher breakdown electric field of 6.1 MV than conventional Al₂O₃ thin film. Hysteresis width from the sweep bias voltage was measured to less than 1 mV which is close to ideal.
MOSCAP electrical characteristics. In addition, Ga2O3 films deposited on PET were used to fabricate for transparent and flexible solar-blind photodetector with metal-semiconductor-metal junction structure. The crystallinity of films was analyzed using Transmission electron microscope (TEM) and X-ray diffraction (XRD). Post annealing (> 800 °C) with argon environment was essential to produce polycrystalline β-Ga2O3. Bandgap was calculated by optical characteristics of the films from UV spectrophotometer. The photoresponse properties of photodetectors were investigated by the current-voltage characteristics and time-dependent photoresponse curves. Various thin film grown by microplasma enhanced ALD demonstrates improved optical and electrical properties. The scientific inspiration of this new deposition technology as well as the prospect for commercial application will be discussed in this presentation.


Plasma assisted atomic layer deposition (PA-ALD) is a low temperature, conformal, layer-by-layer deposition technique that is based on a pair of self-terminating and self-limiting gas-surface half-reactions, in which at least one half-reaction involves species from a plasma. This approach generally offers the benefit of substantially reduced growth temperatures and greater flexibility in tailoring the gas phase chemistry to produce varying film characteristics. The flexibility and lower growth temperatures that plasmas provide come at the cost of a complex array of process variables that often require great care on the part of the user. In response to this challenge, this work focuses on the use of plasma diagnostics to inform the choice of process conditions for PA-ALD systems. In this work we employ VUV-NIR spectroscopy, charged particle collectors near the substrate, and spatially resolved Langmuir probe measurements to characterize the inductively coupled plasma source used in a Fiji 200 (Ultratech/CNT) PA-ALD tool. In particular, we assess the total ion flux reaching the substrate surface, spatial variation of plasma properties, and the relative fractions of atomic and molecular species generated in the plasma under a variety of pressures and gas input flow properties in context of PA-ALD of AlN, InN, TiO2 and Ga2O3 films. Changes in plasma parameters are then linked with changes in film characteristics.


INVITED

Ga2O3 has emerged as a promising material for next generation power electronics. While β-Ga2O3 (monoclinic) is the most stable and studied of five Ga2O3 polymorphs, the slightly less energetically favorable α- and ε-Ga2O3 phases have unique characteristics that can be exploited. α-Ga2O3 (rhombohedral, corundum) has the largest bandgap of 5.3 eV and can be alloyed with α-Al2O3 and α-In2O3 for bandgap engineering. ε-Ga2O3 phase (hexagonal, wurzite) is polar, with a predicted polarization strength that is 10 and times larger than that of GaN and AlN, respectively. Like the III-N system, polarization induced charges can lead to higher charge densities and mobilities in two-dimensional electron channels formed at heterojunctions, which would improve the viability of Ga2O3 electronic devices. Plasma-enhanced atomic layer deposition (PEALD) is a popular, conformal, energy-enhanced synthesis method for thin films due to its many advantages, including: deposition at reduced growth temperatures, access to metastable phases and improved crystallinity, and increased growth rates. In this work, we use PEALD to produce high-quality heteroepitaxial Ga2O3 and (AlGa)2O3 (AGO) films, and investigate phase selectivity as a function of substrate, growth temperature (Tg), plasma gas phase chemistry and gas pressure.

All Ga2O3 films were deposited in a Veeco Fiji 62 reactor equipped with a load lock and turbo pump using trimethylgallium and O2 plasma. Initial studies on c-plane sapphire substrates at 350°C and 8 mTorr, show the phase could be altered from β to α by a varying the O2 flow during plasma pulse from 5-40 sccm. Optical emission spectroscopy indicate that the O2*/O3 ratio is crucial for phase selectivity while the high ion flux to the surface can contribute to the crystallinity at low Tg. To grow ε-Ga2O3 on c-plane sapphire required going to much higher temperature (500°C), pressure (100’s mTorr), and O2 flow (100sccm). Under no conditions was pure ε-Ga2O3 on sapphire achieved. Using optimum growth conditions for the three phases on sapphire, films were deposited on GaN and diamond to determine the effect of substrate structure. While films on diamond resulted in mixed β/ε phases, pure ε-phase films were attained on GaN and the strain varied with pressure and Tg. To investigate favorable heterojunctions for 2DEG formation, AGO films were developed. While the full stoichiometric range could be reached using a PEALD digital alloying method, crystallinity was lost above >30 %Al, independent of phase. Initial electrical results on breakdown voltage and heterojunctions will be shown in order to establish the feasibility of these films in device applications.

Atomic Layer Etching

Regency Ballroom A-C - Session ALE1-TuA

Modeling & Instrumentation I

Moderators: Ankur Agarwal, KLA-Tencor, Alok Ranjan, Tokyo Electron America Inc.

1:30pm ALE1-TuA1 Atomic Layer Etching of Nanostructures, Sabbir Khan, Niels Bohr Institute, University of Copenhagen, Denmark; D. Suyatin, Lund University, Sweden; J. Sundqvist, Fraunhofer Institute for Ceramic Technologies and Systems IKTS, Germany

INVITED

Progress in modern electronics demands atomic precision-controlled fabrication of devices and atomic layer etching (ALE) processes which can assist device trimming with atomic precision. ALE is now becoming a key technique for nanofabrication and the semiconductor industry. In this talk we will demonstrate ALE of thin film Ga-polar GaN (0001) where surface modification is done by Cl2 adsorption and later modified chlorinated layer is removed by low energy Ar ions in plasma environment using standard reactive ion etching (RIE) system (Oxford Plasmalab 100) [1]. Further, using a similar system, Cl2 and Ar based highly anisotropic ALE on crystalline Si (100) with good etch selectivity for SiO2 masks will be discussed. This high material selectivity enables nano-pattern of different geometries on Si wafer and post-ALE patterns inspection allows us to understand different effects (such as, trenching and sidewall tapering etc.) and limitations of the process. We also demonstrate that the ALE processed patterned substrates can be used as molds for high resolution nanoimprinting of features size down to 30 nm [2]. Finally, ALE on semiconductor nanowires will be shown, indicating that the process can be used for damage free processing of semiconductor nanowire devices and precise nanofabrication below 20 nm [3].

Reference:


2:00pm ALE1-TuA3 Selectivity during Plasma ALE of Si-Compounds: Reaction Mechanism Studied by in-situ Surface Spectroscopy, René Vervuurt, ASM; K. Nakane, T. Tsutsumi, M. Hori, N. Kobayashi, Nagoya University, Japan

Plasma atomic layer etching (ALE) processes based on plasma modification and modification layer removal by fluorine radicals have recently been reported, for the etching of SiN and SiC [1-3]. The proposed processes offer advantages in terms of etch process control, uniformity and etch selectivity versus SiO2 compared to more conventional etching techniques. In this contribution the selective ALE of Si-compound films is investigated and the reaction mechanism behind the etch selectivity between compounds is discussed. H2, He and N2 plasma modification and the subsequent etching of the modified layer by F-radicals are studied by in-situ Fourier Transform Infrared Spectroscopy (FTIR) and spectroscopic ellipsometry (SE) for several Si-compounds (SiN, SiC, SiCOH, and SiO2).

in-situ SE measurements show that the selectivity of the ALE process can be controlled by the modification plasma; H2 plasma can be used for the selective etching of SiN, SiC and SiCOH versus SiO2, whereas a N2 plasma makes the selective etch of SiC and SiCOH versus SiN and SiO2 possible. Plasma modification on the other hand did not result in etching by F-radicals.
The origin of the selectivity and underlying reaction mechanism is discussed on the basis of in-situ FTIR measurements. These show that H₂ plasma modification of SiN, creates a H-rich modification layer containing Si-H and N-H groups. Both Si-H and N-H group formation saturate with exposure time. The created Si-H and N-H groups are removed by the subsequent F-radical exposure resulting in the net removal of SiN. The reaction mechanism for H₂ plasma ALE of SiC and SiCOH is found to be similar, a H-rich layer is formed on top of the sample which can be etched using F-radicals, while SiO₂ is not modified. This makes it possible to selectively etch SiN, SiC and SiCOH versus SiO₂.

N₂ plasma can be used to selectively modify SiC versus SiO₂ and SiN by creating a Si-H and C=N rich layer. The Si-H groups are created by the restructuring of the hydrogen already present in the SiC film in the form of C-H bonds. The modified layer can be removed using F-radicals allowing for the selective etch of SiC.

He plasma exposure of SiN, SiC and SiCOH creates a Si-O rich modification layer. This layer cannot be removed by F-radicals and therefore does not result in etching.

The obtained results indicate that the formation of a Si-H rich layer is essential for the plasma ALE of SiN, SiC and SiCOH. By tuning the plasma conditions the formation of this layer can be controlled allowing for the selective ALE between SiN, SiC, SiCOH and SiO₂.


2:15pm ALE1-TuA4 Chamber Vacuum Strategies to Enable High Productivity ALE, Declan Scanlan, D. Stephenson, A. Stover, Edwards Vacuum, Ireland

As device lateral dimensions shrink with each successive technology node, the semiconductor industry is now poised to transition from the nanoscale shrinking CD of devices.

Apart from this extended pumping time requirement, these high-flow steps intensifies this challenge of by-product management within the vacuum system. In addition, the adoption of specific surface passivation and protection techniques, utilising precursor deposition chemistry, (e.g. in-situ ALD / ALE) intensifies this challenge of by-product management within the vacuum system.

This paper will not only discuss how internal pump technology can help address these challenges, but also how different chamber pumping strategies can be deployed to this end.


Due to the possibility of improved electromigration properties and lower resistivity at decreased critical dimensions, Co has been identified as a candidate to replace Cu and potentially W in future semiconductor devices. To enable the use of Co at such small dimensions, monolayer control in process is necessary. Accordingly, Atomic Layer Etch (ALE) is a promising solution towards well-established Atomic Layer Deposition (ALD) methodologies, such that sequential self-limiting etch processes can be targeted with monolayer control for ultra-thin film material removal.

Herein, we present a theoretical analysis using first principles simulations of a thermal ALE process for cobalt metal utilizing a sequential thermal-chemical etch cycle employing propene and carbon monoxide (CO). It is shown that ALE can be achieved via the oxidative addition-H₂ elimination of propene to the Co surface followed by the introduction of CO to generate (η³-C₃H₅)Co(CO)₃ as a volatile etch product at process conditions. It was found that the generation of (η³-C₃H₅)Co(CO)₃ is thermodynamically favourable and necessitates a high CO step coverage. A full proposed mechanism for this potential thermal atomic layer etch process will be discussed.

2:45pm ALE1-TuA6 Selective Quasi-ALE of SiO₂ over SiNₓ via Bottom-up Si₃N₄ Passivation: A Computational Study, Du Zhang, Y. Tsai, Y. Shi, W. Wang, TEL Technology Center, America, LLC

Selective SiO₂/Si₃N₄ atomic layer etching (ALE) has broad applications in both logic and memory device fabrication. Conventional methods of achieving SiO₂/Si₃N₄ selectivity generally employ a preferential top-down carbon-based polymer passivation on Si₃N₄. However, achieving a highly preferential passivation of Si₃N₄ only is challenging in this top-down carbon polymerization approach. To overcome these limitations, we propose a two-step selective SiO₂/Si₃N₄ ALE method that utilizes bottom-up Si₃N₄ passivation. In the first step, the formation of an ammonium (NH₄⁺) salt blocking layer on the Si₃N₄ surface is enabled in a plasma containing H₂ and HF via surface conversion, with its feasibility and reaction pathways demonstrated with thermodynamics and quantum chemistry calculations. The SiO₂ substrate, by contrast, undergoes a partial surface reduction by the H radicals, demonstrated with molecular dynamics simulations. In the second step, the partially reduced SiO₂ surface can be volatilized in a plasma containing fluorine and/or other halogens, leaving the Si₃N₄ underneath the NH₄⁺ salt layer intact. This new approach provides a promising solution toward infinite SiO₂/Si₃N₄ selectivity, thanks to the N atoms for the NH₄⁺ salt passivation layer provided by the Si₃N₄ substrate alone. Moreover, the bottom-up passivation also translates into better pattern fidelity due to precise etch control, which is essential for the ever-shrinking CD of devices.

3:00pm ALE1-TuA7 Insights of Different Etching Properties between CW and ALE Processes using 3D Voxel-Slab Model, Nobuyuki Kuboi, T. Tatsumi, J. Komachi, S. Yamakawa, Sony Semiconductor Solutions Corp., Japan

INVITED

Atomic layer etching (ALE) processes have attracted considerable attention to realize high control etching (layer-by-layer) and very low damage (defect creation) caused by ion bombardment from plasma [1]. To use ALE as a practical process in mass production of semiconductor devices, it is necessary to know how to control process nobs along with the mechanism. To obtain such knowledge in the view point of numerical simulations, we modeled the ALE process of SiO₂ and Si₃N₄ films and simulated etching properties in the cases of conventional continuous-wave (CW) etching and ALE.

We propose a surface reaction model for the ALE process which consists of a deposition step by C₅F₁₂/O₂/Ar plasma and etch step by Ar plasma for SiO₂ and Si₃N₄ film etching. This is based on the slab models of SiO₂ [2] and Si₃N₄ [3], which can give not only the etch rate and thickness of the C-F polymer layer but also the damage distribution described by Si dangling bond density on the etched layers. The surface layer is assumed to consist of two layers: a reactive layer divided by several thin slabs of lattice size order and a deposited C-F polymer layer on the reactive layer. We considered not only outflux of O and N from the reactive layer described previously [2][3] but also the enhancement effects of F from the deposition step and the etched polymer layer by an Ar⁺ ion on the etch yields of SiO₂ and Si₃N₄ films by the Ar⁺ ion. To analyze the 3D etched profile for the self-aligned contact (SAC) process, we developed a 3D simulation technique using an advanced
Atomic Layer Etching

Regency Ballroom A-C - Session ALE2-TuA

Modeling & Instrumentation II

Moderators: Dmitry Suyatin, Lund University, Tetsuya Tatsumi, Sony Semiconductor Solutions Corp.

4:00pm ALE2-TuA11 First-principles Understanding of Atomic Layer Etching of Silicon Nitride using Hydrofluoroarbons, Gyeong Hwang, E. Cheng, University of Texas at Austin; S. Sridhar, TEL Technology Center, America; P. Ventzek, A. Ranjan, Tokyo Electron America Inc.

The removal of thin layers of material with atomic-scale precision and spatial control (area selectivity) is critical for advanced device fabrication, making atomic layer etching (ALE) more attractive due to its ability to tightly control etch rates and to achieve wafer scale uniformity without physical damage. While ALE processes have been widely used to remove Si, Ge, compound semiconductors, and various oxides, only a few studies on ALE of Si3N4 films have been reported despite its technological importance. Recent experimental investigations have demonstrated that ALE of Si3N4 can be achieved via sequential exposure of hydrogen and fluorinated plasma or a cyclic process involving two alternating CH3F gas adsorption and Ar bombardment steps. Both methods are avenues for area selective etch and isotropy control. However, the fundamental mechanisms by which the etching occurs are poorly understood. In this talk, we will present our recent findings regarding underlying mechanisms leading to facile ALE of Si3N4 using hydrofluoroarbons, based on periodic density functional theory calculations. Our study highlights the important role of adsorbates and surface functional groups. For CH3F chemisorption on a N-rich Si3N4 surface, we have found a trimolecular process to be the thermodynamically most favorable pathway for initiation of the process, consisting of a nucleophilic attack of a primary amine site, if available, on CH3F, followed by a stabilization of the fluoride leaving group by an adjacent primary amine site. While this mechanism as is has a relatively high activation energy (~0.9 eV), the presence of products from other reactions on the surface such as HF, F-, and H+ have been demonstrated to lower this activation energy significantly. Furthermore, we find that it is not the methylation of the surface that facilitates etching, but rather the production of H2F+ that helps facilitate formation of volatile N-containing species and Si-F bonds. More importantly, our study also suggests that the surface reaction mechanism responsible for Si3N4 ALE may be altered when CH3F is replaced by CHF3 or CF4.

4:15pm ALE2-TuA12 An Extended Knudsen Diffusion Model for Aspect Ratio Dependent Atomic Layer Etching, Lutz Felipe Aguinsky, P. Manstetten, TU Wien, Austria; A. Hössinger, Silvaco Europe Ltd., UK; S. Selberherr, J. Weinhub, TU Wien, Austria

Atomic layer etching (ALE) is a fundamental part of semiconductor processing as device critical dimensions must be controlled to the order of nanometers [1]. One known issue in ALE, as in other etching processes, is aspect ratio dependent etching (ARDE) [2], which is the reduction of etch rates as the aspect ratio of a feature increases. One of the mechanisms linked to ARDE is the depletion of neutral species towards the bottom of a feature. This phenomenon has been investigated using a three-dimensional Monte Carlo method [3]. However, this method requires a complex setup and it is computationally expensive. For deposition processes, Knudsen diffusion [4] models provide analytical results and are actively developed. These models have been used for estimating surface parameters in some atomic layer deposition processes [5]. The Knudsen diffusion approach arises from physical considerations to the mass balance at each volume element. Alternatively, given isotropic reflections and particle source, the fluxes can be calculated exactly over the whole domain via the radiosity equation [6]. The radiosity approach requires the assembly and inversion of a matrix describing the exchanges, being notably unsuitable for low sticking regimes.

We propose a model extending the standard deposition Knudsen diffusion approach by including the direct flux from a particle source and a geometric factor to enable a more rigorous picture of ARDE in ALE. The inclusion of the direct flux is motivated by the radiosity equation, while avoiding the costly matrix inversion step. The geometric factor enables a more accurate description of the geometry by integrating over the whole feature at each volume element. We compare our extended Knudsen diffusion model against a reference radiosity model [6], achieving good agreement. Our results highlight one shortcoming of the standard Knudsen diffusion model: The flux near the bottom of a high aspect ratio feature is underestimated. We also show that the geometric factor describes the particle transport more accurately near the extremities of finite cylinders.

The financial support by the Austrian Federal Ministry for Digital and Economic Affairs and the National Foundation for Research, Technology and Development is gratefully acknowledged.

References

4:30pm ALE2-TuA13 Thermodynamics-Based Screening Approach for Atomic Layer Etching, Nagraj Kulkarni, Consultant

A thermodynamics-based approach for screening directional or thermal Atomic Layer Etching (ALE) processes is discussed for the purpose of achieving high synergies close to unity. The Ta-Cl system was selected as a test case for this analysis. Reaction equilibria for over 30 condensed-gas species were computed from available thermodynamic data in this system. Suitable process conditions for the formation of stable reaction products or compounds and the corresponding partial pressures of known gas species were first obtained with the aid of volatility diagrams that were calculated using thermodynamic data for all known solid-gas reactions. For optimum conditions during the first stage of a typical ALE process (passivation step), the selection of suitable metal-gas compound/s that have very low vapor pressures and hence negligibly low etch rates was made. For optimum conditions during the second stage (inert ion sputtering) of a directional ALE process, an assessment of the potential for selective sputtering of the selected compound/s relative to the base metal was made from knowledge of the surface binding energies of the base metal and relevant compound/s that are usually considered to be the enthalpy changes of the relevant solid-gas sputtering reactions at room temperature. In the case of an isotropic, thermal ALE process, the selection of suitable temperatures for the direct volatilization of the reaction product layer during the second stage of ALE is also discussed.


One of the main challenges in designing novel atomic layer deposition (ALD) and atomic layer etch (ALET) processes is to ensure the self-limiting (SL) nature of reactions during the individual precursor pulses at the target temperature of interest. It is important to establish a SL temperature window to ensure that the precursors will not produce chemical vapour deposition (CVD) or chemical vapour etching (CVE). To that end, we have developed a first principles based computational methodology to study the competition between continuous and SL reactions when a material surface is exposed to precursor gases.

ALET processes for oxides have been reported using sequential fluorination by HF and ligand exchange reactions at elevated temperatures. Herein, we investigate the nature of the HF pulse when treating a range of materials including SiO2, TiO2, HfO2, ZrO2, Al2O3 and TiN by comparing the free energy
profiles of the potential CVE and SL reactions computed with density functional theory (DFT). In general, elevated temperatures favour CVE of these materials, whereas fluorination of the surface is self-limiting at lower temperatures. HF was computed to continuously etch B₄O and TiO₂ even at temperatures below 100°C by forming volatile fluorides. This is in good agreement with experimental FTIR, where the onset of continuous etching of TiO₂ by HF was found at 80°C - 90°C and where etching of B₄O proceeded even more rapidly than that of TiO₂. However, in another example, HF is predicted to preferentially etch HFO₂ above 160°C, whereas experiment shows the process to be still self-limiting at 200°C. Therefore, this simple thermodynamic analysis, which does not include reaction kinetics, is only able to provide a lower threshold temperature at which a CVE reaction may become favourable, subject to overcoming any kinetic barrier. We also computed that Al₂O₃ resists continuous etching up to 340°C while TiN can not be etched until temperatures exceed 1300°C.

This methodology is also used to understand the competing CVD and SL reactions in the ALD of Ru using the RuO₂ precursor and H₂. The DFT calculations show that RuO₂ undergoes an SL decomposition into RuO₂ on electron-rich surfaces and that this is in competition with CVD.

These examples illustrate that this relatively quick computational approach can be effectively used to screen candidate precursor molecules to be selected for material processing.


5:00pm ALD2-TuA15 Variation of Etched Depth per Cycle and Removal of Reactive Species in Atomic Layer Etching (ALE) - Molecular Dynamics Study. Satoshi Homoguchi, E. T. Tsuchiya, S. Higai, K. Okado, M. Iwasa, T. Ito, K. Karashima, Osaka University, Japan

Alternating application of reactive species from a plasma with no bias energy and Ar plasma with low bias energy to a Si-based film (such as Si, SiO₂, and SiN) can cause atomic layer etching (ALE) of its surface. In this process, the initial application of reactive species to the surface will leave a sufficient number of reactive species (e.g., Cl atoms) bonded with the surface atoms (e.g., Si, forming Si-Cl bonds) and, in the second step where low-energy Ar ions irradiate the surface, a thin mixed layer of the reactive species and surface atoms is formed and volatile molecules (e.g., SiCl₂) desorb from the surface. Since the incident energy of Ar ions is too low to physically sputter surface atoms, etching or desorption of volatile species ends as soon as reactive species are exhausted from the surface - even if Ar ions continue to bombard the surface with low incident energy. This self-limited etched depth of a single cycle (i.e., application of reactive species and application of low-energy ions) allows “nearly” layer-by-layer etching of the material surface. At the end of each cycle, where self-limited etching takes place, some reactive species tend to remain on the surface or in the subsurface region, causing surface roughness. Depending on how deep such reactive species diffuse into the subsurface region or how thick the formed mixed layer becomes, the etched depth per cycle changes. In this study, etched depth per cycle and remaining reactive species are discussed based on the results of molecular dynamics (MD) simulation of single cycles of various ALE processes. Example considered here include Si ALE by fluorne reactions, SiO₂ ALE by fluorocarbon reactions, and SiN etching by hydrofluorocarbone or hydrogen reactions.

Several metal oxide systems, such as Al₂O₃, TiO₂, ZnO, and H₂O₂, have been explored for AS-ALD processes. For a hard mask, Al₂O₃ possesses advantages over other metal oxides due to its high hardness as well as chemical inertness for etching selectivity. However, despite extensive studies on ALD Al₂O₃, there are few studies on AS-ALD of Al₂O₃. Furthermore, literature suggests that Al₂O₃ may be comparatively difficult to block; for example, the blocking selectivity of Al₂O₃ is limited to only ~6 nm due to the formation of a ZnO barrier with a thickness over ~30 nm. The difference in blocking highlights the importance of precursor chemistry for AS-ALD, which motivates the current study to elucidate the mechanism of Al₂O₃ ASALD based on a comparative study of Al precursors.

In this work, we study the growth mechanism of Al₂O₃ with four Al precursors; trichloroaluminum (TCA), dimethylaluminum chloride (DMACl), trimethyloxaluminum (TMA), and triethylaluminum (TEA). They offer a comparative study of precursor ligand properties (reactivity, polarity, and geometric factors) by changing both the number of methyl (Me) and chloride (Cl) group in AlMe₃Clₙ (n=0, 1, and 3) and the chain length of alkyl ligands in AlCl₃Meₙ₋₁ (n=1 and 2). Results of quantum chemical calculations of the reaction pathways show product energetics that are strongly correlated with experimental observations. For example, with increasing number of Cl ligands, the growth rate is found experimentally to increase at low temperature, consistent with a large initial adsorption energy of TCA on Si.

Interestingly, although they have similar geometrical factors, the precursors exhibit different ALD growth rates (0.75, 1.0, and 1.2 Å/cycle for TCA, DMACl, and TMA respectively) corresponding to the calculated trend in activation energies as the Cl number increases. AS-ALD of Al₂O₃ using octadecyltrichlorosilane SAMs as an inhibitor is also investigated; the blocking properties of the four Al precursors will be compared and the results discussed based on the growth mechanism. By pursuing first-principles design of selective ALD processes, this work may enable new methods for additive nanoscale patterning.

Illinois at Urbana-Champaign

Two-dimensional lithography is becoming increasingly challenging due to continued downscaling of modern semiconductor devices. Area-selective deposition of dielectrics and metals can simplify patterning for next-generation devices. A new atomic layer deposition (ALD) approach allows for self-aligned deposition and thereby enables more reliable device fabrication. In our previous work, area-selective ALD of SiO_2 was demonstrated using three-step (ABC) ALD cycles consisting of acetyleneacetonate (Hacac) initiator (A), H_2Si[N(CH_3)_2]_2 precursor (B), and an O_2 plasma co-reactant (C) doses.[1] In this contribution, the reaction mechanisms involved in cyclewise removal and reaplication of inhibitor molecules will be described. Based on the acquired insights, new opportunities and challenges for this approach will be discussed.

The reapplication of the inhibitor allows for the use of oxygen or plasmas as the co-reactant, which is one of the merits of the approach. However, using in situ infrared spectroscopy it was found that the Hacac molecules are not completely removed during the O_2 plasma exposure. Remaining Hacac fragments hinder the Hacac adsorption in the subsequent ALD cycle, and thereby decrease the selectivity. The challenge of reapplying the inhibitor molecules every cycle is therefore to ensure that the non-growth area is returned to its original state before the next inhibitor dose. In order to completely remove all Hacac species, a four-step (ABDC) ALD cycle was developed which employs a H_2 plasma step prior to the O_2 plasma exposure. The added H_2 plasma, significantly improves the selectivity, such that ~2.5 nm SiO_2 can be deposited selectively in the presence of an Al_2O_3 non-growth area.

In general it is challenging to use an O_2 plasma on structures with metal areas, due to potential oxidation of the metal during the plasma exposure which reduces the conductivity. However, the H_2 plasma in the ABDC cycle was found to largely remove the precursor ligands, and therefore only a very mild O_2 plasma exposure is required for SiO_2 deposition. In this way, area-selective ALD was achieved relative to Co as the non-growth area without significant damage to the Co substrate. The application possibilities of this ABDC-type ALD process for reliable interconnect fabrication (i.e. self-aligned VIA) will be discussed.


2:30pm AS1-TuA5 Area-Selective ALD of Silicon Oxide using Inhibitors in Four-step Cycles for Metal/Dielectric Selectivity, Marc Merkx, R. Jongen, Eindhoven University of Technology, Netherlands; A. Mameli, TNO/Holst Center, Netherlands; D. Hausmann, Lam Research Corp.; W.M.M. Kessels, A.J.M. Mackus, Eindhoven University of Technology, Netherlands

The fabrication of nanoelectronics at sub-5 nm dimensions using conventional top-down fabrication schemes is becoming more and more difficult due to the increasingly stringent requirements in alignment. Area-selective ALD deposited films on self-aligned structures and thereby enables more reliable device fabrication. In our previous work, area-selective ALD of SiO_2 was demonstrated using three-step (ABC) ALD cycles consisting of acetyleneacetonate (Hacac) initiator (A), H_2Si[N(CH_3)_2]_2 precursor (B), and an O_2 plasma co-reactant (C) doses.[1] In this contribution, the reaction mechanisms involved in cyclewise removal and reaplication of inhibitor molecules will be described. Based on the acquired insights, new opportunities and challenges for this approach will be discussed.

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such as: (i) lateral overgrowth of an ALD film once film thickness exceeds that of the inhibiting material. A polymer strategy offers the potential to control the polymer film thickness and thus the desired ALD film thickness (ii) On patterned surfaces line edges and corners are sites for significant defectivity in ASD. The surface growth of a polymer readily covers these corners and edges to ensure these features are protected during the ALD process.

3:00pm AS1-TuA7 Area-Selective ALD of ZnO Films Patterned by Electrohydrodynamic Jet Printing of Polymers with Sub-Micron Resolution, Tae Cho, N. Farjamp, C. Panner, C. Huber, O. Trejo, C. Alleman, E. Kayyak, R. Peterson, K. Barton, N.P. Dasgupta, University of Michigan

An increasing demand for customization in manufacturing of integrated nanosystems has motivated the development of printable electronics that can be adapted to the unique requirements of an end-user. The current state-of-the-art in nanofabrication of functional devices involves multiple lithographic patterning steps, combined with thin-film deposition and top-down etching processes. While this has led to tremendous advances in spatial resolution and process reliability, lithographic processes are inherently parallel processes, and not easily customizable. In contrast, additive manufacturing processes enable rapid prototyping of 3-D structures that can be easily tuned, and multiple layers of dissimilar materials can be integrated in a bottom-up manner. Therefore, combining a 3-D printing technology with area-selective ALD could enable a new paradigm in customizable nanomanufacturing.

Area-selective ALD has been previously demonstrated with patterns printed by ink-jet printing, micro-contact printing, directed self-assembly of templates, and a variety of other methods. However, there have been few techniques with the ability to directly 3-D print customizable patterns with sub-micron resolution, as traditional ink-jet printing is limited to a spatial resolution of ~20 microns. In this study, we demonstrate the use of electrohydrodynamic jet (e-jet) printing of polymers with sub-micron resolution [1], which can act as either inhibitors or promoters of ALD growth. The e-jet system allows for 3-D printing of polymers that pattern the surface chemistry by thermodynamically / kinetically activating or passivating local regions to nucleation of inorganic layers by ALD [2]. This enables bottom-up patterning of ALD growth, which can be integrated into 3-D nanosystems without the need for lithography or etching.

A variety of polymers were tested, demonstrating the ability to inhibit or promote the growth of ALD ZnO coatings on the surface by additive and subtractive printing approaches. Auger electron spectroscopy (AES), atomic force microscopy (AFM), transmission electron microscopy (TEM), and x-ray photoelectron spectroscopy (XPS) were used to perform compositional and elemental analysis of the patterned materials. After thin-film deposition by ALD, the electronic properties of the patterned films were characterized, demonstrating a pathway towards additive 3-D nanomanufacturing of customizable electronic devices.


3:15pm AS1-TuA8 Selective Deposition of Silicon Nitride, Han Wong, B. Hendrix, T. Baum, Entegris Inc.

Atomic layer deposition of SiN using Sil and NH₃ was studied. The growth per cycle and initial nucleation of SiN films were analyzed as a function of the deposition temperatures and precursor pulse times on different substrates. The sequential reaction of Sil and NH₃ showed longer nucleation delay on silicon oxide surfaces (native and thermal SiO₂) when compared to metal oxide (ZrO₂ and Al₂O₃) surfaces. This nucleation delay decreased with the increased deposition temperature. By pretreating metal and silicon oxide surfaces with an NH₃ plasma, Sil and NH₃ process showed no nucleation delay on the pretreated silicon oxide surfaces, while a significant delay was observed on the pretreated metal oxide surfaces. By using the definition of selectivity developed by Gladfelner [Chem. Mater. 5, 1372 (1993)], we have achieved tₐₐ₁₀ₓ = 18 Å for the process without NH₃ plasma pretreatment and tₐₐₗ = 74 Å for the process with NH₃ plasma pretreatment. This selectivity was not observed for pretreatment using H₂, N₂, or N₂:H₂ mixtures (50% N₂) plasma. Ex-situ XPS was used to determine the surface species with and without plasma pretreatments.

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Area Selective ALD
Grand Ballroom H-K - Session AS2-TuA1
Area-Selective ALD: Combinations with Etching
Moderators: Silvia Armini, IMEC, Dennis Hausmann, Lam Research Corp.

4:00pm AS2-TuA11 Area-Selective Deposition and Smoothing of Ru by Combining Atomic Layer Deposition and Selective Etching, Martinij Vos, Eindhoven University of Technology, Netherlands; S. Chopra, University of Texas at Austin; M. Verheijen, Eindhoven University of Technology, Netherlands; J. Erkerd, University of Texas at Austin; S. Agarwal, Colorado School of Mines; W.M.M. Kessels, A.I.M. Mackus, Eindhoven University of Technology, Netherlands

Area-selective ALD is expected to become a key technology for fabrication of nano-electronics with sub-5 nm dimensions. The technology is nevertheless in an early stage of development, and one of the main challenges is to obtain a high selectivity. The selective window can however be extended by introducing periodic etch steps that remove defects or nuclei from the non-growth area.

In this work, it is demonstrated that Ru can be grown selectively on top of Pt or Ru (metal-on-metal), by integrating etch cycles into an ALD-etch supercycle. Furthermore, it is shown that this supercycle recipe simultaneously leads to smoothing of the Ru film on the growth area. Area-selective ALD of metal-on-metal is interesting for applications in semiconductor devices, and Ru is specifically relevant since Ru is being considered for the replacement of Cu in small dimension interconnects.

The optimal deposition temperature for the thermal Ru ALD process (without etching) was determined, by maximizing the difference in growth rate per cycle between growth on Pt and SiO₂. Even for the optimized temperature, the ALD process demonstrated a limited growth-selectivity between the two areas. A periodic etch cycle, consisting of an O₂ plasma exposure and a reducing H₂ dose, was therefore introduced to remove unwanted Ru nucleation from the SiO₂, allowing for area-selective deposition with improved selectivity. Both the etch time and frequency were varied to optimize the net growth rate on Pt, while maintaining a clean SiO₂ non-growth area. Using an etch cycle performed after every 100 ALD cycles, 8 nm was deposited with high selectivity on patterned Pt lines, demonstrating the potential of the approach. In addition, it is shown that the inclusion of etch cycles also has the benefit of smoothing of the Ru film, resulting in a lower surface roughness than for the ALD recipe itself. Finally, some guidelines will be discussed for extending the ALD-etch supercycle approach to other material systems.


4:15pm AS2-TuA112 Single Batch Strategies for the Development of an Area Selective Deposition Process with the Deposition/Etch Approach, Christophe Vallée, M. Bonvalot, LTM-UGA, France; R. Gasilloud, CEA-Leti, France; V. Pesce, A. Chakat, LTM-UGA, France; N. Possémé, CEA-Leti, France; B. Pellissier, P. Gonon, A. Beans, LTM-UGA, France

Several approaches are currently being investigated for the development of Area Selective Deposition (ASD) processes. For instance, the use of self-assembled monolayers (SAM) or block copolymers, processing temperatures promoting inherent selectivity, spatial ALD or selective ALD based on ABC-type cycles are common routes under study for this purpose [1-3]. The original approach developed in our group consists in taking benefit from an in situ etching step in a standard ALD cycle [4]. This deposition/etch approach is a simple and effective strategy and recently, two selective depositions have been obtained for two different plasma etching chemistries:

- First, selective deposition on metallic surfaces versus silicon-based surfaces (SiN, SiO₂ and Si) has been demonstrated in the case of Ta₂O₅ and TiO₂ by the application of an extra NF₃ plasma etching step to standard PEALD cycles [4-5];
- Second, geometric selective deposition (also called Topographically Selective Deposition) has been achieved on trench walls by the application of an extra Ar⁺ sputtering step to standard PEALD cycles [6].

In this work, advantages and drawbacks of this deposition/etch approach to ASD processes will be discussed. The following issues will be addressed:

- What is the impact of the extra etching step on the material properties and on the overall throughput of the process? Are there any etching-induced damages to the substrate (etching, roughness...)?
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- Does the deposition temperature have to be determined according to the boiling temperature of etching by-products?
- May the etching step induce any drift of the process?

By addressing these questions, the need for an appropriate specific design of the PEALD reactor will be emphasized so as to provide an efficient strategy for a precise control of plasma parameters. Special attention will be devoted to the role of medium energy ions in the plasma, as illustrated by the following two examples:

- At first, a new route for topographically selective deposition on top and bottom only of trenches will be discussed;
- Second, a surface selective deposition on SiO₂ surfaces versus metallic surfaces using the alternating PEALD/Atomic Layer Etching (ALE) approach will be shown.


4:30 pm AS2-TuA113 Surface Halogenation of Amorphous Carbon for Defect-Free Area-Selective Deposition of Metal Oxides, Mikhail Krichtab, KU Leuven, Belgium, S. Armini, IMEC, Belgium, S. De Gendt, KU Leuven, Belgium

The area-selective deposition (ASD) processes gained recently a lot of attention from the microelectronics industry as a potential solution for the issues associated with top-down pattern formation at nanoscale. As the critical dimensions approach few tens of nanometers, the precise positioning of a pattern becomes essential for reliably functioning devices or connections between them. The area-selective atomic layer deposition (ALD) guided by the contrast in surface functionality allows to circumvent some of the lithography-related issues by introducing self-alignment of adjacent layers. However, the defectivity of typical ASD ALD processes relying on delayed nucleation on a non-growth area is one of the key concerns for the adoption of this technology. Among the strategies addressing the defectivity issue, repetitive refreshment of the non-growth surface and selective etching of undesired nuclei are particularly promising.

In this study, we examined the possibility to combine the two defect-reduction strategies by employing low-power Cl₂ or CF₄ plasmas for both surface functionalization/re-functionalization and for removal of nuclei from a non-growth layer represented by amorphous carbon. We employed prototypical water-based metal oxide processes such as ALD ZnO (DEZ/H₂O) and ALD TiO₂ (TICH/H₂O) to demonstrate area-selective deposition on top of silicon oxide using both blanket films and patterns of amorphous carbon landing on a layer of thermal silicon oxide. At first, the plasma parameters were optimized to minimize etching of amorphous carbon and silicon oxide. Then the selectivity of the ALD processes under study was checked on the plasma halogenated amorphous carbon films using a standard ALD sequence and a sequence interrupted by the appropriate plasma treatment steps. While Cl₂-plasma showed better performance in etching of metal oxide nuclei on top of amorphous carbon, the more hydrophobic fluorinated films exhibited inferior selectivity compared to chlorinated amorphous carbon films for both types of ALD processes. In turn, Cl₂-plasma treated films of amorphous carbon demonstrated outstanding ALD ZnO growth inhibition along with lower tendency to formation of nucleation defects during ALD ZnO and ALD TiO₂. The origin of the defects and of the observed differences in selectivity is discussed in the context of detailed surface composition analysis of the halogenated amorphous carbon films.


Indium aluminum nitride (InAlN) is an attractive material for power electronic applications. However, conventional methods of epitaxial growth of InAlN are challenged by a large miscibility gap and the significant differences in optimal growth conditions for the constituent aluminum nitride (AlN) and indium nitride (InN) binary compounds. Despite these challenges, the epitaxial growth of InAlN alloys throughout the entire compositional range has been demonstrated using plasma-assisted atomic layer epitaxy (ALEP)¹, a variant of atomic layer deposition in which relatively higher temperatures are utilized. In the ALEP growth of InAlN, the desired alloy compositions are achieved by forming ultra-short period superlattices of alternating InN and AlN layers, referred to as digital alloys (DA). In order to further advance these empirical efforts, significant research is needed to better understand the nucleation and growth kinetics of ALEP DA growth. To this end, we employ in situ grazing incidence small angle X-ray scattering (GISAXS) for the real-time study of the evolving ternary InAlN surfaces as has been done previously for binary InN² and AlN³.

Here we present in situ GISAXS studies of ALEP growth of InN, AlN, and a range of InAlN DA on GaN (0001) substrates, which were performed at Brookhaven National Laboratory’s NSLS-II using a custom reactor. The InAlN DA studies included In₃₄Al₆₆N₅ (3 AlN cycles and 2 InN cycles per supercycle), In₇₆Al₂₄N₅ (1 AlN cycle and 3 InN cycles per supercycle), In₄₄Al₅₆N₅ (1 AlN cycle and 5 InN cycles per supercycle) and In₃₄Al₆₆N₅ (1 AlN cycle and 14 InN cycles per supercycle). Preliminary analysis of the data suggests that while the pure InN and AlN grew in 3D and 2D modes, respectively, the InAlN growth mode did not follow a simple trend as the nominal composition was tuned from InN to AlN. Instead, select compositions (50% and 83% In) exhibited predominantly 3D growth, whereas others (19% and 64% In) exhibited 2D growth. Ex situ X-ray reflectivity data show evidence of phase separation in the 83% In DA.


5:00 pm AS2-TuA215 Expanding the Materials Library of Sequential Infiltration Synthesis: Conductive Indium and Gallium Oxides Grown in Polymers, Ruben Waldman, University of Chicago; N. Nean, D. Manodia, O. Heinonen, S. Darling, A. Martinson, Argonne National Laboratory

Over the past decade, researchers have developed a deeper understanding of how the chemistry of ALD can be applied to polymeric substrates. Polymers are fundamentally unlike traditional ALD substrates in that precursors diffuse through the polymer and associate with functional groups that are distributed throughout the volume of polymer, rather than on a two-dimensional surface.

In one implementation of ALD in polymers called sequential infiltration synthesis (SIS), very long static exposures of precursors are used to enable diffusion into the polymer bulk. The published SIS materials library is quite limited compared to the broad ALD materials library. Aluminum oxide (Al₂O₃), as synthesized via SIS with trimethylaluminum (TMA) and water, is by far the most studied system and has been utilized in applications ranging from lithography to oil sorption. Prior attempts to expand this library build upon on a primary SIS cycle of Al₂O₃ to act as a scaffold for subsequent synthesis of other materials. However, the insulating Al₂O₃ is detrimental to the properties of optoelectronically interesting materials. A detailed understanding of the physical and chemical processes of solvation, diffusion, and complexation between ALD precursors and polymer
functionalities is required to engineer hybrid polymer-metal oxide devices and to develop a broader library of SIS materials.

Through a combined experimental and first principles computational study we have developed primary SIS processes for two previously unreported materials – indium oxide (In$_2$O$_3$) and gallium oxide (Ga$_2$O$_3$) – using congeners to TMAl (TMIn, TMGa) and water. Through Fourier transform infrared spectroscopy and density functional theory, we elucidate the binding configuration and affinity of TMAl, TMIn, and TMGa for the carbonyl functional groups in polymethylmethacrylate (PMMA). We find that the three form isoostructurals adducts, though TMAl binds three times more strongly, and observe that the kinetics of adduct formation/dissociation for TMAl are more than ten times slower than for TMIn or TMGa.

With detailed knowledge of the TMIn reaction kinetics we designed an SIS recipe with exposure and purge durations tuned to the time-scales of vapor diffusion in and out of the polymer film. This led to the templated synthesis of In$_2$O$_3$/PMMA hybrid films which are readily converted upon annealing to crystalline, conductive In$_2$O$_3$ films. Notably, we observe substantial SIS growth rates of In$_2$O$_3$ at 80 °C, well below what is possible with these precursors in ALD. This suggests that complexation with polymers can catalyze reactions, opening routes for further exploration of low temperature deposition processes.

S15pm AS2-TuA216 Highly Efficient and Stable Organic – Inorganic Halide Perovskite Solar Cells with ALD-grown Charge Transport Layers. Hyunjung Shin, Sungkyunkwan University, Republic of Korea

CH$_3$NH$_3$PbI$_3$ with perovskite crystal structure has attracted considerable interest for high power conversion efficiency. Metal oxide grown via ALD provides pinhole-free uniform and dense films which are suited to function as passivation layer since ALD is deposited by self-limiting sequential chemical reaction. ALD chemistry for TiO$_2$, SnO$_2$, and ZnO are well known and the process requires relatively low deposition temperature as much as ~100 °C, which is applicable to deposit onto halide perovskite materials. In this presentation, we report highly efficient perovskite solar cells having a long-term stability that adapts uniform and dense inorganic charge transport layer (TiO$_2$, SnO$_2$, Al$_2$ZnO, and NiO) grown by atomic layer deposition (ALD) at relatively low temperature. Ultra-thin undoped NiO films were prepared by ALD with a highly precise control over the thickness. Thin enough (5 ~ 7.5 nm in thickness) NiO films with the thickness of few times of Debye length (1 ~ 2 nm for NiO) show enough conductivities achieved by overlapping space charge regions, which finally exhibited a highest PCE of 17.40 % with a negligible current-voltage hysteresis. Furthermore, highly dense inorganic electron transport layer (ETL) has been deposited onto perovskite using ALD process at relatively low temperature (100 °C). The devices shows excellent water-resistant properties and long-term stability at 85 °C under illumination compared to devices without ETL grown by ALD.

References
AA1-TuP1 Study on Atomic Layer Deposited Al₂O₃, TiO₂, and ZnO for the Application in Silicon Photovoltaics, Arun Haridas, M.G. Greenaway, Hind High Vacuum Company Pvt. Ltd., India; A. Antony, Indian Institute of Technology Bombay, India

We have fabricated a thermal atomic layer deposition (ALD) system with a substrate size of 150 mm diameter. Non-uniformity of 95 nm Al₂O₃ films deposited over polished (100) Si substrate at a temperature of 200°C is ± 0.01% over 150 mm diameter as measured using ellipsometry. The optical properties, i.e. n & k values were found to be very uniform indicating the uniformity of the growth and the quality of the layer over large area. Passivation quality of the Al₂O₃ films over the Si surface is studied by measuring the minority carrier lifetime which can be precisely controlled using ALD.

The material quality and doping level by the oxygen vacancies of the metal oxide layer plays a crucial role in the performance of the carrier-selective silicon solar cells. The high quality films of TiO₂ using Titanium Isoproxide and H₂O as well as ZnO using diethyl Zinc and H₂O are investigated for carrier selectivity. ALD has very good potential as effective tool for depositing ultra thin carrier-selective layers for solar cells.

In this work we are exploring the advantages of the ALD technique to grow pinhole free, conformal and extremely uniform films for improving the performance of silicon solar cells.

AA1-TuP2 Nitrogen-Doped TiO₂ Film Deposited using Plasma-Enhanced Atomic Layer Deposition to Improve the Electrical Conductivity for Surface Passivation of Crystalline Silicon, E.-J. Song, Korea Institute of Materials Science, Republic of Korea; J.-H. Ahn, Korea Maritime and Ocean University, Republic of Korea; Jung-Dae Kwon, Korea Institute of Materials Science, Republic of Korea

For surface passivation with improved electrical conductivity, we investigate nitrogen doped TiO₂ film by combining the TiO₂, TiN sub-cycles using plasma-enhanced atomic layer deposition. For composition control of the TiON films, a n-cycles was adopted which was composed of one cycle of TiO₂ and x-cycles of TiN. The thickness of the TiON films as the nitrogen doping concentration linearly increases with the number of supercycles. We confirm the chemical states, crystalline phase and interface characteristics of these TiON films through the XPS, XRD and C-V analysis. When the nitrogen was doped in the TiO₂: thin film, the carrier lifetime was increased from 30 to 243 μs and the resistivity decreased from 3.1e+08 to 7.1e-01 Ω-cm for the TiO₂:TiN=1:2:0 film.

AA1-TuP3 Multilayer Encapsulation for Highly Stable Perovskite Solar Cells with Atomic Layer Deposited Al₂O₃ and Chemical Vapor Deposited Flowable Oxide, Jungwoo Kim, H. Hwangbo, S.J. Kim, J.H. Jang, H.C. Tran Vo, H. Chae, Sungkyunkwan University (SKKU), Republic of Korea

Perovskite solar cells (PVSCs) are known to be easily deteriorated in atmospheric environment. Many researchers have studied encapsulation technique to protect PVSCs. However, few researchers reported long term stability under severe conditions such as 85 °C with 85% relative humidity (RH). Atomic layer deposited metal oxides are considered to be effective to thin film encapsulation. However, PVSCs can be easily damaged by oxygen radicals during the metal oxide deposition process. In this work, we introduced flowable oxide inter layer for the cell protection before spatially-resolved plasma atomic layer deposition (ALD) process. The flowable oxide layer prevent oxygen radicals generated in N₂O plasma during Al₂O₃ process and the power conversion efficiencies (PCEs) of PVSCs were almost preserved. With flowable oxide and Al₂O₃ double layer, 45% in efficiency drop was observed after 1000 hours in 85 °C/35% RH condition. The PVSCs with multiple stacked flowable oxide/Al₂O₃ layer with glass encapsulation showed less than 10% of efficiency degradation after 1000 hours in 85 °C/85% RH. The multilayer with flowable oxide protection layer and Al₂O₃ moisture barrier layer structure is expected to provide long term stability in ambient condition.

AA1-TuP5 Oxide Buffer Layers for Perovskite Solar Cells Grown with a 200 nm Commercial ALD System Using Low-Temperature Process, P. Rajibhandari, Tara Dholak, Binghampton University

Organic materials provide a very small thermal budget for any post-fabrication treatment or for a subsequent layer in device fabrication. The demand for the low-temperature process has driven the focus of our study to obtain atomic layer deposited oxide buffer layer at temperatures suitable for a perovskite solar cell. The buffer layer will assist in blocking holes, effectively extract electrons, provide better shunt protection and act as a spatter protection layer covering the organic perovskite films from sputter damage from a subsequent layer, such as a transparent conductor. Three different oxide layers, Al₂O₃, ZnO, and TiO₂ are grown at 100°C and studied which is used to enhance carrier selectivity. The ALD (SMFD-ALD) technology optimized in commercial 200 nm ALD reactor from Sundew Technologies. It allows greater precursor utilization and shorter deposition cycle times that in turn reduces thermal processing time compared to traditional ALD processes. These thin films have shown to enhance the fill factor (FF) and high charge extraction from the solar cell. Three oxides are compared on all aspect, among which ZnO (4 nm) along with Al₂O₃ (1 nm) as a buffer layer has shown excellent performance improvement in the device up to 20% power conversion efficiency. In this presentation, ALD growth details of the oxide layers and the resulting perovskite solar cell results will be discussed.

AA1-TuP6 Ultra-thin Nickel Films for Energy Harvesting Applications, Ken Bosnich, P. Motamedi, National Research Council Canada, Canada; K. Cadieu, University of Alberta, Canada; K. Harris, J.-Y. Cho, National Research Council Canada, Canada

The harvesting of ambient heat and light could potentially lead to useful power for driving off-grid, internet-of-things sensors. Recent theoretical predictions suggest that ultra-thin Ni films can show thickness dependent optical properties that can lead to enhanced solar absorptance. The maximum solar absorptance is predicted to occur at a very thin layer thickness of ~12 nm and is attributed to an impedance matching effect [N. Ahmad, et. al. Nano Energy 1, 777 (2012)]. Light absorptance in ultra-thin Ni films can be further enhanced by patterning the Ni films and depositing multi-layer structures. Atomic layer deposition (ALD) produces conformal films with a high level of control and uniformity with respect to the film thickness. While ALD is most widely known for depositing ultra-thin dielectric materials for advanced electronic applications, we have successfully used the technique to deposit ultra-thin Ni films [P. Motamedi, et al., ACS Appl. Mater. Interfaces 9(29), 24722 (2017); P. Motamedi, et al., Adv. Mater. Interfaces 5(24), 1800597 (2018)].

In this study, ALD Ni films are deposited with varying thicknesses onto fused silica and sapphire substrates. Structural characterization indicates that the films are continuous, polycrystalline Ni films with a relatively low degree of roughness and are suitable for comparison with the theoretical predictions. Optical absorptance is measured using an integrating sphere as a function of film thickness and compared with theory. An optimum thickness is found but the experimentally determined absorptance maximum is less significant than theoretically predicted. Possible explanations include surface roughness or deviations from the refractive index of bulk Ni. Nevertheless, the thickness for optimum absorptance is found to be around 10 nm for planar ALD Ni films.

Glancing angle deposition (GLAD) is used to produce quasi-periodic silica pillars on fused silica wafers and ALD Ni films are deposited conformally onto the GLAD pillars. It is hypothesized that the GLAD films with ultra-thin ALD Ni coatings will act similarly to lithographically patterned gratings and lead to enhanced optical absorptance. Optical absorptance measurements reveal a low reflectance at all wavelengths, but an extremely high absorptance in the UV/visible range that decreases to very low values in the NIR. The spectra are seen to have a strong dependence on the ALD Ni thickness but to be less sensitive to changes in the GLAD deposition parameters. Structural characterization, further control experiments, and theoretical modeling are planned to understand these optical results.


Molybdenum [https://www.sciencedirect.com/topics/chemistry/nitride] (MoNx) was directly grown on 3-dimensional nitrogen doped-carbon coated
carbon cloth (NC-CC) at a relatively low temperature of 250 °C by atomic layer deposition (ALD) and then tested as an electrode for supercapacitive charge storage. The charge storage performance of NC-CC and MoN deposited CC have also been evaluated for the comparative studies. The successful formation of MoN@NC-CC and MoN@CC composite was confirmed by several characterization techniques. The scanning and [https://www.sciencedirect.com/topics/chemistry/transmission-electron-microscope] analyses showed the extremely uniform and conformal coating of the MoN on NC-CC. The 3D and porous texture of NC provided the excessive surface area for MoN coating and also granted easy access for the electrolyte penetration. The high areal capacitance of 911 mF/cm² was achieved at a current density of 4 mA/cm² which is 1.3 times higher than that of NC-CC. The negligible charge storage capacity of 7 mA/cm² obtained for MoN@CC highlighted the significance of NC deposition on CC prior to the loading of MoN. The ultra-high stability of MoN@NC-CC (108% capacity retention after 50,000 cycles) further confirmed its exceptional supercapacitive charge storage performance.

AA1-TuP8 ALD Coatings for Nano Imprint Masks, Thomas Seidel, Seitek50 Nano Imprint Lithography (NIL) usage has been limited by mask defects during fill and release process steps. Additionally, for as any process step, it is desirable to improve throughput. The optical intensity in the features of quartz imprint masks with high index conformal coatings was simulated using Maxwell solver software. The index of refraction of the coatings, exposure wavelength, aspect ratio, film thickness and feature size were varied parameters. The simulations indicate the optical intensity may be increased with the mask features using coatings of higher index films relative to the uncoated reference quartz masks for physical feature sizes below 7nm, indicating the possibility of improved productivity. Defectivity is proposed to be addressed by the application of fractional fluorine terminated monolayers of a fluoro-hydrocarbon (FHC) film at the mask feature surface. This approach is intended to address the dichotomy of fill and release type defects in the imprint feature. In addition, ALD conformal films may be used to reduce the critical feature size below that achievable with the state-of-the-art electron beam processes. A matrix of candidate ALD precursors and processes for higher index coating films (Al₂O₃, TiO₂ and Si) relative to quartz, as well as monolayer FHC precursors are reviewed with considerations of quality and throughput. Various ALD wafer systems are considered for process deposition for square mask quartz plates of 6in. x 6in. x 0.25in. geometry.

The support of Nayoa Hayashi and Nobuhito Toyama of Dia Nippon Printing is acknowledged for the simulations.


2. Thomas E. Seidel US 10,156,786B “Method and Structure for Nanoimprint Lithography Masks using Optical Film Coatings,” Dec 18, 2018

AA1-TuP9 The Investigation of Al₂O₃ Passivation Characteristics in the Condition of Growth Temperature and Ozone Concentration, Young Joon Cho, H.S. Chang, Chungnam National Univ., Republic of Korea

The surface passivation for high efficiency c-Si solar cell is a prerequisite for the achievement of high efficiency solar cell. The capability of Al₂O₃ passivation using trimethylaluminium (TMA, Al(CH₃)₃) precursor and H₂O oxidant was presented. Aluminum oxide (Al₂O₃) grown by atomic layer deposition (ALD) was showed excellent passivation performance as good as obtained by thermally grown SiO₂. A superior property of the ALD-Al₂O₃ film appeared to be the field-effect passivation induced by negative fixed charges and the high level of chemical passivation resulting from a low interfacial defect density. ALD-Al₂O₃ film using ozone oxidant showed better thermal stability and no-blistering because of excluding hydroxyl group in ozone oxidant. Therefore, more detail study is required about the effect of growth temperature and ozone concentration on ALD-Al₂O₃ passivation.

AA1-TuP10 Effect of Al₂O₃ Passivation on n-type Si Solar Cell with Passivated Emitter and Rear Cell (PERC), Kiyun Kim, H.S. Chang, Chungnam National University, Republic of Korea

N-type solar cells are immune to LID (Light Induced Degradation) effect, because of the absence of the boron-oxygen defect. However, The fabrication process of n-type PERC includes more steps and makes a solar cell more expensive. Therefore, newer technologies will be needed efficient process steps and structures.

In this study, we investigated n-type PERC cell formed by double-sided Al₂O₃ deposition using ALD. Al₂O₃ films as a passivation layer were grown by ALD at 300°C. After double-sided Al₂O₃ deposition, UV laser ablation with ns pulse performed to make an electrode contact-patternning. Finally, we evaluated passivation performance as a function of emitter sheet resistance and electrode open ratio. In addition, we have evaluated the passivation characteristics affected by electrode materials such as Cu and Al.

The passivation performance of the Al₂O₃ layer was compared with the emitter saturation current (Iₒ) and the implied Voc through Quasi-Steady-State Photoconductance (QSSPC). As a result, We have achieved iVoc of 680 mV through the optimization process.


Calcium fluoride (CaF₂) is highly transparent over a broad range of the electromagnetic spectrum, covering ultra-violet (UV), visible, and infrared (IR) wavelengths. Its high transparency between 150 nm – 12,000 nm and its extremely low refractive index (~1.43 at λ = 500 nm - 600 nm) makes it a well-known candidate for optical applications. In combination with materials exhibiting a higher refractive index, CaF₂ coatings find application in anti-reflective coatings and bandpass filters. Like other fluorides, such as MgF₂ and LaF₃, the ionic bonding situation in CaF₂ enables applications in anti-reflective coatings and bandpass filters. Like other fluorides, such as MgF₂ and LaF₃, the ionic bonding situation in CaF₂ enables applications even below 200 nm (e.g. photolithography). Recently, metal fluoride materials were also suggested to be incorporated in Lithium-Ion-Batteries, acting either as the solid electrolyte or electrode material.[1]

In both cases, i.e. optical applications (such as lenses and three-dimensional structures for optical filters) and coatings in Li-ion batteries, the respective thin film must be of high purity and thickness control is of utmost importance. In consequence, the fabrication of CaF₂ via ALD is the method of choice. Different ALD processes for CaF₂ have been reported in the past, using Ca(thd)₂[2a] and Ca(hfac)₆[2b] as metal source and NH₄F,[2c] TiF₄,[2d] and Hhfac[2c] as fluorine precursor.[2a] These processes showed best results at temperatures around 300 °C.

Herein, we present a new and straight-forward ALD process for CaF₂ thin films using the [Ca(amtd₃)₂]₁−dimer and HF-hydride as precursor, working at temperatures as low as 175 °C. The process was monitored and optimized employing in-situ diagnostics such as FTIR and QCM, and thin films were characterized in terms of their composition (XPS), structure (TEM, XRD, PDF) and optical properties (UVVis, ellipsometry). The process was applied to cathode powers used in Li-ion-batteries and the performance of the respective materials was investigated.


temperature, plasma, and air exposure, and for this reason the work function of MoO$_3$ is degraded and its properties are reduced. In this study, MoO$_3$ is deposited by plasma-enhanced atomic layer deposition (PE-ALD) using Molybdenum hexacarbonyl ($\text{Mo(CO)}_6$) as a precursor for Mo and O$_2$ is adopted as precursor for plasma. Argon was used as a carrier gas of Mo(CO)$_6$ and the gas line and canister temperature was maintained at 40°C and 45°C, respectively. To obtain the best passivation performance, the plasma power was varied between 10W and 500W at PE-ALD process. To investigate the effect of temperature, the sample was annealed at temperature range from 250°C to 500°C.

X-ray photoelectron spectroscopy (XPS) analysis confirmed the chemical state of the MoO$_3$ film. The growth per cycle (GPC) of MoO$_3$ film and MoO$_3$/c-Si interface was investigated by transmission electron microscopy (TEM). The GPC of MoO$_3$ film deposited by PE-ALD was found to be 0.25 Å. The life time and $V_r$ were measured by quasi steady state photoconductivity (QSSPC).

**AA1-TuP13 Understanding and Mitigating F Migration in ALD Nanocomposite Coatings, Anil Mane, M. Gebhard, J.W. Elam, Argonne National Laboratory; M. Papecki, T. Cremer, Incom Inc.; M. Minot, Incom.**

We have developed atomic layer deposition (ALD) processes to synthesize metal-dielectric oxide nanocomposite coatings comprised of conducting, metallic nanoparticles (M) embedded in an amorphous dielectric matrix, nominally Alumina (Al$_2$O$_3$), and where the metallic component is selected from either tungsten (W) or molybdenum (Mo). The nanocomposite layers are prepared using alternating exposures to trimethyl aluminum (TMA) and H$_2$O for the Al$_2$O$_3$ ALD and alternating metal hexafluoride / disilane (MF$_6$/SiH$_4$) or metal hexafluoride TMA (MF$_6$/TMA) exposures for the metal ALD component. By varying the ratio of M:Al$_2$O$_3$ ALD cycles and the order of precursor dosing for the two components, we can tune the composition enabling a wide range of mechanical, electrical, and optical properties of these nanocomposites. We have applied these nanocomposites to a variety of applications, but I will focus this presentation on their use as resistive layers for glass capillary array microchannel plates (GCA-MCPs). These ALD nanocomposite coatings contain residual fluoride (F) from the metal hexafluoride precursor in the form of AlF$_x$. Although we can modulate the F content by adjusting the W nucleation conditions, it is not possible to eliminate the F and this can introduce challenges for device fabrication and integration. For instance, we often deposit ALD magnesium oxide (MgO) following the ALD resistive coating to improve the secondary electron emission (SEE) of the surface. In these cases, we find that residual F can diffuse from the resistive layer into the MgO forming MgF$_2$ and affecting MCP performance. In this presentation, I will describe several strategies we have developed to minimize F migration. I will conclude by showing the enhanced performance and stability of ALD-GCA-MCPs achieved with this technology.

**AA1-TuP14 Ultrathin Metal Oxide Passivation by Atomic Layer Deposition Enhances Stability and Performance of Visible Solar Water Splitting on Solution-Processed Organic Semiconductor Thin Films, L. Wang, D. Yan, Stony Brook University; D. Shaffer, Brookhaven National Laboratory; X. Ye, Stony Brook University; B. Layne, J. Concepcion, M. Liu, Chang-Yong Nam, Brookhaven National Laboratory.**

Solution-processable organic semiconductors have potential for visible photoelectrochemistry (PEC) solar water splitting because of their tunable small band gaps and electronic energy levels. However, the poor stability and photocatalytic activity of organic semiconductors have been posing persistent challenges. Here, we demonstrate that the application of ultrathin metal oxide passivation by low-temperature atomic layer deposition (ALD) enables the direct, visible PEC water oxidation on solution-processed organic semiconductor thin films with enhanced stability and performance. N-type fullerene-derivative thin films passivated by sub-2 nm ALD ZnO allowed the visible PEC water oxidation at wavelengths longer than 600 nm in harsh alkaline electrolyte environments with up to 30 μA/cm$^2$ photocurrents at the thermodynamic water-oxidation equilibrium potential, which is accompanied by the photocurrent half-lifetime extended to 3×10$^4$ s. The investigation shows that the enhanced water oxidation catalytic activity is afforded by the ALD ZnO passivation, and the hole transfer through the passivation layer governs the charge collection process. Further improved PEC water splitting performances were realized by improving the bottom ohmic contact to the organic semiconductor, again via the ZnO interlayer implemented by ALD, ultimately achieving 360 μA/cm$^2$ water oxidation photocurrent at the equilibrium potential, the highest value reported for organic semiconductor thin films to our knowledge. The results not only highlight the significant utility of ALD on improving the stability and performance of organic-semiconductor-based solar water splitting but also provide important design guidelines for optimal ultrathin passivation on organic semiconductor photoelectrodes.

**AA1-TuP15 Enhancement of Photovoltaic Efficiency using a Novel Nickel-4 Mercaptophenol Hybrid Interfacial Layer, Jinseon Park, N.V. Long, H. Thu, Hanyang University, Republic of Korea.**

In this work, we introduced a novel Ni-4 mercaptophenol (Ni4MP) as an interfacial layer in Sb$_2$S$_3$-sensitized mesoporous TiO$_2$ solar cells. Ni4MP thin films with controllable thickness were prepared by an integrated approach via atomic/molecular layer deposition techniques and were systematically characterized. Introduction of the Ni4MP interlayer significantly enhanced the photovoltaic performance and the interfacial charge transfer kinetics of Sb$_2$S$_3$-sensitized solar cells. The augmentation of open circuit voltage and short circuit current density due to the insertion of a Ni4MP interlayer enhanced the power conversion efficiency of the solar cells from 2.07% to 2.79%, corresponding to a 35% increase in efficiency. This improvement in device performance was discussed based on the energy band diagram. We found that the Ni4MP interlayer can effectively extract the photo-generated holes from the Sb$_2$S$_3$ sensitizer due to the excellent band matching and hole scavenging characteristics, thus enhancing the charge transport and suppressing the recombination.

**AA1-TuP16 Enhancement of Photovoltaic Properties of Metal/III-V Schottky Solar Cells using ALD203 Anti-Reflection and Passivation Layer, A. Ghods, V. Saravade, C. Zhou, Ian Ferguson, Missouri University of Science and Technology.**

The metal-semiconductor (M-S) Schottky junction structure is gaining traction in photovoltaic device applications compared to $p$-$n$ junction structure, due to simplicity in device processing, possibility of development of high efficiency multi-junction structures, and also cost-effective large-scale device fabrication. III-V compound semiconductors with direct bandgap and short absorption depth are suitable candidates for fabrication of high efficiency solar cells. Schottky solar cells based on $\text{Al}_2\text{O}_3$/$\text{As/GaAs}$ heterostructure have been fabricated, resulting into short-circuit current density and power conversion efficiency of 19.46 mA/cm$^2$ and 40.84%, respectively.

One of the main issues regarding the M-S structures for solar cells remains about the high reflectivity from the top metal surface. This leads to significant reduction in photon absorption in the active layer of solar cell and, therefore, lowered photo-generated current. Graphene and indium-tin-oxide (ITO), with transmission of more than 80% in the visible region, have been used in conjunction with $n$-GaAs to create Schottky solar cells, leading to short circuit current density and power conversion efficiency of up to 18.95 mA/cm$^2$ and 11.5%, respectively.

Anti-reflection coating (ARC), such as aluminum oxide (Al$_2$O$_3$), has been used to reduce the reflection from top surface of M-S Schottky solar cells, and enhance the photovoltaic properties of these devices. In this work, an 80 nm Al$_2$O$_3$ has been grown on the whole top surface of the Ag/n-GaAs Schottky solar cell using atomic layer deposition (ALD) technique at 200°C, Figure 1 (attachment). The initial optical measurements show the reduction of reflection from the solar cells from 48% (without ARC) to 16% (with ARC), indicating the improvement in photon absorption, Figure 2. JV and EQE measurements will be performed to extract the photovoltaic properties of these devices and investigate the effect of ARC on M-S structure.

Moreover, the effect of Al$_2$O$_3$ as passivation layer will be studied in the full paper. Initial measurements have indicated a decrease in leakage current between the metal contacts, leading to enhancement of shunt resistance from 3×10$^7$ W to 1×10$^8$ W. This will be further investigated, and changes in photovoltaic properties of the solar cells, including filling factor, reverse saturation current, and power conversion efficiency, will be reported.

film transistors (FTTs) to solar cells due to its excellent optical and electrical properties [1]. In the CIGS solar cell device structure, the i-ZnO thin film acts as a buffer layer that reduces the leakage of shunt current paths and also improves p-n hetero-junction quality. In the present study, we deposited the i-ZnO thin films from 80°C to 180°C onto both Si (100) and soda lime glass (SLG) by using atomic layer deposition (ALD) method. The as-grown films were characterized by scanning electron microscopy (SEM), energy dispersive x-ray spectroscopy (EDS), X-ray diffraction, UV-Vis-NIR spectroscopy, and Hall effect measurements. The thickness of as-grown ZnO films is independent of the growth temperatures from 100°C to 180°C. All samples exhibit the optimal bandgap of 3.24 eV. The ZnO buffers show the electrical resistivity of 6 Ohm-cm, 0.29 Ohm-cm, and 0.0058 Ohm-cm for the films-grown at 80°C, 100°C, and 150°C, respectively. In addition, we investigated the I–V characteristics of the fabricated CIGS solar cells using ALD-grown i-ZnO buffers prepared at 80°C, 100°C, and 150°C. The solar cell fabricated with i-ZnO buffer grown at 100°C exhibits the best power conversion efficiency (η) of 8.59% with V oc of 470 mV, J sc of 28.84 mA/cm², and FF of 63.48%.


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AA1-TuP18 Atomic Layer Deposited Zirconium-doped ZnO Transparent Conductive Oxides for Silicon Solar Cells, Geethika Kalidil Poduval, M.A. Hossain, B. Hoex, University of New South Wales, Australia

Transparent conductive oxides (TCOs) are intensively investigated due to their ability to conduct charge carriers and transparency in the visible light in various fields ranging from large scale displays to photovoltaic devices. Currently, the most widely used TCO is indium tin oxide (ITO) which simultaneously offers high optical transparency and high electrical conductivity. Limited reserves, increasing indium prices, and free carrier density limits its use. The optical band gap of ZnO increases with doping levels, up to a value of 3.42 eV at 10% Zr and Zr/ Ti, and the mobility reduces with increased doping. The optical band gap of ZnO increases with doping level up to a value of 3.42 eV at 10% Zr and Zr/ Ti, and the mobility reduces with increased doping.

Among the various kinds of silicon solar cell architectures, heterojunction (HET) silicon solar cells consisting of crystalline silicon absorber and amorphous silicon (a-Si) surface passivation and doped a-Si as the electron and hole selective layers implement TCOs to improve the lateral conductivity of collected carriers. As a-Si degrades at temperatures >200°C and sputtering of ITO damages the interface, leading to increased absorption and recombination, a surface sensitive low-temperature self-limiting process such as atomic layer deposition is very appealing.

In this work, Zr is used as a dopant to increase the mobility and reduce parasitic absorption of earth-ambient ZnO. The recipe for ZrO2 growth using Tetrakis(dimethylamido) zirconium(IV) (TDMAZ) was developed and optimized on a Fiji G2 plasma enhanced ALD tool. The growth properties were studied by in-situ spectroscopic ellipsometry. The effects of doping (0-29 at.% Zr) were investigated for 40 nm thick films. ZnO and ZrO2 superscripts at different ratios were carried out, and their influence on optical and electrical properties was investigated. A slight increase in mobility of “~5% up to 19 cm²V-1s–1” was observed by doping ZnO with 2.4% Zr, and the mobility reduces with increased doping. The optical band gap of ZnO increases with doping level up to a value of 3.42 eV at 10% Zr and reduces for higher Zr concentrations. First-principles density functional theory (DFT) calculations reveal the formation of defects states in the conduction band resulting from the substitutional replacement of Zn by Zr. XPS results indicate that the Zr ions in ZnO are in the Zr4+ oxidation state and also contribute two additional electrons to the lattice. This results in an increase in carrier concentration from 2×10^{19} cm^{-3} to 2×10^{20} cm^{-3}.

Elemental depth profiling using ToF-SIMS is currently ongoing and will be shown at the time of the conference. The improvement in TCO properties of ZnO upon doping with Zr opens the possibility for applications in silicon solar cells as well as thin film solar cells.

Acknowledgment: This research was supported by the Technology Development Program to Solve Climate Changes of the National Research Foundation (NRF) funded by the Ministry of Science, ICT & Future Planning (NRF-2017M1A2A2087577) and (NRF-2016M1A2A936759), also, this research was financially supported by the Ministry of Trade, Industry and Energy (MOTIE) and Korea Institute for Advancement of Technology (KIAT) through the National Innovation Cluster R&D program (P006704).


Solar fuels catalysis is vital to developing new technologies for creating value-added products from alternative feedstocks, such as carbon dioxide and water. Inhomogeneities in typical “state-of-the-art” synthesis techniques for heterogeneous catalysts severely limit the accuracy of determining the composition of active sites and elucidating mechanistic details for catalysis. In the present work, we synthesize discrete, few-atom metal oxide cluster arrays to gain insight into the relationship between cluster size/shape and catalytic activity/efficiency. Clusters are synthesized with exquisite synthetic control via atomic layer deposition (ALD) on chemically modified epitaxial graphene (EG) on SiC. Metal oxide/nitride/sulfide ALD thin film growth is strongly inhibited on graphene. Understanding the factors contributing to unintentional and intentional nucleation and growth on EG will benefit from the use of an accurate, precise imaging technique such as STM. Furthermore, we employ an in-situ plasma treatment (H₂, N₂, O₂) of EG to create attachment points for intentional cluster nucleation via ALD. Discrete, few-atom clusters will be synthesized and cluster size, morphology, distribution, and density of states will be determined via STM/XPS/AFM/Raman mapping. We will correlate these parameters to catalytic activity and efficiency for solar fuels catalysis.

ALD Applications

Evergreen Ballroom & Foyer - Session AA2-TuP

Microelectronics Poster Session

AA2-TuP1 Chemically and Mechanically Activated Carbonaceous Materials for Supercapacitor, D.V. Lam, J.-H. Kim, Seung-Mo Lee, Korea Institute of Machinery and Materials, South Korea

Carbothermic reduction in the chemistry of metal extraction (Mo(s) + C(s) → M(s) + CO(g)) using carbon as a sacrificial agent has been used to smelt metals from diverse oxide ores since ancient times. Here, we paid attention to a new aspect of the carbothermic reduction remained unnoticed till now to prepare activated carbon textile for high rate-performance supercapacitors. On the basis of thermodynamic reducibility of metal oxides reported by Ellingham, we employed not carbon, but metal oxide as a sacrificial agent in order to prepare activated carbon textile. We conformally coated ZnO on bare cotton textile using atomic layer deposition (ALD), followed by pyrolysis at high temperature (C(s) + ZnO(s) → C(s) + Zn(g) + CO(g)). We figured out that it leads to concurrent carbonization and activation in a chemical as well as mechanical way. Particularly, the combined effects of mechanical buckling and fracture occurred between ZnO and cotton were turned out to play an important role in carbonizing and activating cotton textile, thereby significantly increasing surface area (nearly 10 times) compared with the cotton textile prepared without ZnO. The carbon textiles prepared by carbothermic reduction showed impressive combination properties of high power and energy densities (over 20 times increase) together with high cyclic stability.

AA2-TuP2 Diamond Field Effect Transistors with Different Gate Lengths of HfO2 Deposited by Atomic Layer Deposition, Changhi Gu, Institute of Physics, Chinese Academy of Sciences, China

The single crystal diamond was treated in hydrogen plasma formed by microwave plasma chemical vapor deposition equipment, and the normally-off hydrogen terminal diamond field-effect transistors with different gate lengths were prepared by atomic layer deposition of HfO2 as gate oxide. We studied the effect of hydrogen treatment time and HfO2 gate oxide on hydrogen terminal diamond field-effect transistor. The experimental results showed that the HfO2-gate oxide was suitable to fabricate hydrogen terminal diamond field-effect transistor and exhibited a normally-off characteristic, which is advantageous for the fabrication of power devices. Furthermore, with increasing the gate length, the drive current density, threshold voltage, and transconductance of the diamond device decreased.

AA2-TuP3 Atomic Layer Deposition of IGZO Thin Films for BEOL Applications, Shôna Doyle, Tyndall National Institute, Ireland

In the drive for scaling of electronic devices one approach has been the integration of functionality into the back end of line (BEOL). Thin film transistors (TFT) are one such component with high quality devices being realised by PVD indium-gallium-zinc oxide (IGZO). However, the limitations of the PVD deposition process in terms of reliability and coverage in...
developed capacitor with EOT≤2nm shows excellent dielectric integrity, deposited HfO₂ layer: the composite HfO₂/Al₂O₃ remains amorphous at phases of higher symmetry having significantly higher k-value (30-40).2

produced by RTA on the TiN bottom electrode and on the HfAlO (operating voltage 2.5-3.3V) located as DRAM in IMD0, to benefit from the optimized for the required film thickness of the HV MIM capacitor. The engineering of the film growth and its crystallization parameters should be operational voltage of HV MIM entails thicker dielectric layers compared to conventional dielectrics SiO₂ and Si₃N₄. To prevent the uncontrolled crystallization of amorphous HfO₂ film in a monoclinic phase that degrades its electrical parameters, some dopants (i.e. alumina) are introduced in deposited HfO₂ layer: the composite HfO₂/Al₂O₃ remains amorphous at deposition and during BEOL annealing processes. Thus, amorphous materials are usually used in MIM capacitors located in BEOL. Hafnia doping enhances the composite crystallization (T≥600°C) into metastable phases of higher symmetry having significantly higher k-value (30-40).2

Crystalline HfAlOₓ dielectric has been employed in low voltage capacitors used in DRAM. Some CMOS applications (RF, CIS) require HV MIM capacitor (operating voltage 2.5–3.3V) located as DRAM in IMD0, to benefit from the attractive properties exhibited by crystalline HfAlOₓ. The increased operational voltage of HV MIM entails thicker dielectric layers compared to those used in DRAM. To take advantage of crystallinity of the HfAlOₓ film, engineering of the film growth and its crystallization parameters should be optimized for the required film thickness of the HV MIM capacitor. The developed capacitor with EOT≤2nm shows excellent dielectric integrity (Vₜₐₙₖ≈28V) along with the low leakage current.

Table 1 presents the plan of experiment where HfO₂-Al₂O₃ laminated stack (12:1) was deposited by ALD in the same run on two types of substrates: Si/SiO₂/TiN(70nm) – structure A (MIM) and p-Si/thermal SiO₂(6.4nm) – structure B (MOS). The stack thickness is 14nm. Both pre-deposition (PreDA) and post-deposition (PDA) annealing were performed at the same conditions (T>600°C). The RTA processing of the sample A (MIM) was performed for crystallization of thin films. Finally, we analyzed physical and structural study of samples 1, 2 and 3 performed by XRD (Fig.3) and TEM/STEM (Fig.5) techniques. Surface characteristics of the TiN electrode was shown in Fig.4. PreDA process allows to prevent the void formation at the TiN/HfAlOₓ interface and to improve electrical integrity of sample 2.

AA2-TuP6 Improved Performance of GaN Metal-Oxide-Semiconductor Capacitors by Plasma ALD of AlN Interlayer, Dilini Hemakumarika, X. Li, K. Flores, S. Cho, University of Glasgow, UK; I. Guinney, C. Humphreys, University of Cambridge, UK; I. Thayne, University of Glasgow, UK; A. O’Mahony, Oxford Instruments Plasma Technology; H. Knopp, Oxford Instruments Plasma Technology, UK; D. Moran, University of Glasgow, UK

High quality metal-oxide-semiconductor (MOS) gate stacks with stable threshold voltage are required for future GaN-based power transistors [1]. Here, we report a route to the realization of GaN MOS-capacitors (MOSCAPs) with an ALD AlN interlayer between GaN and Al₂O₃ using a FlexAL ALD system. AlN was grown using plasma enhanced ALD at 300°C using TMA and N₂ and H₂ plasma. The GaN samples were first exposed to an N₂ 150W 5min plasma pretreatment followed by in-situ ALD of approximately 2nm of AlN. A 20nm Al₂O₃ was then deposited in-situ using thermal ALD at 200°C using TMA and H₂O. The results from these samples were then compared with MOSCAPs that had only an N₂ 150W 5min plasma pre-treatment followed by a 20nm thermal ALD Al₂O₃ layer. 20nm Pt/200nm Au contacts were deposited ex-situ as the gate contact and the MOSCAPs were measured at room temperature using capacitance-voltage (C-V) and current-voltage (I-V) measurements. The C-V measurements were used to calculate the hysteresis and frequency dispersion of these samples. The hysteresis included the flat band voltage difference between the forward and backward sweep of the C-V curve when swept from -5 to +5V and back to -5V at 1MHz. The frequency dispersion gives the maximum difference in the flat band voltage for C-V curves measured at various frequencies ranging from 1MHz to 1kHz (1MHz, 500kHz, 100kHz, 1kHz and 1kHz). A flat band voltage hysteresis and a frequency dispersion of 200mV was observed for samples that only had an Al₂O₃ gate dielectric while the insertion of an AlN interlayer resulted in a hysteresis and a dispersion of 50mV.

The I-V measurements produced a leakage of 0.016mA/cm² at 1V for the sample with only Al₂O₃ while the one with the interlayer produced a leakage of 0.0096 mA/cm² at 1V. These positive improvements with the insertion of an AlN interlayer could result due to the prevention of GaOₓ sub-oxide formation at the GaN-Al₂O₃ interface [2].

In summary, the insertion of a PE-ALD AlN interlayer between an N₂ plasma treated GaN surface and ALD Al₂O₃ gate dielectric reduces the C-V hysteresis and frequency dispersion by 75% and decreases the leakage current by 40%. Both of these are encouraging for the realisation of high performance GaN power transistors.

characteristics and reliability of SiO$_2$ grown by either thermal or plasma ALD. SiO$_2$ is the most suitable dielectric due to its large bandgap as well as a high conduction band offset to Si resulting in suppression of electron tunneling current in Si CMOS devices. It was found that the channel mobility is similar between thermal and plasma ALD SiO$_2$ but thermal ALD oxide shows lower threshold voltage compared to the plasma ALD oxide. Although ALD SiO$_2$ provides positive threshold voltage and good gate insulating property, the Si/C/SiO$_2$/interface requires further treatment to enhance the mobility. We have recently demonstrated a novel interface engineering technique to improve the MOSFET mobility by combining ultrathin lanthanum oxide (LaO) at the SiC/dielectric interface and ALD SiO$_2$. In this study, we deposited ultrathin 1nm LaO followed by 30nm SiO$_2$ using ALD tool without breaking the vacuum. It was found that the channel mobility is enhanced with the incorporation of 1nm LaO between SiC and SiO$_2$ as compared to the device without LaO layer. This combination of ultrathin LaO and SiO$_2$ provides an effective solution to challenges of Si CMOSFETs for power applications.

AA2-TuP9 Atomic Layer Deposted TiO$_2$-Based Memristors using In-situ Fabricated Al Doped ZnO Thin Film as Electrodes, Kei Zhang, P. Liu, Old Dominion University, A. Pradhan, Advance Material Solution LLC, H. Baumgart, Old Dominion University

Memristor is a nonlinear and two terminal passive device, which has the ability to change the resistance between high resistive states and low resistive states by applying bias voltage. This property called resistive switching makes the memristors suitable for a wide range of applications in non-volatile memory, dynamic random-access memory, and flash memory. In recent years, Metal-oxide-based memristive devices have drawn significant attention due to their high-density integration, high endurance, fast switching behavior, low power consumption and simple structure. In addition, among the promising binary transition metal oxide materials, such as nickel oxide, zirconium oxide, zinc oxide, hafnium oxide, tantalum oxide, TiO$_2$ films are extensively used to fabricate the nonvolatile memristor device due to its simple structure and compatible with CMOS integration process. Recently, ZnO has been widely used for various applications due to its good electrical conductivity, wide band gap (3.37 eV), high exciton binding energy (50 meV), low cost, nontoxicity, high mechanical and thermal stability. When doped with Aluminum ZnO grown via atomic layer deposition (ALD) has been reported to show resistance values ranging from insulating to on the order of 10$^{-3}$ Ω·cm, which is suitable for memory device electrodes.

Currently, the most common methods used were magnetron sputtering, pulsed laser deposition, thermal oxidation, electrodeposition, chemical vapor deposition, sol gel chemical reaction, and atomic layer deposition. The ALD is a self-limiting technique that allows atomic layer growth each cycle, ALD can precisely control the film layer thickness, stoichiometry, composition, uniformity, and sharp interface. ALD also shows perfect conformal coverage when it deposits thin film on complex surface structures. Therefore, ALD is considered as a novel and competitive method to deposit IMEM memory structures. To create such devices, transparent Al/ZnO film was grown on Si wafers as a transparent electrode followed by an active layer of TiO$_2$ film, then the other layer of Al/ZnO was deposited on Si/Al/ITO$_x$-layers to form a memristor structure. All the thin films in the structures were synthesized by the ALD system sequentially.

Several physical characterization techniques have been employed to determine the ALD films of memory devices. The crystal structure was analyzed by X-ray diffraction. The film morphology was determined by field emission scanning electron microscopy. The surface roughness was analyzed by atomic force microscopy. The electric properties were measured by semiconductor analyzer. The results demonstrate a fairly good memristive device.

AA2-TuP10 Homogeneously Doped Atomic Layer Deposition Zinc Tin Oxide Thin Films for Improving Contact Resistance in Semiconductor Device Applications, Alex Ma, University of Alberta, Canada; T. Muneshwar, Synthetry Inc., Canada; D. Barlage, K. Cadien, University of Alberta, Canada

For thin film semiconductor device applications, the formation of high quality contacts is critical. Currently, it is difficult to realize ohmic contacts on zinc oxide (ZnO) thin films especially for applications that require more resistive active layers e.g. thin film transistors (TFTs) and Schottky diodes. In this work, we investigate the contact resistance in thin film devices that employ ZnO active layers grown by low temperature plasma-enhanced atomic layer deposition (ALD) with the gated transmission length method (TLM). The contact performance in intrinsic ZnO devices are compared to identical devices but with a homogeneously doped ALD zinc tin oxide (ZTO) interlayer inserted between the semiconductor body and metal contact. By incorporating a small percentage of tin (Sn) in the ZnO during ALD growth, we observed an increase in the film’s electron concentration resulting in lowered contact resistance.

AA2-TuP11 ALGa/NbN Films Obtained by Atomic Layer Deposition Targeting Thin Film HEMT, Joaquin Alvarado, M. Chávez, Benemérita Universidad Autónoma de Puebla, Mexico; S. Gallardo, CINVESTAV-IPN, Mexico; Y. Sheng, D. Muenstermann, Lancaster University, UK

ALGa/N and NbN films were obtained using Plasma Enhanced Atomic Layer Deposition (PE-ALD) at 300 °C; we study the effect of Al content variation on the optical and structural and electrical performance. XRD measurements show the hexagonal structure, SIMS profile signals reveals the main components of AlGa/N.

Experimental

ALGa thin films were deposited on silicon wafers via atomic layer deposition using a mega cycle which consists of sub cycles of AlN and GaN to obtain the AlGa/N alloy. The AlN sub cycle consist of (1) pulse of Trimethyl Aluminiun (TMA), (2) Ar purge, (3) H$_2$/N$_2$ plasma and (4) Ar purge, the growth rate is 0.5Å/cycle at 300°C, the total number of megacycles were 215. GaN sub cycles consist of (1) pulse of Trimethyl Gallium (TMGa), (2) Ar purge, (3) H$_2$/N$_2$ plasma and (4) Ar purge, the growth ratio is 0.3Å/cycle at 300°C, the total number of megacycles was 131. The number of megacycles were calculated in order to obtain ~20 nm.

Results

The XRD patterns of Al$_x$Ga$_{1-x}$N on silicon substrates growth with 0.3 and 0.6 Al content were performed. Two peaks were observed in the sample Al$_{0.5}$Ga$_{0.5}$N the peak located at 2θ=34.5° (002) is assigned to hexagonal phase of GaN and a second peak at 2θ=32.3° (100) correspond to the hexagonal phase of AlN. The sample Al$_{0.6}$Ga$_{0.4}$N show peaks at 2θ=34.3°, 37.0° assigned (002), (100), (101). Furthermore, from photoluminescence characterizations it is possible to observe in the Al$_x$Ga$_{1-x}$N sample a yellow luminescence band situated at 2.32 eV, which is related to Gallium and N vacancies, carbon defects, as well as to the high concentrations carriers 10$^{18}$ cm$^{-3}$ [1]. The peak observed at 2.32 eV is associated to dislocations defects [2]. However, a sample which contains higher content of Al didn’t show PL signal.

On the other hand, by SIMS sputtering time profile it is possible to observed that the sample with Al$_{0.5}$Ga$_{0.5}$N show a non-uniform Al content, although Al$_{0.6}$Ga$_{0.4}$N show a better Al distribution film. Electrical characterizations of the deposited films will be also included.

AA2-TuP12 High-Temperature Thermal Stability of ALD-TIN Metal Gate on In-situ AlOx/YrOx/(In)GaAs(001): Toward the Self-Aligned Gate-First Process, Lawrence Boyu Young, H.-W. Won, J.-H. Huang, K.-Y. Lin, J. Liu, Y.-H. Lin, National Taiwan University, Republic of China; J. Kwo, National Tsing Hua University, Republic of China; M. Hong, National Taiwan University, Republic of China

High-k metal gate (HKMG) technology has been introduced since the 45nm node complementary metal oxide semiconductor (CMOS). The gate-first process was replaced by the gate-last process because of the threshold voltage pinning causing by the subsequent high-temperature process$^1$. The gate-first process provides a capability to reduce the process complexity, and is more economic than the gate-last process. To realize high-performance MOS field-effect transistors (MOSFETs) using self-aligned gate-first process, the thermal stability of MOS structure must be excellent to sustain the subsequent high temperature process. With the higher electron mobility, GaAs-based III-V semiconductors have potential to replace the current Si-based CMOS technologies. However, the reported thermal stability between high-k/III-V was limited to 500°-600°C caused by the interface oxidation. In our previous study, ultra-high thermal stability above 850°C between in-situ grown oxide/III-V interface was attained$^2$, critical for the present study of atomic layer deposition (ALD)-TIN/oxide/(In)GaAs thermal stability at temperatures ranging from 850 to 950°C. Here, we have studied the samples with different post-metallization annealing (PMA) using transmission electron microscopy (TEM), J-E, and C-V characteristics of the MOS capacitors (MOSCAs). The samples were prepared in a ultra-high vacuum (UHV) multi-chamber growth/analysis system (Fig. 1). The detailed fabrication process and the schematic structure of the MOSCAPs are shown in Fig. 2. The TEM shows the smoothness in an atomic scale of the ALD-TIN/high-k/(In)GaAs interfaces. The interface remained intact without degradation after 800°C 5s in He ambient (Fig. 3). From the J-E
curves (Fig. 4), the leakage current densities of the MOSCAP with different PMA in N₂ show no degradation after 900°C annealing for 10s. The leakage current density of the MOSCAPs maintained below 10⁻⁷ A/cm² at electric fields of ± 4 MV/cm, which is the same with that of the MOSCAP without PMA. A different behavior was found in the MOSCAP with PMA in He. The leakage current density raised sharply in the negative bias region, probably resulted from the generation of nitrogen vacancies during the high temperature annealing in He. Similar features were found in the CV characteristics (Fig. 5). With the PMA in N₂, the C-Vs showed no degradation after 900-950°C annealing, while the MOSCAP was too leaky to measure the C-Vs for the MOSCAP with PMA in He with temperatures above 900°C. The excellent electrical and thermal stability of the MOS structures with TiN gate are vital to realize high performance GaAs inversion channel MOSFETs using a gate-first process.

AA2-TuP13 Identification of Interfacial Defect in ALD Grown Al₂O₃/GeOₓ/Ge Gate Stack, Jinjuan Xiang, L. Zhou, X. Wang, X. Ma, T. Li, W. Wang, Institute of Microelectronics of Chinese Academy of Sciences, China

Germanium (Ge) has attracted tremendous interest as a channel material for high performance complementary metal-oxide-semiconductor (CMOS) devices. The interfacial cided charges are detrimental to the performance of Ge MOSFET devices as they can form Coulomb scattering center to reduce channel carrier mobility and device reliability. Thus we experimentally investigate the interfacial defect in the GeOₓ/Al₂O₃ gate stack grown by ALD using X-ray photoelectron spectroscopy (XPS) and electrical characteristics by capacitance-voltage (C-V) measurement. For GeOₓ interlayer by ozone oxidation, oxygen vacancies exist and show positive charges at the Ge/GeO interface. The O₂ annealing is helpful to decrease the oxygen vacancy defect. For the GeOₓ/Al₂O₃ interface, oxygen dangling bonds exist, and show negative charges. This work can be effectively applied to engine the interface promotion and enhance the performance of Ge-based devices.

AA2-TuP15 Effect of Metal-insulator Interface on Dielectric Properties of Ultrathin Al₂O₃ and MgO Fabricated using In-situ Sputtering and Atomic Layer Deposition, Jagarana Acharya, J. Will, R. Goul, B. Liu, J. Wu, The University of Kansas

We have investigated the properties of ultrathin Al₂O₃ and MgO in metal-insulator-metal (M-I-M) trilayers fabricated using in situ integrated sputtering and atomic layer deposition (ALD). The quality of ultrathin Al₂O₃ was found to be significantly dependent on the pre-ALD conditions which lead to extremely different M-I interface. After optimization of ALD processing parameters, M-I interfacial layer (IL) was reduced to a negligible level obtaining a dielectric constant (ε) up to 9.8 on the Al₂O₃ films in a thickness range between 3.3-4.4 nm, corresponding to an effective oxide thickness (EOT)=1.4-1.9 nm respectively compatible to high-k dielectrics. While ε decreases at a smaller Al₂O₃ thickness, the hard-type dielectric breakdown 32 MV/cm and in situ scanning tunneling spectroscopy (STS) revealed band gap ~2.63 eV confirming high quality dielectric as good as an epitaxial Al₂O₃ film. This result suggests that the IL is unlikely a dominant reason for the reduced ε at the Al₂O₃ thickness of 1.1-2.2 nm and is due to electron tunneling as supported by transport current-voltage measurement. However, non-optimal conditions result in the growth of significant IL with drastically reduced ε~0.5-3.3. The properties of MgO with and without SC-ALD Al₂O₃ studied in the thickness range 2.5-5 nm point out significance of seed layer in fabrication of high-quality dielectrics, approaching ε~9 for SC-ALD-Al₂O₃/ALD-MgO at thickness 3.8-4.9 nm corresponding to EOT=1.6-2.1 nm respectively. But, 40C-ALD MgO without seed layer has unexpectedly lower ε~3.4 possibly due to poor nucleation forming an interfacial layer, and correspondingly increase in the leakage current. The similar decreasing trend in ε with decrease in MgO thickness is observed but at thickness greater than that of Al₂O₃ due to higher leakage current observed for MgO dielectrics and also confirmed by in situ STS analysis. Our results demonstrate the significance of controlling the nucleation in ALD to achieve better M-I interface in order to fulfill the demand for leak-free and defect-free high-quality ultrathin dielectrics as an alternative for low-cost gate dielectric for CMOS, and tunnel junction for quantum computing and memory applications.

AA2-TuP16 Thermal and Plasma ALD Al₂O₃ Gate Insulator for GaN Electronic Devices Characterized by CV-Stress Measurements, Nicole Bickel, E. Bahat Treidel, I. Ostermay, O. Hilt, O. Krüger, Ferdinand-Braun-Institut, Germany; F. Naumann, H. Gargouri, SENTECH Instruments GmbH, Germany; J. Würft, G. Tränkle, Ferdinand-Braun-Institut, Germany

The technology of atomic layer deposited (ALD) Al₂O₃ films is ideally suited for fabrication of high quality GaN MISFET’s gate insulator especially in vertical GaN n-channel transistor technology (Fig. 1). The gate oxide technology is a very crucial process step as it influences transistor functionality such as normally-OFF operation, hysteresis and low positive threshold voltage shift. Furthermore, dependent on the transistor design the gate oxide/channel interface may also determine ON-OFF-Ratio. For qualifying and characterizing the gate insulator film technology, circular-planar MIS-capacitors were formed on a n-GaN layer (Fig. 2). The 25 nm thick Al₂O₃ films were deposited by plasma enhanced atomic layer deposition (PEALD) and thermal atomic layer deposition (ThALD) in SENTECH ALD system SI PEALD. Different in-situ surface pre-treatment conditions such as NH₃-plasma, NH₃-flow and without any pre-treatment were tested to optimize the GaN/Al₂O₃ interface. After top electrode metallization the capacitors were annealed at 350°C in N₂-ambient to achieve a large ΔC/COX. Accumulated capacitance-voltage(CV)-scans were performed to evaluate the insulator charging effects, to identify possible shifts in the CV-profile and to gain insight into bulk and interface charging phenomena (see Figs. 3 and 4). While measuring the accumulated bidirectional scans the maximum positive stress bias voltage was increased in 2 V steps from 0 V to 16 V after each bias sweep. The capacitance was measured at 1 MHz and 1 V AC amplitude. According to Figs. 3 and 4 a negative bias down to -15 V has turned out to be sufficient to empty the interface traps. PEALD and NH₃-plasma treated samples show a significant broadening of the positive bias stress CV-profile. Furthermore the flat band voltage shifts up to 7.2 V (Fig. 5). In contrast, the ThALD films with NH₃-plasma pre-treatment show a reduced broadening with a flat band voltage shift of only 2.9 V. When using NH₃-plasma pre-treatment, the calculated maximum negative fixed-oxide charges are less for ThALD (ΔN̄₂O₃ 5.1×10¹² cm⁻²) as compared to PEALD (ΔN̄₂O₃ 1.1×10¹³ cm⁻²), see Fig. 6. Therefore thermal ALD in combination with NH₃-plasma pre-treatment is very suitable for GaN MISFET technology.


Atomic layer deposition (ALD) of metallic ternary TiSiN films is associated with a variety of morphological and structural variations. Among these phenomena are the thickness and stoichiometric-dependent amorphous to crystalline phase transitions, film density changes, surface roughness and film resistivity variations. In the case of TiSiN films deposited via thermal ALD at temperatures of about T=600°C, using chlorine-based Si precursors, titanium tetrachloride and ammonia, the film structure is highly dependent on the total Si incorporated in the film. In this work, we demonstrate the tunability of crystalline phase highly conformally TiSiN films with variable Si content. TiSiN films were deposited on high aspect ratio structures using a Eugenus 300nm commercial QXP mini-batch system. Film thickness and Si content were varied, and corresponding structural analysis was performed using multiple characterization techniques. X-ray diffraction and reflectivity studies of these films showed a reduction in film density and transition from nano-crystalline to pure amorphous phase with increase in Si fraction. Cross-section high resolution transmission electron microscopy (HRTEM) and selected area electron diffraction (SAED) pattern analyses corroborates with the X-ray analysis that high-Si TiSiN films exhibit a fully amorphous structure. Moreover, control of Si fraction in the film enables tuning of the morphology from polycrystalline to fully amorphous; in all cases, excellent step coverage on high aspect ratio structures were obtained.

AA2-TuP18 Room Temperature Deposition of Hafnium Oxide by Atomic Layer Deposition for Gating Applications, Pragya Shekhar, S. Shamin, K. Hartinger, J. Kleinlein, R. Schlereth, H. Buhmann, L. Molenkamp, University of Wuerzburg, Germany

The advancement of fabrication techniques for nanostructures devices has led to technological breakthrough in semiconductor industries. Apart from the lithographic developments, high-k materials like ZrO₂ and HfO₂ have been employed as gate dielectric for efficient control of the carrier density. In this regard, atomic layer deposition (ALD) has been used to grow these insulators as it produces highly uniform and conformal layer with precise thickness. Previous works to grow HfO₂ by ALD require higher temperature (~1000°C) for microelectronics devices has been done. However, many
devices and materials have additional constraints that their properties degrade at higher temperatures. This limits the operating temperature at which the various fabrication processes can be carried out. For our research in the field of topological physics, mercury telluride (HgTe) topological insulators (TIs) are significant due to its versatility and tunability from trivial to 2D TI to 3D TI to Weyl by tuning the thickness and applied strain (compressive or tensile). However, the transport properties degrade when the HgTe wafer are heated above 80 °C. To overcome this problem, we have developed a room temperature ALD process for growing HfOx. A comprehensive study of structural and transport properties of devices containing HfOx gate dielectric was carried out and results have been compared to device containing conventional SiO2/Si3N4 multilayers insulator films grown by plasma enhanced chemical vapour deposition (PECVD). This comparison demonstrates that our ALD grown insulator is superior in terms of structural properties. We have already shown that microstructures fabricated with ALD grown insulator show quantum spin Hall effect for 2D HgTe based devices. This capability is critical for understanding the properties of microscopic devices and may provide new insights in the field of topological insulator. Our process is not limited to HfOx (it is used for process control) but can be easily adapted to other material systems which also require low temperature lithography process in order to retain the intensive property of material.

AA2-TuP18 Influence of Surface Cleaning Process on Initial Growth of ALD-Al2O3 and Electrical Properties of Pt/Al2O3/β-Ga2O3 MOS Capacitors, Mafuura Hirose, National Institute of Technology, Japan; T. Tobotoke, National Institute of Materials Science, Japan; E. Maeda, Shiba Institute of Technology, Japan; A. Ohi, N. Ikeda, Y. Irokawa, Y. Kode, National Institute for Materials Science, Japan; H. Kyono, Shiba Institute of Technology, Japan

β-Ga2O3 power device with metal-oxide-semiconductor (MOS) structure have been widely investigated. Al2O3 is leading candidate as gate insulator because of relatively stable amorphous structure, a high dielectric constant (k) of 8 - 9 and a large bandgap of 6.5 - 6.8 eV. Al2O3 films are generally formed by atomic layer deposition (ALD). However, it remains big issues such as an abnormal flatband voltage (Vfb) shift and a large interface state density (DOI). To improve these electrical properties, various surface cleaning techniques of the substrate have been considered. In this study, we investigate how the surface cleaning technique affects to morphology of the surface of β-Ga2O3 and electrical properties of Pt/Al2O3/β-Ga2O3 MOS capacitors.

At first, n-β-Ga2O3 epilayer (2.0 × 10^17 cm^-3) / n'-β-Ga2O3 (3.7 × 10^20 cm^-3) substrates (n-β-Ga2O3) were cleaned under four conditions: just a SPM for 5 min and SPM for 5 min (SPM), followed by BHF for 1 (BHF1), 10 (BHF10), and 30 min (BHF30). 25-nm-thick Al2O3 films were deposited on n-β-Ga2O3 substrates by ALD at 300 °C using TMA precursor and H2O gas. Finally, Pt gate electrodes and Ti/Pt ohmic electrode were deposited.

The minimum root mean square (RMS) value (0.36 nm) of the n-β-Ga2O3 substrate was observed after SPM treatment. The RMS values (~0.6 nm) increased drastically when BHF treatment carried out even for 1 min and the value was unchanged even if treatment time was longer. In addition, the n-β-Ga2O3 substrate was etched by 0.9 nm for the BHF30. This is because the increase of the surface roughness is due to the heterogeneous etching of the n-β-Ga2O3 substrate. The Al2O3 XPS intensities of the Al2O3 films after ALD 5 cycles for the BHF10 and BHF30 decreased by about 25% compared to the SPM and BHF1, suggesting that the surface roughness affects to the initial growth of the Al2O3.

The MOS capacitor exhibited similar J-V properties regardless of the surface treatment techniques, indicating that the characteristic of the Al2O3 films were unchanged. On the other hand, the Vh, hysteresis (Vh-Vh) due to the trapped/detrapped electrons increased as the BHF treatment time increases. The Dv energy distribution due to the fixed charge, which was calculated using conductance method, increased with increasing the BHF treatment time. These Vh and Dv behaviors are in good agreement with the data of the surface roughness of the n-β-Ga2O3 substrate. Considering to these data, note that the fixed charge and trapped/detrapped electrons occur at the Al2O3/n-type β-Ga2O3 interface. Therefore, the BHF surface treatment technique is not necessary promising from the viewpoint of the interface characteristics.

AA2-TuP20 Reliable Gate Stack Development Employing Plasma Assisted Atomic Layer Deposition HfOx on InGaAs, Seung-Jeong Oh, M.-Kong, K. Seo, Seoul National University, Republic of Korea

We developed an advanced plasma-assisted atomic-layer deposited (PA-ALD) HfOx process targeted on InGaAs substrate. The developed ALD process is consisted of isopropyl oxidant precursor and in-situ cyclic N2 plasma nitridation that improves both interface and dielectric bulk quality as well. The interface chemistry and capacitance-voltage characteristics of HfOx/InGaAs MOS devices are investigated. Clear oxide-related elements were eliminated using our ALD process confirmed by XPS and STEM measurements. The IPA-based HfOx/InGaAs MOS capacitor exhibited a significant decrease in the 〈Dv〉 of 4.5×10^10 cm^-2·e^-1·eV^-1 for 0.3 eV and outstanding inversion behaviors. Moreover, substantial improvement was found not only in n-type substrates but also in p-type substrates as well. The significant mid-gap Dv decrease is responsible for inversion behavior. The improvement mechanism of the proposed technology is assumed to be that nitrogen incorporation reduces oxygen vacancies which act as oxygen diffusion paths and with the use of IPA oxidant the interface would be strongly protected during pre- and post- dielectric deposition. Detailed electrical characteristics such as positive-bias temperature instability characteristics were investigated.

AA2-TuP21 Stabilizing Ultrasmall Colloidal Platinum Diphosphide (PtP2) Nanocrystals with Atomic Layer Deposition Oxide for Neutral H2O2 Electrosynthesis, Hui Li, S. Geyer, Wake Forest University

Despite recent demonstrations of various electrocatalysts for small amount hydrogen peroxide (H2O2) production with rotating ring-disk electrode technique, it is still a great challenge to develop an efficient, selective, and stable O2 to H2O2 electrocatalyst for realizing continuous on-site production of neutral hydrogen peroxide. Here we synthesize ultrasmall and monodisperse colloidal PtP2 NCs which achieves nearly zero-overpotential and unit H2O2 selectivity at 0.27 V vs. RHE for ORR. DFT calculation suggests that the P plays a key role in promoting associative hydrogenation of OOH* to H2O2 and suppressing the dissociative OOH* to O2. With precise ALD Al2O3 overcoat and activation, the proton-exchange membrane fuel cell (PEMFC) with 42Al2O3/IRP-600 catalyst achieves a maximum iR(H2O2) of 2.26 mmol h^-1 cm^-2 and a highest current efficiency of 78.8% for 120 h. Under recycle mode, the accumulated neutral H2O2 concentration reaches up to 3% for 65 h and 1.21 mol% for 120 h, and which can be readily used for medical, food, and environmental applications.

AA3-TuP1 Highly Dispersed Uniform Pt Catalysts on Carbon Support by Atomic Layer Deposition Fluidized Bed Reactor (FBR), Jang-Yeon Park, W.P. Hong, J.Y. Park, Hyundai Motor Group, Republic of Korea; W-J. Lee, S.-H. Kwon, Pusan National University, Republic of Korea

One of the key issues for fuel cell applications is to increase the active surface area by controlling the size of Pt catalyst and reduce Pt loading to achieve high performance and cost savings. Atomic layer deposition (ALD) has recently received attention as an effective method for synthesis of nanocatalyst since it allows precise control at the atomic level. In this study, Pt catalyst is synthesized using ALD directly on the surface of porous carbon support floated by fluidizing bed reactor (FBR). The oxygen functional group introduced on carbon surface through acid solution treatment provides reaction site of Pt precursor. In initial cycle, nucleation occurs on carbon surface, and high density 1-2 nm size uniform nanoparticles is formed. The Pt precursor adheres to the surface of already generated Pt and grows the Pt nanoparticle. Because of this growth mechanism, the size distribution of the particle is slightly wider at high cycles, but the size of the particle is controlled by the cycle and grows up to about 4 nm in 30 cycles. About 1 nm size particles have the highest active surface area, but in terms of catalyst performance, about 3 nm size particles show the best results under the Pt loading fixed condition. When the size of particle is not less than 3 nm, Pt exhibit physical properties as a catalyst and agglomeration of particles can be suppressed. To evaluate the catalyst performance of new processes, MEA optimization is important and this remains as a future plan.
emission characteristics. Despite its great advantages, it is difficult to commercialize due to high stack cost. Among the parts, Platinum(Pt) catalyst is expensive and scarce, so it is important to maximize the catalyst activity with minimal usage. Many researchers have significantly focused on core shell nanocatalysts due to their great activity, selectivity and stability with reducing the Pt loading. To optimize the characteristics of core shell nanocatalysts, it is necessary to precisely control shell composition and thickness. With the Atomic Layer Deposition(ALD) process, the size of nanocatalysts and shell thickness could be finely tuned at atomic scale. In order to uniformly deposit the nanocatalysts on the porous carbon support with large surface area, ALD with Fluidized Bed Reactor(ALD-FBR) offers the solution. By dispersing the carbon powder in the chamber, particle agglomeration is prevented and nanocatalysts can be uniformly deposited.

In this work, we synthesized core shell nanocatalysts using ALD-FBR. We utilize Nickel(Ni), Ruthenium(Ru) for the core materials, and Pt for the shell material. Ni(1-dimethylamino-2-methyl-2-butanolate), \( \eta^2 \)-1,3-cyclohexadiene ruthenium tricarbonyl, and Trimethyl(methylcyclopentadieny)platinum(IV) are used as Ni, Ru and Pt precursor, respectively. The size of nanocatalysts and shell thickness is controlled by changing each ALD cycles. TGA, XRD and HRTEM are used to examine the structural and chemical properties of core shell nanocatalysts. From EDX line profile analysis, shell material(Pt) is preferentially deposited on core nanoparticles(Ni, Ru). Electrochemical Surface Area(ECSA) and cell performance were measured by Cyclic Voltammetry(CV) and MEA test. Core shell nanocatalysts by ALD-FBR show higher ECSA and cell performance than commercial catalyst.

AA4-TuP6 Porous Nanomembranes Grown by Atomic Layer Deposition: Self-Rolling in Solvent and their Sensing Applications, F.-M. Ye, Y-Y. Zhao, G. Huang, Yong Feng Mei, Fudan University, China

Tubular microstructures of various materials have emerged as active agents for large-scale detoxification, sensing, and many other promising applications.[5] Generally, for sensing application, binding of specific recognition sites on tubular structures for target molecule is engaged to achieve capture and detection of certain molecular.[2] The rolled-up technology,[3,4] provide the possibility of producing microtubular structures with desired geometries and surface decoration on surface, which should be of great importance for real-time bio-sensing. In this study, porous nanomembranes were fabricated with high productivity by depositing active material on the surface of 3D polymer porous template with rough surface. Then, by atomic layer deposition technique,[5] the free-standing porous ZnO nanomembranes were obtained after the sacrificial template was removed at high temperature in oxygen. The rough surface of the template and the high-temperature treatment make the surface of the nanomembrane with porous microstructure. Self-rolled porous ZnO nanomembranes were then prepared by sonication in chemical solvent. The porous surface was used as cytosine recognition sites for effective and selective binding of neurotransmitter compounds like dopamine (DA). Such selective binding is significantly enhanced by the high surface-to-volume ratio of the porous structure. For sensing applications, dispersion solution containing rolled-up structures was dropped on the surface of glassy carbon electrode, and then cytosine recognition sites was self-assembled on porous ZnO nanomembrane to capture target DA molecules which induces concentration-dependent electrical signals. Detailed analyses demonstrate that increased mass transfer leads to the enhanced sensitivity for DA. The current strategy provides an opportunity to develop 3D biosensor for high-affinity capture-based detection of nerve agents and can be extended to environmental contamination field.

References:

AA4-TuP7 Fabrication and Characterization of Atomic Layer Deposited ZnO-based Ultra-Thin Films for Hydrogen Sensing, Yan-Qiang Cao, A.-D. Li, Nanjing University, China

As a high-energy density, non-polluting renewable energy source, hydrogen is widely used in many fields such as industrial synthesis, fuel cells, and rocket propulsion. It is of great importance to develop reliable, fast, and precise hydrogen sensors so as to avoid possible explosion risks and harm. Due to the low cost, chemically and thermally stability, extremely abundant nanostructures and simple fabrication technique, ZnO as n-type semiconductor is widely used to detect reductive gases, such as hydrogen. Usually thin film-based sensor is more effective for improved gas sensing performance due to its small size, larger surface to volume ratio, and feasibility in integrated circuits. To date, research on ZnO ultra-thin film-based H2 sensor is still lacking.

In this work, the ZnO ultra-thin films with varied thicknesses from 5 nm to 30 nm were grown on SiO2 substrate at 200 °C using diethyl zinc (DEZ) and H2O by atomic layer deposition (ALD), which could precisely control the thickness of the films down to values comparable to the Debye length. The effect of ZnO thickness and post-anneal on H2 sensing, such as detection concentration, work temperature, and sensitivity has been carefully investigated. It is found that H2 sensor based on 10 nm-thick ZnO ultrathin film exhibits better room temperature sensing performance with Rair/Rgas of 29 in 4000 ppm H2. We also attempted to prepare Pt nanoparticles-decorated ZnO ultra-thin films by ALD. The impact of Pt NPs size and areal density on enhanced H2 sensing of ZnO film sensor has been evaluated. The improved mechanism has been proposed.

ALD Applications
Evergreen Ballroom & Foyer - Session AA4-TuP

Protective Coatings, Barrier Films, Membranes and Flexible Substrates Poster Session

AA4-TuP1 ALD for Membrane Applications, Matthieu Weber, M. Bechelany, Institut Européen des Membranes, France

Atomic layer deposition (ALD) is a technology allowing for the preparation of conformal ultrathin films with a sub-nanometer thickness control, a unique capability. Therefore, this route is particularly suited for the structural modification and pore tailoring of porous structures. ALD can be advantageously applied to the area of membranes by fine-tuning their surface properties, and by controlling the diameter and the aspect ratio of the pores with (sub)nanoparticle precision. The precise control over the chemical and physical nature of the pore surface provided by ALD makes this route extremely valuable for membrane science. Thus, ALD coatings have been prepared on a wide variety of membrane substrates, from inorganic templated substrates to porous polymers.

This presentation aims to provide a summary of the advances of ALD applied to membranes. Based on a wide literature data survey including some of our recent data,[1-3] the application of ALD for different types of membranes will be described and illustrated using relevant examples, and the main challenges and opportunities of the ALD route will also be assessed.


AA4-TuP2 Nano-Hardness of ALD Films, James Daubert, W. Sweet, J. Kellner, Northrop Grumman

In this presentation, we will explore different films (Al2O3, ZrO2, Ta2O5) deposited using atomic layer deposition (ALD) to compare how the processing conditions (i.e. deposition temperature, material interfaces, and annealing temperatures) effect hardness. The mechanical and electrical performance of materials used in microelectronics are often dependent on the processing conditions of material, but extensive testing after device manufacturing is often required to determine these relationships. Bulk, macroscale measurements, such as thickness, index of refraction, and sheet resistance can easily be measured, but often do not translate well to the performance of the final device, because the devices are often dependent on nanoscale properties of the materials (i.e. defects). If the nanoscale properties of the materials can be measured before final device fabrication, then correlations can be established linking material processing conditions with device performance.

One method to measure nanoscale properties of materials is through nanoindentation. Nano-indentation is a method to measure the hardness of
AA4-TuP3 High Acid Corrosion Resistance of NbOx Thin Film Deposited by Room Temperature ALD, Kazuki Yoshida, K. Saito, M. Miura, K. Kanomata, B. Ahmmad, S. Kubota, F. Hirose, Yamagata University, Japan

Metal oxide thin films like aluminum oxide (Al2O3), silicon oxide (SiO2), and titanium oxide (TiO2) have been well known as gas barrier materials for moisture. For acid corrosion, Al2O3 exhibits a slight deliquescence against hydrochloric acid. On the other hand, niobium pentoxide (Nb2O5) has been studied as a cathode protective layer of a fuel cell and a corrosive barrier film for metal. By laminating Nb2O5 on Al2O3 using thermal ALD, the corrosion resistance was enhanced to a certain degree. However, the deposition temperature was over 2000°C although the high-temperature process is not acceptable for not heat-tolerant flexible electronics. In this study, a laminated film of Al2O3 and Nb2O5 was deposited by room temperature atomic layer deposition (RT-ALD) and we report the improved acid corrosion resistance.

We used plasma excited humidified Ar as an oxidizing gas, trimethylaluminum (TMA) and tert-butylimidotris-(ethylmethylamido) niobium (TBTEMEM) as precursors of Al2O3 and Nb2O5, respectively. The RT-ALD system is shown in Figure 1. We prepared SUS 304 plates with a size of 20 x 50 mm² as samples. The SUS plates were cleaned by ultrasonic cleaning with using acetone, isopropyl alcohol, and deionized water to remove organic impurities. The surface was slightly etched with dilute hydrochloric acid to remove the surface scratches. For the corrosion resistance test, we immersed substrates into the concentrated hydrochloric (36 wt%).

Figure 2 shows the anti-corrosion film coated substrate immersed in concentrated hydrochloric acid for 30 minutes. Al2O3 thin films were deposited 30 nm both (a) and (c). The Nb2O5 was deposited with a thickness of 5nm both the substrate(b) and (c). The substrate (c) is laminated Nb2O5 on Al2O3. As we can see from Fig.2, the corrosion resistance for hydrochloric acid is clearly improved by laminating Nb2O5. We consider the RT deposited Nb2O5 is applicable for not heat tolerant flexible and MEMS application.

AA4-TuP4 Effects of Composition Ratios on Mechanical and Electrical Properties of AZO – Zincone Composite Thin Film Deposited on Transparent Polyimide Film Using Atomic and Molecular Layer Depositions, Seung Hak Song, B.-H. Choi, Korea University, Republic of Korea

The combination of ALD and MLD techniques enables the fabrication of various functional organic – inorganic composite thin film structures. It is possible to fabricate thin films with various mechanical and electrical properties by adjusting the ratio of organic / inorganic components. In this study, a composite thin film composed of Al-doped zinc oxide (AZO) and the zincone organic film were deposited on a transparent polyimide substrate using diethylzinc (DEZ) with H2O and hydroquinone (HQ) precursors. The characteristics of the hybrid thin film are varied significantly with the change of composition ratios, so the change of mechanical and electrical properties of the thin films according to the ratio of zincone organic film were measured. Various nano-structures of hybrid thin film were fabricated by controlling the composition ratio and process conditions, and their morphology and characteristics were analyzed. To investigate the ratio of thin films with high durability and electrical conductivity, the variation of electrical resistivity of thin films according to bending was measured.

AA4-TuP5 Room-temperature Atomic Layer Deposition of Aluminoisilicate Thin Film on Flexible Films, Yoshiharu Mori, K. Yoshida, K. Kanomata, M. Miura, B. Ahmmad Arima, S. Kubota, F. Hirose, Yamagata Univ., Japan

In recent years, aluminoisilicate thin films are applied in various fields such as ion absorbers. Aluminoisilicate is generally prepared by hydrothermal synthesis. However, it is based on high temperature and pressure processes. It is also not suited for the fabrication on electronic devices. To solve these problems, we newly developed room temperature ALD of aluminoisilicate using tris (dimethylamino) silane (TDMAS), trimethylaluminum (TMA) and plasma excited humidified argon. We realized deposition of aluminoisilicate on flexible films at room temperature as shown in Fig.1. Fig.2 shows a wide scan XPS spectrum measured from the RT grown aluminosilicate on a PEN film. We confirmed significant peaks of Si, Al and O. The aluminosilicate film thickness was measured by spectrophotometric ellipsometry that exhibited the growth per cycle of 0.16 nm/cycle at room temperature. This suggest the possibility of the film thickness control with a precision of nanometer. We confirmed the ion absorption ability of the film. It was confirmed that Na and K cations were effectively absorbed on the film. The ion exchange properties from Na to K was also confirmed. The present RT-ALD offers the ion exchange reaction on flexible films. This research is expected to be applied as heavy metal ion filters and ion sensitive field effect transistors.

AA4-TuP6 ALD Layers for Reduced Wear on Micro Cutting Tools, T. Junghans, Hans-Dieter Schnabel, Westsächsische Hochschule Zwickau, Germany

In modern life, the usage of electronics is increasing day by day. Therefore, many circuit boards need to be machined. One of the major problems in circuit board manufacturing is the wear of micro cutting tools used for it. Hard and corrosion resistant coatings might be a good opportunity to reduce the wear of these tools. To the small size of the tools, with diameters of 300 µm and 3 mm, most traditionally used coating techniques are unable to produce conformal coatings on them. This is why the works presented in a poster aimed for thin wear reducing films generated with atomic layer deposition.

The materials used were Al2O3 and TiN in various thicknesses from 20 nanometer to 150 nanometer. Those were used because of their properties, like hardness and corrosion resistance and the well-established ALD-processes. In order to achieve dense films and low deposition temperatures the processes were plasma enhanced. Al2O3 was deposited with TMA as precursor in combination with an oxygen-argon plasma. The TiN films were generated by reacting TDMAT with an ammonia-argon plasma.

The poster shows that Al2O3 and TiN do not differ in wear behavior. Therefore, the focus is on Al2O3, due to the more stable and less time-consuming process. As the film thickness becomes bigger than 50 nm the Al2O3-layers are spalling off of the tools. Therefore, a lower or none reduction of wear was achievable with films as thick as or thicker than 50 nm. The work also shows that especially thin films of about 20 nm thickness achieved high reduction in tool wear. This shows that ALD-layers have promising properties in the field of wear reducing coatings for micro cutting tools.

AA4-TuP7 Fabrication of Atomic Layer Deposited Alumina as Protective Coating of Silver, Gwon Deok Han, J.S. Park, J. Koo, J.H. Shim, Korea University, Republic of Korea

Silver is one of the precious metals widely used in human life. Silver has the disadvantage of being easily corroded or discolored when exposed to moisture and oxygen. Protective coatings of thin oxide films are effective in preventing corrosion and discoloration of silver products such as cookware, coins and jewelry. It is especially important to make a thin, uniform protective coating to protect the silver products from external environments. In this respect, atomic layer deposition (ALD) is considered the best technique for forming a protective oxide layer. ALD has an excellent function to form a uniform film without pinholes even in a complex three-dimensional (3D) structure with a high aspect ratio.

In this study, we evaluated the anti-corrosion performance of ALD alumina coatings for silver products. The protection stability of the alumina coating layer was tested using an artificial sweat solution. The stability of the protective layer was evaluated by depositing alumina layers of changing thicknesses of 20-80 nm on silver samples and immersing the coated samples in artificial sweat solutions. We have demonstrated that a relatively thick alumina layer is effective in protecting the original properties of silver samples. In this meeting, we will discuss the protection performance of ALD alumina including its microstructure, optical properties and corrosion resistance.


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Tuesday Evening Poster Sessions, July 23, 2019

OLEDs (Organic Light-Emitting Diodes) are used in display devices such as mobile and TV, and next-generation OLED displays should be flexible and foldable. Flexible and foldable OLED displays require curvature radius less than 2.5R. In addition, a good encapsulation property is required in a thin thickness. Therefore, it is essential for OLED to realize these characteristics through laminated thin film rather than single thin film. The laminated thin film can reduce the diffuse reflection by generating the antireflection film effect due to the difference of the refractive index of each single layer film. It is also effective in reducing stress in the film and blocking ultraviolet rays.

Recently, the ALD process has been applied as a method of depositing thin films with excellent film quality. These ALD methods are used to develop thin film encapsulation technology because of the self-limiting surface reaction and the advantages of the reaction fraction.

In this paper, structure of the SiO2/SiNx stack films were fabricated by using PEALD (Plasma Enhanced Atomic Layer Deposition) method at low temperature (90 °C) using a single precursor, N2Si:O1. The thickness and refractive index of the thin film were measured using a Woollam M2000D spectroscopic ellipsometer. In addition, WVT (Water Vapor Transmission Rate) was measured using MOSCON Aquatran 2 for thin films deposited on polyethylene naphthalate (PEN). The structure of the SiO2/SiNx stack film, the refractive index was measured to be 1.47 / 1.85, confirming the possibility of antireflection effect through the multilayer. The WVT characteristics were measured over 100 hours according to the thickness of the thin film. At a thickness of less than 150 Å, the SiO2 thin film or SiNx thin film had poor WVT characteristics. In order to overcome this problem, SiO2/SiNx structure was deposited. It is also expected that 2 to 3% of carbon in the deposited SiNx film will lower the film stress and maintain the flexibility of the entire film (Figure 1). The SiO2/SiNx/SiO2 laminated thin films exhibited excellent WVT characteristics with the prevention of destruction of the encapsulation characteristics at a thin thickness (Figure 2). From this work, we confirmed the possibility of a laminated thin film consisting of a silicon oxide film and a nitride film by PEALD in one chamber using one precursor. In particular, the production of a laminated thin film can prevent both reflection and stress absorption, and it is expected that the next generation OLED encapsulation will be applicable.

AA4-TuP9 Low-cost Fabrication of Flexible Transparent Electrodes based on Sprayed Nanocomposites Silver Nanowires and AI Doped ZnO Deposition by Spin Coating, H.O. Nguyen, L.D. Nguyen, C. Jimenez, D. Bellet, LMGP, Grenoble INP/CNRS, France; S. Aghazadehchors, LMGP, France; N.D. Nguyen, Université de Liège; David Muñoz-Rojas, LMGP Grenoble INP/CNRS, France

We report the study of nanocomposite transparent electrodes based on Aluminum doped Zinc Oxide (ZnO:AI) thin films and silver nanowire (AgNW) networks. The electrodes are fully fabricated by low-cost, open-air techniques, namely, atmospheric pressure spatial atomic layer deposition and spray coating. We show that the transparency and the conductivity of the ZnO:AI/AgNW nanocomposites can be tuned by controlling the AgNW network density. We also demonstrate that the thermal, electrical and mechanical stabilities of the composites are superior to those of AgNW networks or ZnO:AI thin films separately. We have also developed a theoretical model to explain the relationship between the conductivity of the composites and the AgNW network density. Our results provide a means to predicting the physical properties of such nanocomposites for applications in solar cells and other optoelectronic devices. Finally, the deposition methods used open the way towards stable, low-cost flexible and transparent electrodes for industrial application.

AA4-TuP10 Nanomechanical Properties of Crystalline Anatase Titanium Oxide Films Synthesized using Atomic Layer Deposition, Yousuf Mohammed, R. Lin, K. Zhang, H. Boungart, A. Elmusto, Old Dominion University

Titanium dioxide (TiO2) thin films have received significant attention due to their remarkable biocompatibility, stability, nontoxicity, and excellent photocatalytic properties. TiO2 films are used in artificial heart valves, photocatalyst in solar cells. The photocatalytic activity of titanium dioxide is exhibited in both the anatase and the rutile phases. Likewise, the photocatalytic properties of TiO2 thin film coatings are noticeable in medical applications in bacterialic coatings of wound care gauze or in coatings of surgical instruments to be sterilized and for antimicrobial surfaces in hospitals. Fabrication of TiO2 films has intensified in the last two decades due to their notable optical and electronic properties and their excellent potential applications for gas sensing. Another application for anatase TiO2 in photovoltaics, when their team realized impressive photovoltaic performance advances with perovskite TiO2 heterojunction solar cells, which were fabricated with pure phase anatase TiO2 nanosheets with dominant (001) facets serving as the electron collector.

Several deposition techniques have been used in the past to deposit TiO2 films on silicon substrates, including reactive DC sputtering, RF magnetron sputtering, focused ion beam Induction, chemical vapor deposition, atomic layer deposition, chemical vapor deposition, mist CVD and the atomic layer deposition (ALD). The ALD has emerged as a modern chemical reaction based technique to deposit monolayers of inorganic compounds. ALD possesses unique film deposition uniformity and exact composition control with atomic precision and absolute conformity. Crystalline TiO2 films of 500 nm thickness were synthesized using ALD on p-type Si (100) substrates. The crystal structures of the TiO2 thin films were characterized by the X-ray diffraction (XRD). The film thickness and surface morphology were inspected using field emission scanning electron microscopy (FE-SEM) and AFM. The nanomechanical properties were measured using a nanodenter equipped with a three-sided Berkovich diamond tip to evaluate the hardness and modulus of the TiO2 thin films. Due to low temperature ALD deposition, the X-ray diffraction revealed a single phase TiO2 anatase growth and the FE-SEM images indicate columnar grain structure growth with primarily vertical directions of the polycrystalline TiO2 films. The measured hardness of the anatase ALD TiO2 films at 20% film thickness has been measured as 5 Gpa, which is considerably softer compared to the reported benchmark values of the better-known rutile phase of ~ 12 Gpa. The elastic modulus of the TiO2 thin films was estimated as 138 and 145 Gpa.

AA4-TuP11 Encapsulation of Magnetic Nanostructures by ALD for Improved Stability and Performance, Devika Choudhury, Y. Zhang, K. Gao, A. Mane, J.W. Elam, Argonne National Laboratory

Morphology of magnetic nanoparticles is an important aspect responsible for controlling the optical, electrical and magnetic properties. Their interesting shapes and sizes result in novel properties significantly different from their bulk counterparts. For example, 1D magnetic nanostructures often exhibit significantly modified properties and enhanced coercivity as compared to the bulk magnets thus making them attractive for wide range of applications. These materials are not only extensively used in high-density magnetic data-storage mediums, magnetic sensors and spintronic devices, but also suitable for valuable biomedical applications as well.

Metal alloys such as PtCo, SmCo, FeNi and FeCo are well known for their magnetic properties such magnetization values obtained from SQUID measurements.

Atomic Layer Deposition (ALD) has emerged as one of the most widely accepted techniques to provide conformal coating of controlled thickness on high aspect ratio microstructures, and a popular method for encapsulation of various type of microstructures. In this work, we report the coating of magnetic metallic alloys using ALD method to improve stability and performance of the nanostructures. Different chemistries are used for the deposition of a variety of protecting layers. Comparison on the effectiveness of the coatings are drawn from the stability and their magnetic properties such magnetic saturation values obtained from SQUID measurements.


The decreasing feature sizes and increasing aspect ratios in semiconductor process flows have imposed stringent requirements on the physical and electrical properties of metal-to-semiconductor interfaces. This has resulted in fundamental material challenges for low-resistance contacts and ultra-thin diffusion-barrier films. Physical vapor deposition (PVD) based TiN film is a widely used diffusion barrier layer. However, deposition of ultra-thin TiN exhibits pronounced islanding which leads to rough film with polycrystalline grain structure. Furthermore, inhomogeneities due to grain boundaries offer diffusion pathways and lead to device degradation. In the current study, we present our findings on the diffusion barrier properties of amorphous ternary alloy films composed of Ti, Si and N (TiSIN), an excellent alternative to TiN films. These films were grown using Atomic Layer Deposition (ALD) technique on the Eugeusen 300mm QXP commercial mini-
batch reactor. In one set of experiments, TiSiN films were deposited on highly-doped polycrystalline Si:B films followed by diffusion studies of boron. In another set of experiments, fluorine precursor based CVD WSi2 film was deposited on TiSiN, followed by diffusion studies of fluorine. Secondary Ion Mass Spectrometry (SIMS) and High-resolution electron energy loss spectroscopy (HREELS) were utilized to detect the effectiveness of the barrier film to prevent boron and fluorine diffusion.

**ALD Applications**

**Emerging Applications Poster Session**

**AA5-TuP1 Bottom up Stabilization of Perovskite Quantum Dots LED via Atomic Layer Deposition, Rong Chen, K. Cao, X. Xiong, B. Zhou, Huazhong University of Science and Technology, China**

Flexible displays are becoming the most promising and attractive techniques in the future. Quantum dots(QDs) have attracted great attention due to their excellent optical properties, such as tunable wavelength, narrow emission, long carrier diffusion length, and high photoluminescence quantum efficiency. These properties make QDs the most promising optical materials for flexible displays. However, as the instability of QDs based light emitting diodes limits their practical applications, QDs based LEDs are still under laboratory developments.

In this talk, we will discuss ALD based protection approaches from the nano scale QDs passivation to macroscopic encapsulation to improve the stability and boost its performance of QD-LEDs. First, the low-temperature selective ALD method has been developed for defects elimination. This protection method can preserve QDs monomers without damaging surface ligands and improving the quantum efficiency. For the QD light emitting layers, voids are formed during the stacking which may induce instability from electric, heat transfer. The ALD based filling process has been developed to improve charge transport within the layer. To study the surface interaction mechanisms of ALD precursors with the QDs layers, in-situ characterizations such as quartz crystal microbalance (QCM), infrared spectrometer (IR) are utilized to monitor the ALD process and the interactions with QDs layers. The oxides filling between quantum dots could reduce the carrier transport barrier and enhance carrier injection. Finally, it is imperative to develop efficient and ultrathin encapsulation to improve the stability towards ambient environments and flexibility of displays. Ultrathin multi-stacking films are designed and fabricated based on the combination of spatial ALD, molecule layer deposition and chemical vapor deposition. Such composite films could greatly enhance the water and oxygen resistance, while retain low stress and flexibility of the devices. It has demonstrated that the ALD approaches are versatile and useful for several fabrication steps in flexible QDs displays.


X-ray-emitting devices require a window transparent to low energy X-rays while keeping the device at vacuum. Polycrystalline Be windows are often used since they have high X-ray transparency due to the low atomic number of Be. However, Be is sensitive to environmental moisture and shows degradation over time via two routes. Firstly, ambient gas can penetrate the Be window through the crystalline grain boundaries deteriorating the vacuum. Secondly, water vapor reacts with Be material causing corrosion and forming an oxide layer which can delaminate and reduce the window thickness over time. The window can become so thin that it can no longer hold a vacuum inside the X-ray device — effectively ending the lifetime of the tube. Here, we show how the application of conformal, pinhole-free ALD bilayer coatings can extend the lifetime of X-ray windows more than five times with negligible influence on X-ray transmittance.

We have developed and patented (US20180061608A1) a robust solution using a combination of Al2O3 and TiO2 less than 200 nm in thickness. The ALD coatings were deposited in an Oxford Instruments Plasma Technology FlexAL™ system at 350 °C. Thermal Al2O3 (~40 nm) was used as an adhesion layer, followed by in-situ deposition of thermal TiO2 (~80 nm) as a harder, protective layer, using trimethylaluminum and tetraakis(dimethylamino) titanium, respectively. The relatively low atomic numbers of Al and Ti mean that the maximum allowed film thickness to maintain clarity of the X-ray spectra is 800-1000 nm, which is much higher than the used thickness. This window coating is an effective moisture barrier and attenuates the transmitting X-rays by less than 5 % compared to the attenuation of an uncoated window. Importantly, the ALD coating does not contaminate the output X-ray spectra. No fluorescence contamination of Al and Ti could be detected. The lifetimes of ALD coated windows were compared with that of uncoated window by determining how long they could sustain ultra-high vacuum. For all sixteen coated samples, the windows survived the test at least 5 times longer and, in many cases, >15 times longer.

The ALD coating of the X-ray windows increases lifetime of X-ray emitting equipment by more than five times minimising specialist maintenance. The excellent conformality of ALD is furthermore expected to help close off grain boundaries present in the Be windows which can be up to 100 nm deep and could otherwise be pathways for gas diffusion into the vacuum of the system. Future options include making the coating conductive as a further advantage for X-ray equipment.

**AA5-TuP3 ALD for 3D Nano MEMS Applications, Dorothee Dietz, Fraunhofer Institute for Microelectronic Circuits and Systems IME, Germany**

In the area of MEMS and nano sensor structures, the ALD becomes ever more important. Because of the highly isotropic and highly conformal deposition method, ALD is the best choice for structures with large aspect ratios or structures with complex cross sections. Moreover it is possible to deposit several different materials in the same tool, so that the functionality of the material can be tuned by stacks or doping as good as possible. Because of the low deposition temperature, ALD can be applied in post-CMOS-processes.

ALD techniques enable the fabrication of free standing 3D structures as follows: In a first step, a sacrificial layer is deposited onto a (CMOS-) substrate. Small holes or trenches are etched through it as pillars and an ALD layer is deposited and structured. In the end, the sacrificial layer is removed. This technique can be used e.g. for the processing of different gas sensors or for realizing 3D multi electrode arrays (MEA).

The first type of gas sensor, which is based on conductometric semiconductor gas sensing, operates with metal oxide (MOx) nanowires, 350 nm in width and 150 μm in length. The metal oxide (e.g. ZnO or SnO2) is used as the functional layer but also for forming the 3D structure. Because the metal oxides need to be heated for gas sensitivity, a heater is realized with the same technology as described above. In this case, Ru, TiN or TiAlCN, is used as heater material, deposited also by ALD.

The second gas sensor is acting as a nano pellistor. The heater has to be a free standing 3D structure, because the sensor has to be thermally decoupled from the substrate underneath. All materials are deposited with ALD to achieve the high aspect ratio and because of the material properties. The heater consists of Ru, the surrounding isolation layer can be Al2O3 and the catalytic layer is made of Ru again.

To increase the sensitivity of the sensor, the surface of the catalyst can be increased by using a porous Al2O3 layer instead of a solid one. A porous Al2O3 layer can be achieved by doping it during the ALD in a first step e.g. with ZnO and by a selective etching of the doping material in a second step.

Another application for using this technology is processing 3D MEA. They can penetrate biological cell membranes for measuring intracellular electrical signals directly. As a conductive and biocompatible material, Ru is used for these electrodes. They are 200 nm in diameter and a few microns in height. With an additional step, the diameter at the tips can be reduced so that they can penetrate membranes easier, without the risk of destroying them.

**AA5-TuP4 Tribological Properties of Plasma Enhanced Atomic Layer Deposition TiMoN, Mark Sowa, Veeeco-CNT; A. Kozen, U.S. Naval Research Laboratory; B. Krick, N. Strandwitz, Lehigh University**

In our previous study, we demonstrated a tertiary plasma enhanced atomic layer deposited transition metal nitride (TiVN) with exceptional wear rates and friction coefficients. We have extended that work with an investigation of another tertiary transition metal nitride system, TiMoN. For films deposited at 250°C and 300W on a Veeeco CNT G2 Fiji PEALD system, we have demonstrated how the ratio of Ti:Mo:N cycles (1:0, 3:1, 1:1, 1:3, 0:1) provides linear control of the Ti:Mo in the resulting film. Through application of an 13.56MHz RF substrate bias (0-250V) during the plasma step, ion bombardment energy of the substrate can be varied, providing a means for tweaking the films physical and chemical characteristics which in turn are shown to impact the resulting film’s tribological properties. As PEALD metal nitrides have broader interest than wear layers and to gain insights on the interrelationships of the mechanical properties, the...
AAS-TuP5 Thickness Optimization of Alumina Thin Film for Microchannel Plate Detector. Boaqun Yan, S. Liu, Institute of High Energy Physics, Chinese Academy of Sciences, China
Conventional lead glass microchannel plate (MCP) detector has been used in a variety of applications. The MCP performance can be improved by coating high secondary electron emissive layers, such as alumina (Al₂O₃) and magnesium oxide (MgO), via atomic layer deposition (ALD). In this poster, the alumina thin films with varied thicknesses were deposited by ALD on polished Si substrates and MCPs, respectively. The secondary electron yield (SEY) of the alumina thin films on silicon substrate were measured by using electron beam. The MCPs used in our experiment had a high length to diameter ratio ~80:1 and worked in photon counting mode. The optimal thickness of alumina was obtained through comparative study the MCP performance before and after coating. In addition, the DC gain variation as a function of total charge per unit area Q (C/cm²) were investigated.

AA-TuP6 Optical Coatings Deposited on Nonlinear Crystals by Atomic Layer Deposition. Ramotis Drazdys, R. Buzely, M. Drazdys, Center for Vacuum Physics, Faculty of Physics, University of Warmia and Mazury, Olsztyn, Poland
Growing requirements for optical coatings deposited on temperature and environment sensitive crystals force to look for alternatives to conventional physical vapor deposition technologies. KDP, DKDP, LiNBO₃ are nonlinear optical materials that have been difficult to coat due to specifics of surface adhesion and thermal properties. Atomic layer deposition (ALD) is widely used in nanotechnology and semiconductor devices [1] and recently attracted more interest in manufacturing of optical components [2,3]. The main goal of our research was to develop antireflection (AR) coatings on nonlinear crystals with high laser-induced damage threshold (UDD) HfO₂ and Al₂O₃ thin layers deposited using TDMAH and TMA precursors and H₂O as oxidant by Savannah 200 system from Ultratech at low temperature (<100 °C). UDD experiments were performed, Experimental deposition processes of HfO₂- and Al₂O₃-thick layers 150 nm thickness single layers were made at temperatures from 40°C to 100°C with different pulse and purge time duration parameters. To prevent the HfO₂ layer crystallinity we used the nanolaminate concept [4] where each HfO₂ layer with thickness of 20 nm incorporated a certain number of Al₂O₃ monolayers. Growth rates, dependency on precursor pulse and chamber purge durations were determined by using quartz crystal monitoring and optical spectrums data. Reflective index and absorption dispersions were determined. Setup with the Nd:YAG laser (from EKSPLA co.) generating pulses with repetition rate 15 Hz, pulse duration ~2 ns was used for UDD measurements. The investigation of the optical transmission and reflection of produced-thin layers allowed to determine optical losses in UV region. These results gave us the possibility to choose optimal technological parameters for AR-coating formation on nonlinear crystal substrates. The following design of experimental AR coating was selected: substrate / 75nm HfO₂ / 200nm Al₂O₃. In previous investigations determined growth rates per pulse cycle were used for layers thickness control. The same coating design was used to manufacture AR coatings by IBS and e-beam evaporation. The UDD measurements of AR coatings demonstrated comparable or higher damage levels for ALD coatings.


AAS-TuP7 Atomic Layer Deposition of Nickel and Nickel Oxide Thin-Films for Astronomical X-ray Optics Applications. Hossein Salami, A. Uy, A. Vadapalli, University of Maryland; V. Dwivedi, NASA Goddard Space Flight Center; R. Adamowits, University of Maryland
Nickel and nickel oxide films have optical, electrical and magnetic properties that when combined with good chemical stability makes them attractive for many applications. Nickel oxide is a p-type semiconductor that can be used as a transparent electrode, or in manufacturing nonvolatile resistance random access memories, or for chemical sensing purposes. In its pure form, nickel film can be used as adhesion layer for copper interconnects [1]. Because of its X-ray reflecting property, another application of pure nickel film is in multi layer coatings for X-ray optics [2,3].

In this talk, we will discuss atomic layer deposition process for Ni and NiO thin-films using two different metal precursors, nickelocene and nickel acetylacetonate, in combination with ozone as the oxygen source. We will present two different routes to depositing metallic Ni: direct metal deposition or metal-oxide deposition with a subsequent reduction step. Our initial results confirm the deposition of NiO film and its reduction using molecular hydrogen predicted by thermodynamic analysis. Advantages of each route and their effect on the properties of the final product will be presented. Furthermore, specifically for astronomical applications, roughness and X-ray reflectivity of the prepared thin-films and the conformal coating of high aspect-ratio X-ray optics will be discussed in detail.


Zirconium boride is an attractive material for microelectronic, hard coating, and other applications. Because, it has high melting point (3040 °C), a high mechanical hardness, excellent wear properties, and excellent corrosion resistance toward molten metals [1]. In this work, we talk about new applications of ZrBₓ for new work function, barrier metal, hard mask and area selective deposition (ASD). ZrBₓ film have been deposited both by sputtering and chemical vapor deposition (CVD) routes. An inherent shortcoming of sputtering is its non-conformal nature. In conventional CVD of ZrBₓ, films, the ZrClₓ and BClₓ precursors are reduced with H₂, but the incorporation of residual chlorine atom has proven to be detrimental to film properties. In addition, thermal atomic layer deposition (ALD) was not studied in detail [2,3]. In this study, ZrBₓ films have been deposited by thermal ALD and CVD process using single precursor Zr(BH₄)ₓ for new work function, barrier metal, hard mask and ASD. The work function of deposited ZrBₓ film by ALD at 250 to 350 Å is 3.93 to 3.96 in the bulk and 3.86 to 3.64 in the surface respectively (Fig. 1). The step coverage was showed 100 % in aspect ratio 19:1 pattern at 250 Å(Fig. 2). The resistivity of ZrBₓ film was about 450 µΩ cm and showed amorphous structure.

The deposited ZrBₓ film on Si(100) by CVD is sufficient to prevent copper diffusion into silicon during a 600 °C anneal for 30 min (Fig. 3, 4). The ZrBₓ film on SiO₂ by CVD has a very slow etch rate for CF₃, while a very fast etch rate for BCl₃ (Fig. 5). The wet etch was not showed in 0.5% HF solution (Fig. 5). The ZrBₓ film has resistance to oxygen. ASD of Zr(BH₄)ₓ was showed selectivity of W metal and SiO₂ substrate for ZrBₓ film (Fig. 6). The deposited ZrBₓ films were showed amorphous phase. The possibility of applying a new work function, barrier metal, hard mask and ASD is expected.


AAS-TuP9: Comparative Study of Mo, W, S, Alloy Gas Sensor by Atomic Layer Deposition. Minjoo Lee, Y. Kim, J. Dark, H. Kim, Yonsei University, Republic of Korea
Two-dimensional (2D) Transition metal dichalcogenides (TMDCs) are a layered structure, which stacked via weak van der Waals interactions. 2D TMDCs have attracted great attention because of their remarkable electronic and optoelectronic properties such as indirect-to-direct bandgap transition with reducing layers, superior electrical properties and strong spin-orbit coupling. Furthermore, recently the 2D TMDCs have shown the potential as a gas sensing material due to their very large surface-to-volume ratio, semiconducting property, and low-power consumption. Thus, Tuesday Evening Poster Sessions, July 23, 2019 127
the WS₂ or MoS₂, that is one of the most popular 2D materials has been studied for its gas sensing properties and demonstrated an excellent response to various gas molecules, such as nitrogen dioxide (NO₂), ammonia (NH₃), acetone, etc. However, due to the difficulty of uniform synthesis of 2D TMDC's and the highly sensitive characteristic of these 2D-gas sensors, there are few researches about direct comparative study of such materials. Although only a theoretically calculated study on the lateral heterostructures of dielectrics were reported, the result is often different according to adapted model.

In this study, layer controlled 2D MoS₂ and WS₂, synthesized with Mo(CO)₆ and W(CO)₆ as precursors and a reactant using ALD in situ. Ultrathin films of MoS₂ and WS₂ were fabricated with multiple patterning and etching steps to achieve area-selective deposition. Compositional and property differences between conformal ALD-deposited MoS₂ and WS₂ alloys using ALD super-cycle and confirmed that composition in alloys can be controlled by changing super-cycle configuration. Synthesized 2D TMDC's were fabricated for gas sensors for comparison of gas sensing property and showed different response and response time according to composition in alloy.


High-aspect-ratio gold gratings have broad applications in x-ray optics, and their quality and aspect ratio strongly affect the quality of the generated images. To fabricate the gratings, two key technological challenges must be addressed: (i) creating a high-aspect-ratio trenches with smooth vertical walls, and (ii) filling the trenches uniformly with gold.

We report fabrication of 450 nm half-pitch gold gratings with an aspect ratio of 26 using laser interference lithography (LIL), reactive etching (RIE), atomic layer deposition (ALD), and gold electroplating techniques. In the first step, gratings are patterned on the resist/chromium coated silicon wafer via LIL. Then, the chromium, which served as a hard mask for silicon etching is etched using RIE. This step is followed by cryogenic RIE to create deep trenches in silicon. Then, a platinum seed layer is deposited by ALD, and finally the mold is electroplated with gold.

RIE of high-aspect-ratio dense and narrow trench/wall structures of gratings imposes significantly more difficulties than the etching of isolated narrow lines or trenches, since the undercut and the negative taper can damage the thin walls. High-aspect-ratio nanoscale silicon gratings were obtained by carefully tuning all etching parameters (Figure 1a).

A continuous, conductive and conformal seed layer is essential for uniform electroplating. We performed ALD of platinum as a seed layer. To improve platinum adherence, a 10 nm alumina adhesion layer was deposited by ALD as well. The high-exposure platinum ALD was optimized to assure conformal coating of the high-aspect-ratio trenches. The nanometric trenches were filled with gold via conformal electroplating, when plating occurred from all surfaces. The method has an advantage of much shorter electroplating time, compare to bottom-up plating technique. However, it is challenging to avoid voids formation due to premature trench sealing, and achieve uniform plating over the entire trench depth because of the gold ions depletion inside the narrow and deep trenches (Figure 1b).

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Area Selective ALD

Evergreen Ballroom & Foyer - Session AS-TuP

Area Selective ALD Poster Session

AS-TuP1 Laterally-Structured Dielectrics by Area-Selective Atomic-Layer-Deposition on 3D Substrates, Philip Klement, D. Anders, F. Michel, J. Schörmann, S. Chatterjee, Justus Liebig University Giessen, Germany

Industrial semiconductor fabrication combines lithography, etching, and deposition processes to create electronic devices. The quest for miniaturization of those devices has led to complex fabrication processes with multiple patterning and etching steps to achieve area-selective deposition. However, with conventional top-down fabrication reaching its limits in patterning resolution and alignment, a tool for bottom-up processing in advanced technology must deposit different combinations of materials area-selectively. Atomic-layer-deposition (ALD) is a technique for depositing high-quality, ultrathin films of dielectrics with the potential of area-selective deposition. It could reduce the number of manufacturing steps and allow for continued miniaturization, yet no area-selective deposition of lateral heterostructures has been realized.

Here, we show the successful direct patterned deposition of TiO₂ on complex SiO₂ substrates creating smooth surfaces of alternating dielectrics. Our approach demonstrates area-selective deposition on three-dimensional substrates, and we identify factors to consider that are not present in area-selective deposition on conventional two-dimensional substrates. We use a combination of electron beam lithography using a polymer mask, ion beam etching, plasma treatment, and ALD similar to established semiconductor fabrication processes to realize lateral heterostructures of dielectrics. Several process parameters were varied, and their effect on the resulting structure was investigated by atomic force microscopy, scanning electron microscopy, and X-ray photoelectron spectroscopy. We investigated different polymer mask surfaces and precursor diffusion in terms of area-selective deposition, and found that a number of factors must be considered in design, patterning, and deposition to achieve reproducible results. Our work enables the realization of lateral heterostructures of dielectrics as building blocks for advanced technology applications.

AS-TuP2 Area-specific ALD Poster Session

Plasmonic Nanoantennas, Chengwu Zhang, T. Gao, B. Willis, University of Connecticut

Plasmonic nanoantennas, especially with gaps less than 10 nm, can greatly enhance electric fields through excitations of surface plasmons, which are collective oscillations of electrons excited by light. Arrays of plasmonic nanoantennas can be designed to concentrate and manipulate light at the nanoscale, and have wide applications such as surface enhanced spectroscopy, photo-driven chemical conversion, and optical information processing. Atomic layer deposition (ALD) is a thin-film deposition technique capable of producing conformal thin films with precise control of thickness and composition at the atomic level. Area selective ALD provides a way to precisely tune nanogaps to enhance their optical and electronic properties. The optical properties of plasmonic nanostructures offer the possibility to enhance selective growth through resonant excitations. In this work, we investigate the effect of light in area selective ALD on plasmonic nanoantennas.

We present a case study of Cu-area selective ALD on Pd nanoantennas. The sizes of antenna dimers range from 25 nm to 200 nm, with 20 nm gaps. The gaps are measured and compared before and after thermal ALD with and without light irradiation. Results show GPC (growth per cycle) is enhanced at lower temperatures using irradiation, which yields better selectivity. As an example, for nanoantennas with lengths of 75 nm and widths of 25 nm, ALD growth at 150° with light yields almost the same GPC as 230° without light. Compared with thermal ALD, only 1/3 number of cycles are required for the same growth with irradiation. Using various nanoantenna designs and array configurations, we analyze the role that plasmonic heating or hot electrons may contribute to the enhanced growth.

AS-TuP3 Area-Specific Atomic Layer Deposition (ALD) of Cobalt As Mediated by Thermally Induced Dehydrocoupled Self-Assembled Monolayers (SAMs), Barry Arkles, I. Goff, C. Brick, Gelest, Inc.; A. Kaloyeros, SUNY Polytechnic Institute

Organic trihydroxilanes can provide an elegant route for generating self-assembled monolayers (SAMs) by vapor phase transport on a variety of substrates. Under mild conditions, these precursors can be made to interact with a variety of clean metal and hydrogenated metalloids surfaces, including those of interest for nanoscale integrated circuitry (IC) applications, such as titanium, copper, and silicon, to form near-zero-thickness SAMs. As shown in the figure below, the resulting SAMs can be customized with specific functionality (depending on the choice of the R substituent) to activate or deactivate subsequent ALD Co on the underlying substrate of choice, leading to area-specific Co deposition. In this work, negative and positive ALD Co protocols under low substrate temperature conditions will be presented and fabricated.

AS-TuP4 Investigation of In-situ Surface Cleaning of Cu Films using O₃/O₂ and NH₃, Su Min Huang, A.L.N. Kondusamy, Q. Zhiyang, H.S. Kim, L.F. Peña, K. Tan, J. Veyan, University of Texas at Dallas; D. Alvarez, J. Spiegelman, RASIRC; J. Kim, University of Texas at Dallas

Copper is widely used in semiconductors as interconnects due to its low resistivity, high resistance to electromigration, low temperature coefficient of resistances, and good thermal stability. Recent demonstration of atomic layer deposition (ALD) of Cu thin films is expected to overcome the limitations of the PVD process and could be used to deposit a highly conformal film over high-aspect ratio structures with precise thickness control. Several processes on ALD Cu have been reported requiring an additional reduction step to obtain metallic Cu. Therefore, it is imperative
to explore reducing agents capable of reducing the oxide on Cu at low temperatures. Among the various available reducing agents, N\textsubscript{2}H\textsubscript{4} (Hydrazine) can be used in the reduction of copper oxide due to its higher reduction capability.\textsuperscript{1} Inspired by Hydrazine’s unique characteristics, we explore the feasibility of vapor-phase reduction of copper oxide using N\textsubscript{2}H\textsubscript{4} to achieve an ideal metallic Cu film in an ALD environment. Additionally, a detailed in-situ surface analysis of the reduction with N\textsubscript{2}H\textsubscript{4} has not been reported yet.

In this work, Cu samples were oxidized using an O\textsubscript{2}/O\textsubscript{3} mixture, followed by N\textsubscript{2}H\textsubscript{4} using a rapid thermal ALD system to investigate the reduction effectiveness of N\textsubscript{2}H\textsubscript{4}. From the XPS analysis, Cu samples treated with O\textsubscript{2}/O\textsubscript{3} showed the diffusion of oxygen into the sample and the formation of Cu\textsubscript{2}O layer that is approximately 4 nm thick. With N\textsubscript{2}H\textsubscript{4} treatment, a significant amount of copper oxide was reduced to metallic copper with approximate thickness of 1 nm, the comparable reduction capability of N\textsubscript{2}H\textsubscript{4} agent. In addition, in-situ reflection absorption infrared spectroscopy (RAIRS) was employed to elucidate the individual surface chemistry of copper films during the oxidation (O\textsubscript{2}/O\textsubscript{3}) and reduction (N\textsubscript{2}H\textsubscript{4}) step. The detailed experimental results will be presented.

This work is partially supported by Basirc Inc. by providing N\textsubscript{2}H\textsubscript{4}. We also acknowledge TMEIC (Toshiba Mitsubishi-Electric Industrial Systems Corporation) for providing the O\textsubscript{3} generator.

\textsuperscript{1}P. Poodt et al., \textit{P. Poodt et al.}, 10.1007/s10681-014-9883-z (2014). 

\textbf{AS-TuP5 Area-Selective Deposition of SiO\textsubscript{2} based on Spatial ALD with Interleaved Etching Steps to Obtain High Selectivity, Alfredo Mamell, TNO/Holst Center, Netherlands; F. Rozeboom, Eindhoven University of Technology and TNO, Netherlands; P. Poodt, TNO/Holst Center, Netherlands}

Area-selective atomic layer deposition (AS-ALD) has been envisioned as a potential technological solution for advanced patterning. However, the selectivity that can be obtained is often very limited and the throughput of most AS-ALD methods is low, which hampers its industrial acceptance.\textsuperscript{1,2} In this work, we present a process for AS-ALD of SiO\textsubscript{2} using intermitting plasma etching steps to obtain high selectivity.\textsuperscript{3} At the same time, the deposition process itself is performed in a spatial ALD mode at atmospheric pressure that allows for achieving high throughput.\textsuperscript{4} AS-ALD of SiO\textsubscript{2} on a pre-patterned substrate with SiO\textsubscript{2} and ZnO was demonstrated using a chemoselective inhibitor that chemisorbs preferentially on the non-growth area (ZnO) while it allows for depositing SiO\textsubscript{2} on the growth area (SiO\textsubscript{2}). In order to obtain high selectivity, a blanket fluorocarbon plasma etching step was interleaved after every 110 ALD cycles. This way, up to ~30 nm-thick selective SiO\textsubscript{2} deposition was demonstrated, as shown in Figure 1 of the supplemental PDF file. Furthermore, X-ray photoelectron spectroscopy was carried out to verify the selectivity of the process. No Si was detected on the non-growth area, demonstrating the high selectivity of this process.

The process presented in this work combines selective inhibitor chemisorption, plasma-based spatial ALD at high deposition rates and plasma etch-back steps to correct for selectivity loss. Being compatible with roll-to-roll and sheet-to-sheet concepts, this approach can enable high-throughput AS-ALD on large-area and flexible substrates as well.

\textsuperscript{1}A. Mamell et al., ACS Nano, 2017, 11, 9303-93 
\textsuperscript{2}F.S.M. Hashemi et al., ACS Nano, 2015, 9, 8710-8717 
\textsuperscript{3}R. Vallat et al., JVSTA, 2017, 35, 01B104 
\textsuperscript{4}P. Poodt et al. JVSTA, 2012, 30, 01B022(1-10)

\textbf{AS-TuP6 Defect Mitigation Solution for Ru on TiN/SiO\textsubscript{2} Nanopatterns, J. Soethoudt, K.U. Leuven – University of Leuven/IMEC, Belgium; F. Grillo, ETH Zurich, Switzerland; E. Marques, R. van Ommeren, Delft University of Technology, Netherlands; B. Briggs, H. Hody, V. Spampinato, P. Poodt, B.T. Chan, J. Macak, University of Pardubice, Czech Republic}

Area-Selective Deposition (ASD) receives increasing attention as a bottom-up approach for nano patterning. Implementation of ASD is however limited by undesired particle growth on the non-growth surface. This work provides a demonstration of defect mitigation strategies based on insight into the particle growth mechanism on the non-growth surface. Ru is selectively deposited by 1-(ethylbenzyl)-1,4-ethyliclohexadienyl) ruthenium (EBECHRu) and oxygen atomic layer deposition on TiN/SiO\textsubscript{2} nanopatterns pretreated with dimethylamino-trimethylsilylane. This material system is relevant for a tone inversion patterning application, where a hard material (Ru) is selectively deposited inside holes in a soft material (SiO\textsubscript{2}) which is more straightforward than patterning the hard material directly.\textsuperscript{1} Ru films are selectively deposited on TiN, while particle growth of Ru is observed on dielectrics (Figure 1a). The thickness of the selectively deposited Ru layer on TiN is independent of feature dimensions in the entire investigated size range of 90µm-25nm (Figure 1b). We propose two strategies to mitigate defectivity based on the first stages of EBECHRu/O\textsubscript{2} growth on dielectrics. Initially, the Ru particles are too small to catalytically dissociate oxygen, thereby suppressing direct deposition on the particles.\textsuperscript{1} Ru particles at first grow only through surface diffusion and coalescence until they reach a sufficient size for catalytic O\textsubscript{2} dissociation, at which point the particles start to rapidly grow through direct deposition on the particles. A first defect mitigation strategy employs the initial growth regime in which particles are smaller compared to the ASD-grown film. During this regime, the particles can be fully etched with limited thickness reduction of the ASD Ru layer.

The discovery and success of graphene paved the way for developing two-dimensional materials with outstanding properties.\textsuperscript{1} In particular, monolayers of two-dimensional transition metal dichalcogenides (2D TMDCs) possess a direct band gap\textsuperscript{2} that is crucial for optoelectronic applications. Additionally, the direct band gap can be easily tuned by either chemical composition or external stimuli. In parallel to monolayer TMDCs structures, a high surface area layer of TMDCs flakes shows promising properties for hydrogen evolution\textsuperscript{3}, photodegradation of organic dyes\textsuperscript{4} or as electrodes in Li ion batteries\textsuperscript{5}.

To date, various top-down (e.g. exfoliation) and bottom-up techniques, such as chemical vapor deposition (CVD) and atomic layer deposition (ALD) have been reported for the preparation of 2D-TMDCs\textsuperscript{1}. However, ALD is the only technique enabling sub-nanometer thickness control, which is revealed as a crucial factor in the properties of 2D TMDCs materials. In the last years, it has been reported the possibility to employ ALD as a technique to grow MoS\textsubscript{2}, which has been extensively studied for many different applications. In these works (CH\textsubscript{3})\textsubscript{2}S\textsubscript{2}[6] or H\textsubscript{2}S[7, 8] were used as the S precursor and MoCl\textsubscript{5} or Mo(CO)\textsubscript{6}, respectively, as the Mo precursors. Further, important efforts have also been devoted to attain the ALD fabrication of MoSe\textsubscript{2}, since it possesses higher electrical conductivity than MoS\textsubscript{2}[9, 10]. Recently, we have shown that ALD deposition of MoSe\textsubscript{2} or MoO-S-Te [12] is feasible using (CH\textsubscript{3})\textsubscript{2}S\textsubscript{2} as the Se precursor and MoCl\textsubscript{5} or Mo(thd)\textsubscript{4} as the Mo precursors.

The presentation will focus on the synthesis of MoSe\textsubscript{2} and MoS\textsubscript{2} by ALD, their characterization and applications in various fields. Experimental details and some recent photocatalytic, battery and hydrogen evolution results will be presented and discussed.
performance. The FET on/off ratio was about ~10^4 with decent mobility. To understand and overcome these obstacles, we examine NPs coated in a hexamethyldisilathiane (HMDST) were used as ALD precursors to deposit MoO3 film by plasma enhanced ALD followed by sulfurization in a reactor with two agitation modes, rotation and vibration. We analyze high-speed videos of NP motion while varying agitation parameters (velocity, frequency, timing) as well as NP material and size. After pALD, we weigh the coated powders and study core-shell NP composition and morphology via TEM and N2 adsorption measurements.

**NS-TuP5 Density Function Theory for Nucleation of MoF6 with Oxide Surfaces in Atomic Layer Deposition of MoS2, Matthew Lawson, Boise State University**

Several two-dimensional (2D) atomic-layered transition metal dichalcogenides (TMDs) are of great interest for electronic and optoelectronic applications due to their wide direct band gaps for few layer materials. Beyond mechanical or liquid exfoliation of bulk materials, high quality 2D TMDs have been grown via chemical vapor deposition (CVD) but growth is typically performed at high temperatures. Several studies have reported atomic layer deposition (ALD) of thin TMD films at lower temperatures, but as-deposited films are typically amorphous our nanocrystalline. Complementary to *in-situ* experimental studies of the growth and nucleation of nanoscale films, we have employed density functional theory (DFT) to understand the nuanced interactions during precursor nucleation. Hydroxyl groups are commonly found on metal oxide surfaces and play an important role during many ALD processes. To develop a deeper understanding of the ALD of MoS2 from MoF6 and H2S, we studied the reactivity of MoF6 with three substrates: Al2O3, MgO, and HfO2 without hydroxyls and fully saturated with hydroxyls using DFT. We calculated the electronic distribution of the surfaces, how the electronic structures changed with single MoF6 precursors, and calculated the valence electron transfer. Our calculations support the important role of hydroxyls in the nucleation of MoF6 with oxide surface and provide insight into the formation of precursor bonds at the surface.

**NS-TuP3 ALD-based Synthesis of Few-layer Transition Metal Disulfides with Wafer-scale Uniformity for Device Integration, Tao Chen, Y. Wang, H. Zhu, L. Chen, Q.Q. Sun, D.W. Zhang, Fudan University, China**

Different transition metal disulfides (TMDs) ultra-thin films with wafer-scale uniformity have been successfully synthesized by ALD-based process. Two growth routes have been developed: sulfurizing transition metal oxides deposited by ALD, and annealing amorphous TMD films deposited by ALD. Molybdenum hexacarbonyl and ozone were used as precursors to deposit MoO3 film by plasma enhanced ALD followed by sulfurization in a tube furnace to form MoS2 TMD films. Tungsten hexachloride and hexamethyldisilathiane (HMDST) were used as ALD precursors to deposit WS2 films which were further annealed at high temperature to improve crystallinity. Both approaches can produce high-quality and thickness-controllable TMD films with wafer-scale uniformity, which have been confirmed by AFM, XPS, Raman and TEM characterizations. Field-effect transistor (FET) device arrays have been further fabricated based on both films showing excellent homogeneous and reproducible electrical performance. The FET on/off ratio was about ~10^4 with decent mobility over 10 cm^2/Vs. These experimental results demonstrated attractive and promising potentials of the novel two-dimensional TMD films in future micro-/nanoelectronics device integrations and applications by using ALD-based techniques.

**NS-TuP4 Overcoming Agglomeration and Adhesion in Particle ALD, Benjamin Greenberg, J. Wollmershauer, B. Feigelson, U.S. Naval Research Laboratory**

The fundamental challenge of particle ALD (pALD) is that small particles are sticky. Nanoparticles (NPs) in particular are highly susceptible to van der Waals, dipole-dipole, electrostatic, and chemical forces. When NPs are fluidized or agitated to expose their surfaces to ALD precursors, these forces can cause persistent agglomeration and adhesion to reactor surfaces, preventing conformal coating and reducing core-shell NP yield. To understand and overcome these obstacles, we examine NPs coated in a...
In 2018, we saw the introduction of a new generation of logic products, featuring FinFET transistors from Intel with their 10 nm generation microprocessor, followed by 7nm devices from competing foundries, primarily targeting high-end application processors in mobile devices. We also saw memory product manufacturers Samsung, Hynix, Toshiba and Micron introducing 64- to 72- stacked layer 3D-NAND devices, and move into 1x generation DRAM devices.

As a supplier of competitive intelligence to the semiconductor and electronics industries, Techninsights performed structural analyses to examine the features and manufacturing processes of all of these innovative devices.

This presentation will examine some of the different structures we have seen through the evolution of these technologies, in particular 7nm and 10-nm logic, 3D-NAND and DRAM parts, that have been introduced. We will also look at several historical applications of ALD/ALE technology that have been observed through reverse engineering. We will highlight the importance of ALD/ALE process in advanced logic and memory devices. In many cases, the technology could not have advanced without the implementation of ALD technology.

Along with the growth of emerging non-volatile memory (NVM), developing an outperforming selector is also required to pave the way for innovative devices.

This work shows for the first time ternary ALD chalcogenide films with statistical analysis is presented.

References:
3) A. Velea et al., Scientific Reports 2017, 7, 8103.
and Se source, respectively. TEM images reveal that ~20 nm grown GeSe layer is amorphous while EDX and RBS measurements revealed stoichiometric GeSe films with traces of Cl impurities. EDX mapping revealed uniform Ge and Se distribution throughout the film. Elastic recoil detection (ERD) measurements show ~5% carbon inside the grown GeSe film. AFM images show an RMS surface roughness of 1.7-1.9 nm. GeSe grown on 3D test structures showed excellent film conformality. Currently work is ongoing to apply conformally grown GeSe layers as OTS selector devices in electrical test vehicles. We will report electrical switching and endurance characteristics of conformal, pulsed CVD grown OTS GeSe selector layers and bench mark these with PVD grown GeSe layers.

9:15am AA1-WeM6 Thin Film Challenges in 3D NAND Scaling, Jessica Kachian, D. Pavlopoulos, D. Kiousis, Intel Corporation

In today’s datacenteric society, 3D NAND has become a storage architecture of focus through increased bit density, relative to 2D architectures. Continuing bit density increase through 3D NAND scaling requires clever manufacturing strategies, centered on discovery and patterning of target materials. Thin film deposition steps face daunting aspect ratios with unforgiving quality specs. The inherent conformality afforded by ALD makes it an attractive process for 3D NAND. However, many relevant ALD processes do not deliver film quality as-deposited. This talk focuses on general material and patterning requirements for key steps in 3D NAND fabrication and considers how ALD may address these challenges, with attention to target properties towards performance.

ALD Applications
Grand Ballroom H-K - Session AA2-WeM

ALD for ULSI Applications I
Moderators: Ravindra Kanjolia, EMD Performance Materials, Jae Hyoung Choi, Samsung Electronics

10:45am AA2-WeM12 The Journey of ALD High-k Metal Gate from Research to High Volume Manufacturing, Dina Triyoso, R. Clark, S. Consiglio, K. Tapily, C. Wajda, G. Leusink, TEL Technology Center, Amentum LLC

In the early days of the search to find a replacement for SiO2-based gate oxides the goal was to find a material with a very high k value which could be incorporated into CMOS production for multiple technology nodes. A historical overview of the many promising high k materials considered for SiO2 replacement leading to the selection of ALD HfO2 as “the winner” will be presented. ALD HfO2 has successfully been implemented in CMOS production for over a decade, starting at the 45nm node. There are two general integration approaches for implementing ALD High-k/Metal Gate stacks (HKMG) in production: gate first and gate last. Challenges with each integration approach, leading to the wider adoption of gate last will be discussed. Furthermore, as the dielectric constant of HfO2 is only ~20 and a thin SiO2-based interface was still required to maintain mobility and reliability, HfO2 provided essentially a one-time scaling benefit. Further thinning of HfO2 resulted in unacceptable leakage and thus to continue transistor scaling fully depleted devices such as FINFET and Ultra Thin Planar SOI (FDSOI) were pursued. High volume manufacturing flows for FINFET (with gate last integration) and FDSOI (with gate first integration) come with their own unique challenges. For example, with FINFET maintaining gate height uniformity is crucial for VT targeting and control. With FDSOI, maintaining gatetack stability at high temperature is key. To continue future scaling, new device architectures (e.g. GAA, Vertical FETs, etc.) will pose further challenges for gate stack integration. Recent and historical progress in HfO2 growth, interface control, selective deposition, morphology and etching will be discussed with respect to the possibility for future gate stack engineering.

References:

Wednesday Morning, July 24, 2019

11:15am AA2-WeM14 Effects of Er Doping on Structural and Electrical Properties of HfO2 Grown by Atomic Layer Deposition., Soo Hwan Min, B.-E. Park, C.W. Lee, Yonsei University, Republic of Korea; W. Noh, Air Liquide Laboratories Korea, South Korea; I.-K. Oh, Yonsei University, Republic of Korea; W.-H. Kim, Hanyang University, Republic of Korea; H. Kim, Yonsei University, Republic of Korea

Gate dielectric materials with high-k are required for further scaling down in future years. As an alternative of conventional high-k materials such as HfO2, the addition of elements to host high-k materials has attracted attention. Among various elements, rare-earth elements, such as Y, La, Dy, or Er has been known to transform the crystal structure of HfO2 from the first-principles study. The theoretical study showed that the doping into HfO2 can energetically stabilize the cubic or tetragonal phase at lower temperature than thermodynamic conditions of pure HfO2. Since cubic (k≈29) or tetragonal (k≈70) HfO2 has much higher dielectric constant than that of amorphous (k≈16-19) and monoclinic (k≈20-25) phases, it is noteworthy that the structural modulation by doping of rare-earth elements can enhance the electrical properties of HfO2. In this work, Er doping into HfO2 was experimentally carried out using atomic layer deposition (ALD) super-cycle process with Er(MeCp)(N-iPr-amd), HfCl4, and H2O co-reactant. ALD Er-doped HfO2 with a variety of Er/Er+Hf) compositions were systematically examined, mainly focusing on structural and electrical properties. X-ray photoelectron spectroscopy (XPS) and X-ray diffraction (XRD) were utilized to investigate the film composition and crystal structure. In addition, MOS capacitors were fabricated with various compositions to evaluate the electrical properties from capacitive-voltage (C-V) and current-voltage (I-V) measurements. In specific ratio, the dielectric constant and the interface trap density of Er-doped HfO2 were found to have significantly improved compared to undoped HfO2. Structural and electrical characterization revealed that the addition of Er to HfO2 induces phase transformations from the monoclinic to the cubic or tetragonal phases, even at low post-annealing temperatures of 600°C. This study identifies optimum conditions to improve the electrical properties of Er-doped HfO2 films which have potential applications in future nanoscale devices.

11:30am AA2-WeM15 Improvement of Electrical Performances of Atomic Layer Deposited ZrO: MIM Capacitors with Ru Bottom Electrode., Jaehwan Lee, B.-E. Park, Yonsei University, Republic of Korea; W. Noh, Air Liquide Laboratories Korea, South Korea; I.-K. Oh, Yonsei University, Republic of Korea; W.-H. Kim, Hanyang University, Republic of Korea; H. Kim, Yonsei University, Republic of Korea

With accelerated scaling down and three-dimensional structuring of integrated circuits, it becomes very challenging to fabricate metal-insulator-metal (MIM) capacitors with low leakage current and high capacitance density. Specifically, the introduction of high-k dielectrics in conjunction with TiN electrodes has improved electrical properties in sub-100 nm processes. Various high-k dielectrics layers combined with TiN electrodes in MIM capacitors were studied for further improvement of MIM capacitors. Controlling an interfacial layer formation between dielectric layer and metal electrode is essential for depositing high-k dielectric thin film on a TiN electrode. When high-k dielectric films were placed on the TiN, interfacial layer was formed due to high reactivity of TiN. The interfacial layer acts as charge traps causing degradation of electrical properties. Surface treatment like plasma treatment on the TiN has been known to help suppress formation of an interfacial layer, but it would be hard to apply for mass-production of DRAM process due to difficulty of uniform treatment without damage caused by energetic species such as ions and radicals on the devices formed inside deep trenches with high aspect ratio. Alternatively, selection of stable metal electrodes with high work function is required to improve electrical properties. Among several metals, Ru electrode can be appropriate option due to its good thermal and chemical stability, low resistivity, high work function. In this paper, we investigated effects of bottom electrodes on the thin film properties of atomic layer deposited (ALD) ZrO, concentrating on correlation between interfacial layer formation and electrical properties. Transmission electron microscopy (TEM) showed thinner thickness of the interfacial layer on the Ru electrode than TiN electrode. Chemical composition of the interfacial layer was analyzed by x-ray photoelectron spectroscopy (XPS) analysis, and ZrO on Ru was less intermixed with bottom electrode due to good thermal and chemical stability of Ru electrode. Introducing Ru electrode improved symmetry of the normalized C-V characteristics. Simultaneously, the introduction of Ru electrode affects decrease of leakage current density from ~10−7 A/cm2 to ~10−9 A/cm2 in I-V characteristics. These results are very meaningful capacitor with Ru electrode can be a very promising device for MIM capacitor in DRAM production.
High-performance metal-oxide-semiconductor field-effect transistors (MOSFETs) require the semiconductor/high-k interface with high-temperature thermal stability and a low interfacial trap density ($D_i$). Previously, in-situ atomic layer deposition (ALD) or molecular beam epitaxy (MBE) $Y_2O_3$ has effectively passivated GaAs(001) surface. The growth was achieved in an integrated ALD/MBE ultra-high vacuum (UHV) system. Despite the difference in deposition, both $Y_2O_3$/GaAs interfaces withstand 900 °C annealing, and the $D_i$'s lie below $5 \times 10^{11}$ eV/cm$^2$. MOS capacitors (MOSCAPs) with such interface outperform those with ex-situ deposited Al$_2$O$_3$. By in-situ synchrotron radiation photoemission study on ALD-$Y_2O_3$/GaAs(001)-$x$-$x$, we found that the surface As atoms were removed and lines of Ga-O-Y bonds stabilized the interface. The interfacial Ga-O-$\gamma$-like state explains the low $D_i$. In this work, we have improved the electrical characteristics in ALD-$Y_2O_3$/GaAs by in-situ UHV annealing the initial 1-nm $Y_2O_3$. The idea is motivated by removing the freed As atoms and hydrocarbons remained in the ALD layer. Note that, an amount of hydrocarbons at such critical interface can degrade the device performances. ALD-$Y_2O_3$ was grown by thermal ALD with sequential $Y(Et)Cl_3$ and $H_2O$ pulses, and in-situ UHV annealing up to 600 °C was conducted in another chamber in our system right after the ALD growth. MBE-$Y_2O_3$ is relatively pure and employed as a reference.

Fig. 1 shows the capacitance-voltage (CV) and quasi-static CV (QSCV) curves for MOSCAPs. The UHV-annealed ALD-$Y_2O_3$/GaAs was improved with a reduced frequency dispersion (F.D.) in the accumulation/depletion region, and a lowered trap-induced hump in the inversion region. Fig. 2 presents the $D_i$ spectra extracted from QSCVs. The UHV-annealed ALD-$Y_2O_3$/GaAs shows a reduced $D_i$, also hinted by the sharp transition of QSCVs and the narrow gap between QSCVs and CVs. Fig. 3 shows the O 1s core-level spectra, where O-Y is from the stoichiometric $Y_2O_3$ and O* is from the interfacial Ga-O-Y and the surface Y-O-H. Note that the ratios of O-Y of our 1-nm $Y_2O_3$ films are significantly higher than the one reported. Upon UHV annealing, the residue O* may be attributed to the interfacial Ga-O-Y with the surface Y-O-H mostly removed. This UHV annealing approach is significant in perfecting ALD-$Y_2O_3$/GaAs and is applicable to many other material systems.

References:


Atomic Layer Etching

Regency Ballroom A-C - Session ALE1-WeM

Integration & Application of ALE

Invited Moderators: Bert Ellingboe, Dublin City University, Wei Tian, Applied Materials

8:00am ALE1-WeM1 ALD and Etch Synergy to Enable the Next Scaling Innovations, Angelique Kyle, K.L. Lee, X. Sun, Q. Lou, Y.T. Lu, M. Edley, S. Oyola-Reynoso, P. Ventzek, R. Clark, P. Biolsi, H. Masanobu, A. Ranjan, TEL Technology Center, America, LLC

As logic nodes continue to scale below 7 nm, the back-end-of-line (BEOL) critical pitch has moved to sub-40 nm and is forecasted to scale down to 14 nm according to the latest International Roadmap for Devices and System (IRDS). In addition to the patterning and integration complexities that arise with scaling, pitch reduction has a direct impact on the plasma-processing window. Continuous conventional wave processes can no longer achieve stringent aspect ratio dependent etching (ARDE), selectivity and profile control requirements and have gradually given way to pulsed plasma processes, decoupled process sequence plasmas or remote plasmas to widen the process space. In this talk, we will discuss implementation of atomic layer deposition (ALD) and decoupled or cyclic plasma etch in the BEOL to overcome challenges of mask loss, ARDE, low k damage and LER/LWR and look to future technology enablement with area and topographically selective processes.

ALD processes are achieved by using sequential, self-limiting reactions. ALD technology is widely used to go beyond lithography resolution limits, to increase selectivity and to enable self-alignment. For dielectric etches with fluorocarbon plasma chemistry a decoupled plasma etch process can achieve the benefits of an ARDE free etch with improved mask selectivity. Integrations combining ALD and etch can yield further improvements in profile such as chamfer control and via CD control which have a direct impact on device reliability and yield. Finally, cyclic combinations of ALD and etch can drive down line width roughness through smoothing benefits of front growth merging and preferential etching of asperities.

8:30am ALE1-WeM3 On the Role of Individual Etching Components in Selective Atomic Layer Processing: Etch and Deposit to Obtain High Selectivity, Alfredo Mameli, TNO/Holst Center, Netherlands; F. Roozeboom, Eindhoven University of Technology and TNO, Netherlands; P. Poort, TNO/Holst Center, Netherlands

In the domain of Atomic Layer Processing both Atomic Layer Etching (ALE) and area-selective Atomic Layer Deposition (ALD) are becoming increasingly popular because of their potential in advancing nanomanufacturing. Yet, the selectivity in terms of layer thickness and defectivity requirements has major limitations to overcome. Here, the combination of selective deposition and etching can play a key role in tackling these challenges. The complementarity of deposition and etching techniques offers great potential for reaching the targeted requirements for advanced applications.

In this presentation, the combination of spatial area-selective ALD using chemoselective inhibitors and interleaved etching steps to increase the process selectivity will be discussed. The focus will be on two different etching steps: the self-limiting etching of the inhibitor and a blanket etch-back step of the growing material. The former enables cyclic selective deposition when using a plasma-based ALD process while the latter allows for further maximizing the selectivity.

Finally, the concept of area-selective ALD combined with etching techniques in an integrated cyclic etch/dep spatial-tool for high-throughput Atomic Layer Processing will be presented.


9:00am ALE1-WeM5 Area-Selective Deposition of TiO$_2$ on Various Surfaces by Isothermal Integration of Thermal TiO$_2$ ALD and ALE, Seung Keon Song, G.N. Parsons, North Carolina State University

As transistor size is shrinking, area selective deposition process is becoming more important than before. Atomic Layer Deposition (ALD) and Atomic Layer Etching (ALE) are promising processes for area selective deposition of metallic and dielectric materials as they can deposit and etch nanoscale thickness of thin film conformally. ALD precursors usually have different affinity to solid surfaces, which enables ALD processes to have surface dependent selectivity. For examples, thermal TiO$_2$ ALD, employing sequential doses of TiCl$_4$ and H$_2$O, shows initial growth delay on hydrogen-terminated silicon (Si-H) but rapid growth on oxide silicon surface (SiO$_2$) at 150-190°C. To extend this surface dependent selectivity, we created isothermal integrated ALD/ALE process, where TiO$_2$ ALD cycles are combined with a few cycles of thermal TiO$_2$ ALE, employing sequential doses of WFs$_6$ and BCl$_3$ under isothermal condition. Using the integrated ALD/ALE sequence, we achieve ~7 nm of TiO$_2$ on SiO$_2$, before noticeable TiO$_2$ nucleation on Si-H, as determined by SEM, ellipsometry and TEM analysis. Process and materials analysis using in-situ QCM and ex-situ AFM and XPS further confirm our findings. Beyond TiO$_2$ selectivity on Si/SiO$_2$ surfaces, some metal surfaces (Cu, Au, Co) showed some extent of initial growth delay during TiO$_2$ ALD cycles, as observed by in-situ QCM. Thus, TiO$_2$ selectivity on various kinds of surfaces was also studied with ex-situ XPS, SEM, and ellipsometry. We expect that this demonstrated ALD/ALE process on various surfaces provides useful information about ALD/ALE precursors reactions on various surfaces, and this information offers opportunities to integrate ALD and ALE process with optimum process controls.
The use of limited dose ALD and ALD are described for producing localized film coatings on 3D, non-planar structures such as trenches and fins. Limited dose ALD (LD-ALD) has been described for improved ALD film deposition rate (thickness/unit time)\(^1\) and for local masking applications of DRAM bottle trenches.\(^2\) In this paper we describe Limited Dose Atomic Layer Etching (LD-ALE) to obtain localized films on trenches and fins using various combinations of standard ALD, LD-ALD and LD-ALE. Three cases for localized film coatings are described:

(i) a film localized at the bottom of a trench or fin, by using standard ALD followed by LD-ALE,

(ii) a film localized at the center of a trench or fin, using LD-ALD followed by LD-ALE, and

(iii) a film localized at the top and bottom of a trench or fin, using ALD followed by LD-ALE, and this in turn followed by LD-ALD.

In case (i), the LD-ALE step is carried out using a prescribed limited ALD precursor modification\(^2\) dose. The limited dose is prescribed to attain the desired local film etching and removal of a specified depth near the top of the non-local feature. As an application example, the local doping at the bottom of a bulk finFETs, is described using doped ALD films\(^3\) at the bottom of a fin to counter dope the base of the fin. Separately, doping the source – drain region at the top of the fin is described. Examples of mask applications on trenches and fins will be described, as well as film localized thickness adjustments. Limited Dose implementation challenges as well as various equipment opportunities are briefly discussed. If experimental demonstrations are available, they will be presented.


9:30am ALE1-WeM7 Formation of Ohmic Contacts to Si using In-situ Chemical Cleaning of the Substrate, Sara Iacopetti, Technion – Israel Institute of Technology, Israel; R. Torafdar, S. Loi, M. Danek, Lam Research Corp.; M. Eizenberg, Technion - Israel Institute of Technology, Israel

The implementation of novel device geometries in CMOS technology such as FinFETs, allowed a further downsizing of the logic nodes to 45 nm and below, reaching nowadays mass production of devices of 7 nm and studies on sub-5 nm nodes. To such feature sizes and complex geometries, the well-established technology of Source and Drain (SD) contacts by metal silicide formation produces bulky contacts that cause short-channel effects, detrimental to the transistor performances. Shallow ohmic contacts must be implemented in the future.

This work focuses on the feasibility of producing ohmic contacts using in-situ chemical cleaning (CC) of the native SiO\(_2\) layer prior to the deposition of the contact metal (Co) without air break. The two main aspects investigated are the amount of Si consumption as a function of heat treatment, and the resultant contact resistivity.

Si blanket wafers were exposed to different number of cleaning cycles (increasing: No CC, CC, CC and CC++); Co was deposited by PVD to isolate the effect of cleaning on the interface. Compositional and microstructural studies were carried by ToF-SIMS, XRD and HRTEM (STEM-EDS) on Si + 30 nm PVD Co, as-deposited and vacuum annealed. The CC removes completely the native oxide but creates a disordered interlayer of 2 nm thickness at the metal/semiconductor interface. Cobalt silicides formation is accelerated as a consequence of the removal of the native oxide, leading to the formation of a Co and Si intermixed layer from 200°C, and the onset of crystalline CoSi\(_2\) and CoSi formation as early as 350°C and 450°C, respectively. As the resulting contacts are very thick (> 60 nm for the low thermal budget annealing), the approach to shallow contact fabrication moved to Si/Co + PVD Co 10nm/TiN 30 nm/Co 200nm, without air break between depositions. The thin silicide formation with annealing of the contacts was checked by TEM and XRD and it follows the same silicide formation as seen in the Si + PVD Co 30nm case.

The contact resistivity was studied by fabrication of structures for transmission line measurement (TLM) by photolithography on Si/Co/TiN/Co, followed by wet or reactive ion etching of the metals. The contacts are ohmic and specific contact resistivities of 10\(^{-6}\) Ohm cm\(^2\) were measured, higher for the C++ samples with respect to the non-cleaned and other cleaned samples, suggesting that the disordered interface plays a role as a thin dielectric barrier across the interface.

The ongoing research is focusing on the quantitative study of the interface composition and its influence on the contact resistivity, crucial for moving to an ALD metallization scheme.

5.5:45am ALE1-WeM8 SADP Spacer Profile Engineering by Quasi-Atomic Layer Etching, Tsai Wen (Maggie) Sung, C. Yan, H. Chung, J. Lo, D. Desai, P. Lembesis, R. Pakulski, M. Yang, Matsson Technology, Inc.

As the size of modern device shrinks, self-aligned double patterning (SADP) and quadruple patterning (SAQP) has gained increasing interest in the fabrication of 14nm technology node and beyond. Plasma reactive ion etching (RIE) with inductively coupled plasma (ICP) is a common technique utilized in the SADP/SAQP process flow because of its etch anisotropy and tunability. Higher bias power is usually employed to achieve sufficient directionality; however, it can lead to sloped, sharp, and asymmetric spacer profiles. These undesired profiles may cause inadequate pattern transfer and the error may be amplified as it moves down the process line, such as pitch-walking and nonuniform fin formation. Furthermore, a high bias power can also severely damage the bottom substrate due to strong ion bombardment, resulting in an uneven etch. Recently, a method for quasi-atomic layer etching (QALE) was developed where it was found that the reactivity of a material increased with exposure to an active species.\(^1\)

1. In this work, a chemical dry etch (CDE) equipment with an ICP radical source and a capacitive coupled plasma (CCP) plasma source was utilized to perform QALE. A RF bias was applied to the substrate to produce highly selective radicals and to promote vertical implantation of the active species into the top surface of SADP spacers. The implantation “activates” the spacer top surface by increasing itsetch rate during a subsequent etch step, while keeping the etch rate of the unexposed sidewalls at a minimum, thereby improving the etch anisotropy. The activation-etch process is self-limiting and the etch depth scales linearly with the activation-etch cycles. By modulating this QALE method, we successfully demonstrated a significant reduction of the spacer shoulder slope and tip angle, thus flattened the spacer profile. Moreover, the QALE technique can be further developed and utilized to engineer the spacer surface profile and applied in other device fabrication processes.

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**Atomic Layer Etching**

**Regency Ballroom A-C - Session ALE2-WeM**

**Materials Selective ALE**

Moderators; Fred Roozeboom, Eindhoven University of Technology and TNO, Geun Young Yeom, Sungkyunkwan University

10:45am ALE2-WeM12 Dynamic Temperature Control Enabled Atomic Layer Etching of Titanium Nitride, He Zhang, Y.S. Kim, D. Paeng, Lam Research Corp.

TIN ALE was achieved with Rapid Thermal Sources using O\(_2\) plasma and Cl\(_2\). TIN surface was oxidized to TiO\(_2\), and the following Cl\(_2\) flow absorbed Cl on the oxidized surface. This modified layer can be thermally removed under intense light source irradiation. Full removal of few nm blank ALD TIN layer is demonstrated. XPS observed surface composition change after each step. Surface smoothen was also observed after etching. The ultra-short thermal pulses enabled fine control of surface reactions in each ALE steps. Thermal ALE of Ge under similar approach will also be discussed.

11:00am ALE2-WeM13 Rapid Thermal-Cyclic Atomic Layer Etching of Thin Films with Highly Selective, Self-Limiting, and Conformal Characteristics, Kazunori Shinoda, Hitachi, Japan; H. Kobayashi, Hitachi; N. Miyoshi, M. Izawa, Hitachi High-Technologies; K. Ishikawa, M. Hori, Nagoya University, Japan

Invited

Etching processes with atomic level precision are important in order to provide next-generation of semiconductor devices that have densely arrayed high-aspect-ratio structures. There is thus considerable interest in the development of isotropic atomic layer etching (ALE) for a variety of materials used in semiconductor manufacturing. One approach for isotropic ALE is rapid thermal-cyclic ALE, which consists of cyclic repetitions...
of plasma exposure at lower temperature and infrared (IR) lamp annealing. The plasma exposure produces self-limiting modified layers on the surface of the target materials, and the IR lamp annealing removes the modified layer by thermal desorption. The authors demonstrated rapid thermal-cyclic ALE of a variety of materials such as Si$_3$N$_4$, SiO$_2$, TiN, and W over the last several years.

Rapid thermal-cyclic ALE processes were originally developed on the basis of an understanding of plasma-surface reactions using in-situ analysis. As for Si$_3$N$_4$, in-situ x-ray photoelectron spectroscopy (XPS) analysis revealed that hydrogen and fluorine containing plasmas produce a self-limiting layer of ammonium hexafluorosilicate on the surface of Si$_3$N$_4$. Thermal desorption spectroscopy (TDS) analysis showed that lamp annealing decomposes the ammonium hexafluosilicate into Si$_3$F$_4$, HF, and NH$_3$. The result of TDS is consistent with the result of thermodynamic calculation of the decomposition of ammonium hexafluorosilicate. This technology is also applicable to other nitride films besides Si$_3$N$_4$. The authors have demonstrated self-limiting isotropic ALE of TiN using this technology.

A 300-mm ALE apparatus that consists of an inductively coupled plasma (ICP) source for downflow radicals, IR lamps for rapid thermal annealing, and in-situ ellipsometry for thickness monitoring was developed for rapid thermal-cyclic ALE. A self-limiting nature in both the plasma exposure step and the lamp annealing step has previously been demonstrated for Si$_3$N$_4$, TiN, and W. Conformal, highly selective etching for patterned samples was confirmed by transmission electron microscopy (TEM). Layer by layer ALE for Si$_3$N$_4$ of more than 100 cycles was confirmed by in-situ ellipsometry. Moreover, it was demonstrated that etching selectivity between different materials could be switched from infinitely selective to nonselective by adjusting the lamp annealing time. In this talk, applications of rapid thermal-cyclic ALE for a variety of dielectric and metal films will be presented.

11:30am ALE2-WeM15 Atomic Layer Etching of HfO$_2$ with Selectivity to Si by Utilizing Material-Selective Deposition Phenomena, Kang-Yi Lin, C. Li, University of Maryland; S. Engelmann, R.L. Bruce, E.A. Joseph, IBM T.J. Watson Research Center; D. Metzler, IBM Research - Albany; G.S. Oehrlein, University of Maryland

Atomic layer etching (ALE) applies sequential deposition, reactant purge and etching steps with a short processing step length to establish self-limited material removal and atomic scale precision. The reactants during the ALE deposition steps may exhibit material-selective deposition based on the chemical affinity of precursor gases to the substrate material and nature of interfacial bonding. Integrating the feature of material-selective deposition with an etching step opens a new processing window for selective ALE. In this work, we evaluated the deposition behaviors of different hydrocarbon (HFC) precursors, i.e. mixtures of methane (CH$_4$) with trifluoromethane (CHF$_3$) and mixtures of methane with octafluorocyclobutane (CF$_8$)$_2$, on Si and HfO$_2$ surfaces, respectively. This is followed by the investigation of substrate-dependent selective deposition using a mixture of HFC precursors to achieve HfO$_2$ etching and etching selectivity relative to Si. Our results show that during the purge step of ALE sequences using CH$_4$/CHF$_3$ selectively deposit a fraction of a nm thick FC layers on Si surface while self-desorption is observed on the HfO$_2$ surface. In contrast, mixtures of CH$_4$ with CF$_8$ etch do not show this self-desorption behavior for HfO$_2$. By utilizing the selective deposition behavior seen for CH$_4$/CHF$_3$-based ALE in conjunction with low energy Ar ion bombardment, we were able to remove the top HfO$_2$ layer while simultaneously forming a FC passivation layer on the underlying Si surface. In order to confirm the etching performance of CH$_4$/CHF$_3$-based ALE of HfO$_2$, X-ray photoelectron spectroscopy (XPS) was used to study whether any HfO$_2$ remains on the sample at the end of the processing cycle where the in-situ ellipsometry indicated a depletion of the HfO$_2$ layer. The XPS results show that after the ALE processing the Hf-O peaks no longer exist in the HF$_4$ and O1s spectra. Instead, a weak intensity of the fluorinated Hf peaks are observed, suggesting the HfO$_2$ layer with an initial thickness of 2.9 nm was removed and a few hafnium etching byproducts were left on the substrate. These results support the concept that gas pulsing of complex HFC precursors during ALE sequences provides the opportunity to achieve material-selective deposition and enable ALE selectivity of HfO$_2$ relative to Si.

11:45am ALE2-WeM16 Enhancing Etch Selectivity in Plasma-Assisted ALE of Silicon-Based Dielectrics using Surface Functionalization, Ryan Gasvoda, Colorado School of Mines; S. Wang, E. Hudson, Lam Research Corp.; S. Agarwal, Colorado School of Mines

Stringent processing windows are required for the fabrication of sub-7-nm semiconductor devices, which in turn places severe constraints on conventional plasma-assisted etching. Atomic layer etching (ALE) is a promising etching technique that can provide high etch fidelity, directionality, layer-by-layer removal, and selectivity to meet the stringent processing demands. Plasma-assisted ALE of SiO$_2$ and SiN typically consists of two sequential half-cycles: fluorocarbon (CF$_x$) deposition from a fluorocarbon plasma followed by an Ar plasma activation step. Typically, selectivity is achieved through manipulating the plasma and processing parameters. Recently, we proposed a methodology to further increase etch selectivity by selective prefunctionalization of the SiO$_2$ or SiN$_x$ surface with hydrocarbons. We show that the abundance of hydrocarbon on the prefunctionalized surface promotes the formation of an etch inhibiting graphic carbon film after just a few ALE cycles.

In this study, we used in situ attenuated total reflection Fourier transform infrared (ATR–FTIR) spectroscopy and in situ 4–wavelength ellipsometry during ALE to monitor the surface reactions, film composition, and net film thickness. We show that cyclic azasilanes can be used to selectively functionalize SiO$_2$ over SiN$_x$. Our results show that during the purge step of ALE cycles of SiO$_2$ etching with (blue) and without (black) surface prefunctionalization. For the prefunctionalized surface, we observe an increase in absorbance from ~1500 – 1800 cm$^{-1}$, assigned to a graphitic hydrofluorocarbon film. After just 4 ALE cycles, this graphitic hydrofluorocarbon film reaches a thickness that acts as an etch stop layer. As a result, after 10 cycles, the etched thickness of SiO$_2$ was ~23% of the case where there was no surface functionalization. This methodology can therefore be used to enhance overall etch selectivity for SiN$_x$ over SiO$_2$.

Further, we will discuss the role of Ar$^+$ ion energy during the Ar plasma activation step on graphitic hydrofluorocarbon film formation. The length and structure of the hydrocarbon chain on the prefunctionalized surface will also be addressed.

ALD for Manufacturing

Grand Ballroom E-G - Session AM1-WeM

Spatial ALD, Fast ALD, and Large-Area ALD

Moderators: John F. Conley, Jr., Oregon State University, Paul Poott, TNO/Holst Center

8:00am AM1-WeM1 Impact of Operating Parameters on Precursor Separation in “Air Hockey” Spatial Atomic Layer Deposition Reactor, John Grasso, B. Willis, University of Connecticut

A defining characteristic of atomic layer deposition (ALD) is the sequential exposure of a surface to self-limiting, saturating reactions. Temporal ALD operates through intermittent purge cycles, while spatial ALD relies on physical separation accomplished by delivering reactants through a deposition head located in close proximity to the substrate’s surface. An inert gas stream placed between precursors acts as a diffusion barrier to prevent mixing. A dysfunctional barrier results in gas phase reaction and non-ALD growth. To understand the impact system parameters have on the efficiency of the gas barrier, this work presents a COMSOL Multiphysics study of the fluid dynamics and concentration diffusion for the system.

We present a case study for ALD of alumina by trimethylaluminum (TMA) and water using a novel spatial ALD system analogous to an air hockey table. In contrast to other spatial ALD reactors that are limited by mechanical constraints, dispersed nitrogen inlet and substrate gas throughput and injector region to deposit films within a deposition gap of less than 100 μm. The rotation height, or deposition gap, is a function of the fluid pressure underneath the substrate. An accurate height estimation from the parameters is necessary to evaluate the efficiency of the gas barrier. In-situ -height measurements are used to validate the COMSOL model, and the results are in good agreement for different operating conditions.

This work investigates how diffusivity, deposition gap, inert flow rate, and geometric design influence the effectiveness of precursor separation by evaluating the concentration of the precursors at the substrate surface. Small deposition gaps prevent precursor intermixing, however the diffusional barrier is not effective when the inert flow rate is low. Specifically, high diffusivity enables the precursors to readily diffuse beyond their ideal zone, cause gas phase reactions, and lead to CVD
growth. Additionally, the uniform surface exposure of reactant is altered, leading to non-uniform growth at the edges of the deposition area. Successful precursor separation can be achieved at large fluctuation heights when the inert flow is large; however, the precursor concentration at the surface becomes low. These conditions may lead to insufficient saturation of the surface and non-ideal ALD growth. Stationary deposition experiments are utilized to demonstrate the ability of the model to predict non-ALD behavior. Additionally, the geometric design of the reactor plays a critical role in preventing precursor intermixing.

8:15am AM1-WeM2 Plasma Enhanced Spatial ALD of Silver Thin Films at Atmospheric Pressure, Tim Hasselmann, University of Wuppertal, Germany; N. Boysen, Ruhr University Bochum, Germany; D. Theinich, University of Wuppertal, Germany; A. Devi, Ruhr University Bochum, Germany; T. Riedl, University of Wuppertal, Germany
A wide range of opto-electronic devices, such as solar cells and light emitting diodes, require electrodes that are highly conductive and at the same time transparent. Ultra thin (thickness < 10 nm) silver (Ag) films can provide these properties.[1,2] Plasma enhanced atomic layer deposition (PE-ALD) would be a suitable coating technique that allows for homogenous film growth on large areas at low temperatures with precise thickness control. Since ALD is originally a vacuum based technique, limitations towards high throughput processing and low-cost manufacturing occur. These drawbacks can be overcome by spatial PE-ALD at atmospheric pressure.[3] In our earlier work, we have shown outstanding (conductive) gas diffusion barriers and more recently, the growth of Ag films from a novel halogen-free precursor, by spatial PE-ALD at atmospheric pressure.[4-6] In this work, we provide detailed growth studies of Ag thin films grown from this novel 1,3-di-tert-butyl-imidazolin-2-ylidene silver(I) 1,1,1-trimethyl-N-(trimethylsilyl) silanaminide [(NHC)Ag(hmds)] precursor by spatial PE-ALD. An atmospheric pressure dielectric barrier discharge with Ar/H2; as working gas is used. Saturating behavior with growth rates of about 2.4×10^-3 atoms/(cm^2)s (corresponding to an equivalent of 0.42 Å/cycle), determined by RBS, at a very low deposition temperature of 100°C is shown, with only small amounts of residual carbon (~1.5 at.%), and Si (~0.8 at.%). In the films. Percelated and conductive Ag films with a low sheet resistance of 0.3 Ω/sq (resistivity: 10^{-5}Ωcm) are demonstrated. Furthermore, the influence of the deposition temperature in a range from 80°C to 120°C on the growth characteristics is discussed. All results are compared to those obtained from the more established precursor [Ag(fod)2(Pet)][(FOD)].[7] The prospects to use these ALD grown Ag layers to create highly conductive electrodes for perovskite solar cells are discussed.


8:30am AM1-WeM3 Low Temperature Spatial PEALD of Silicon Nitride Films from Aminosilane Precursors and DC Direct Plasma, Eric Dickey, Lotus Applied Technology
INVITED PEALD of silicon nitride using aminosilanes in precursor combination with N2, N2:H2, or NH3 plasma has been widely studied in recent years. Most of this research has been conducted in conventional pulse-purge reactors, employing RF power for plasma and the direct Inductive Coupled Plasma (ICP) or direct Capacitively Coupled Plasma (CCP). While the use of RF plasma is a necessity for pulse-purge ALD reactors, Spatial ALD provides an opportunity to use a simple DC direct plasma. This is due to the fact that most interior surfaces of the reaction chamber, including the plasma electrode, are not coated with the dielectric film, as growth occurs only on the surfaces that are exposed to both the plasma and the precursor. In this work, a spatial ALD system incorporating a rotary disc substrate holder and DC diode plasma was used to deposit silicon nitride at temperatures between 300 and 350°C. From bis(diethylamino) silane (BDEAS), bis(tertbutylamino)silane (BTBAS), disopropylamino silane, (DIPAS), and "New SAM" supplied by Air Liquide. N2 and N2:H2(4%) were used as the plasma gas, with an operating pressure between 0.5 and 1.2 Torr. Refractive index values as high as 1.94 at 633 nm were attained, and wet etch rates in dilute hydrofluoric acid (1%) as low as 1 nm per minute were measured. RBS compositional analysis for stoichiometry and contamination was performed on a subset of samples, and showed significant variation depending on the precursor and plasma gas used.

9:00am AM1-WeM5 Development and Characterization of an Atmospheric Pressure Plasma Reactor Compatible with Open-Air Spatial ALD, H. Rabat, F. Zoubian, O. Aubry, N. Dumuis, S. Dozias, GREMI University d’Orléans/CNRS, France; C. Masse de la Huerta, A. Sekkat, V.H. Nguyen, LMGP Grenoble INP/CNRS, France; M. Bonvalot, C. Vollée, LTM-UGA, France; D. Hong, GREMI University d’Orléans/CNRS, France; David Muñoz Rojas, LMGP Grenoble INP/CNRS, France
Dielectric Barrier Discharge (DBD) plasma are widely used for atmospheric pressure plasma generation. The possibility of their adaptation in custom-made configurations makes them potential candidates to assist deposition processes. In fact, the increased need of high-quality thin films forces to improve the deposition techniques. New processes should be able to work in less constrained conditions such as atmospheric pressure rather than vacuum and to have faster deposition rates while respecting the same high quality of the deposited films. In this paper we present the development of a surface dielectric barrier discharge plasma reactor to assist an atmospheric spatial atomic layer deposition process. The plasma was generated by a surface dielectric barrier discharge powered by a microsecond pulsed high voltage power supply. The dissipated power was measured for different configurations, and thanks to the micro discharges imaging, it was observed that the thickness and the shape of the dielectric barrier influenced the micro discharges distribution on the dielectric surface. The plasma reactor exhaust gas was chemically analyzed by FTIR spectroscopy and micro gas chromatography. The ozone concentration was determined as function of frequency of the power supply. Initial results of utilization of the new compact atmospheric plasma head to deposit functional materials by open-air high-throughput plasma-activated SALD will be provided.

9:15am AM1-WeM6 Fast Plasma ALD Employing de Laval Nozzles for High Velocity Precursor Injection, Abhishekkumar Thakur, J. Sundqvist, Fraunhofer Institute for Ceramic Technologies and Systems IKTS, Germany; S. Wege, Plasway Technologies GmbH, Germany
AlD based self-aligned multiple patterning (SAXP) has been the key process to continued chip scaling. SAXP demands PEALD for low temperature and conformal deposition of spacers on photoresist features for the subsequent etch based pitch splitting. ALD is limited by low thru put that can be improved by raising the growth per cycle (GPC), using new ALD precursor, preforming batch ALD or fast Spatial ALD, shrinking the ALD cycle length, or omitting purge steps to attain the shortest possible ALD cycle. Today’s latest and highly productive platforms facilitate very fast wafer transport in and out of the ALD chambers. Current 300 mm ALD chambers for high volume manufacturing are mainly top-down or cross-flow single wafer chambers, vertical batch furnaces, or spatial ALD chambers. In our research developing fast PE ALD processes, we use top down gas flow via showerhead to ignite a 60 MHz plasma (CCP) in a 300 mm chamber. The chamber has been modified to attain ultra-short (<10 ms) ALD precursor pulses along with good uniformity using a ring injector (W02017194059A1) with integrated de Laval nozzles enabling high speed, all-round precursor injection across the wafer. We used the well-known TMA-O2 PEALD process to deposit Al2O3 for the hardware development and the productivity benchmarking.

Initially we used a single capillary injector for PEALD of Al2O3 at room temperature (30 °C), wherein we shrunk the TMA pulse length from 2000 ms down to 15 ms maintaining the constant 1.7 Å GPC (Fig. 1), which confirmed the self-limiting nature of the TMA half-reaction. With the de Laval ring injector the saturation started at 10 ms of TMA pulse length (Fig. 2), as this is the tested switching limit of the electro-pneumatic ALD valve. The process linearity (Fig. 3) and the saturation curve indicated the ALD nature of the process. For 50 ms of TMA pulse, a wide ALD temperature window (30-120 °C) with constant 1.3 Å GPC was achieved (Fig. 4). Even with very short pulses we achieved a very good uniformity from wafer center to the edge. XPS analysis of the deposited Al2O3 indicated that the film deposited at 120 °C were more oxidized than the films at 30 °C with the single injector. However, the elemental composition for films deposited with TMA pulse of 10 ms vs. 50 ms was indistinguishable. A surface carbon contamination (Table 1) was observed due to the wafer exposure to the outside atmospheric post processing. However, angular XPS depth profiling revealed no detectable amount of carbon in the “bulk of the film”. The complete ALD process optimization results including plasma pulse optimization, conformality and 300 mm wafer scale uniformity will be presented at the conference.
Atomic Layer Deposition (ALD) is best known for depositing electronic device films, but it also offers great promise for producing transparent barrier films on optics—such as large concave metal-coated astronomical observatory telescopes. To date, ALD coatings on mirrors has been limited to relatively small-sized optics and certainly not ones with their mounting hardware attached. We have designed, constructed, and tested a new ALD tool to apply uniform ALD coatings on planar and curved substrates up to 1m in diameter. The new tool has been named the Meter Scale ALD (MS-ALD) tool. The MS-ALD tool employs a unique chamber design that isolates a large substrate surface to be coated by utilizing the substrate itself as an internal wall of the process chamber. This configuration allows the backside of the optic to be isolated from the front side process environment allowing robust transparent uniform protective dielectric coatings to be grown on telescope mirrors with their backside support hardware in place.

Robust and scalable thin film deposition methods are key to realize the potential of the combined nanoporosity and hybrid organic-inorganic chemical modularity of metal-organic frameworks (MOFs) in electronic devices [1]. Here, we report the first fully integrated and highly-controllable vapor deposition process for MOFs (MOF-CVD) [2], as recently implemented in a 200 mm modified commercial ALD reactor. The process consists of two-steps: (1) atomic layer deposition for the metal oxide precursor, and (2) subsequent stop-flow reaction with the sublimated organic linker at elevated pressure and non-isothermal temperature conditions. As our selected test case, the optimized MOF-CVD process for ZIF-8 (zinc-2-methylimidazolate) showcases smooth, pinhole-free and large-area uniform ultrathin films that are highly nanoporous. Our process distinguishes itself from previous works as it permits single-chamber deposition, under mild conditions and without the need for a separate post-deposition crystallization steps; to the best of our knowledge, it is the only MOF thin film deposited via an integrated ALD-CVD method on large area substrates to date. Through its implementation in a single-chamber, the MOF-CVD reaction mechanism was studied using a combination of time-resolved in situ ellipsometry and QCM monitoring, and ex situ thin film characterization techniques. We will present the impact of relevant deposition parameters in the form of a MOF-CVD deposition rate process chart. Our method shows great promise to ease the manufacturing of devices based on MOF thin films, as will demonstrated by a sneak preview of ongoing application projects.


since Cu ions can diffuse into the deposited film and further catalyze and/or stabilize the inter-chain polyimide by forming metal-organic complexes with the partially ordered system inside. However, at 170 °C ring-closed imidization seems to dominate, whereas at 200 °C inter-chain PI formation dominates.

References:

8:30am EM1-WeM3 Integrated MLD Supercycle for the Direct Deposition of Zeolitic Imidazolate Framework Films, Alexander John Cruz, I. Stassen, R. Ameloot, KU Leuven, Belgium
Intrinsic nanoporosity and synthetic tunability position porous materials, such as metal-organic frameworks (MOFs) at the center-stage of some emerging applications in microelectronics [1,2]. For example, these materials have shown promising properties for device integration ranging from gas sensing to low-k dielectrics for future logic microprocessors. Essential for capitalizing on the disruptive potential of MOFs on such device-oriented valorization is a solvent-free process for the deposition of ultrathin, defect-free films with unprecedented control over thickness and properties [2]. We herein present an ongoing proof-of-concept study on the direct molecular layer deposition of thermally and chemically stable nanoporous MOFs using a modified commercial ALD/MLD reactor. In our ZIF-8 (zinc-2-methylimidazolate) test case, sequential reactions of diethylzinc, water, and 2-methylimidazole are assembled into a supercycle to yield layer-by-layer deposition of films that are crystalline and nanoporous as-synthesized, in the absence of separate post-deposition treatments. To explore a variety of chemical handles for molecular-level control of the thickness and film characteristics, we introduced modulators such as water, methanol and ethylene glycol during different stages of the supercycle by means of ALD pulses. The present contribution will highlight our most recent works on MLD ZIF-8 and a brief introduction on a catalog of new MOF chemistries via integrated ALD-MLD-CVD processes, as well as a demonstration of potential integration routes to applications in microelectronics. Furthermore, we will elaborate the steps on how we took advantage of in situ ellipsometry and QCM in combination with complementary ex situ techniques for unraveling mechanistic insights into the reaction-crystallization processes. We will clarify and explain optimization guidelines and high-level design rules on how to implement MOF-MLD formulations to other laboratory setups and fabrication facilities.

9:00am EM1-WeM5 Molecular Layer Deposition of Indicone Thin film using Indium Precursor and Hydroquinone, Seung-Hwan Lee, G.H. Baek, J.-H. Lee, Hanyang University, Republic of Korea; T.T. Ngoc Van, B. Shong, Hongik University, Republic of Korea
Flexible electronics are obtaining attention for potential to be used in various applications because of their light, thin, conformable design advantages.[1] However, most inorganic materials have limitations to be used for flexible devices due to high elastic modulus and weakness on external stress or strain, regardless of their superior electrical properties. On the other hand, organic materials are often elastic so that they are resistant to external stress or strain, but with poor electrical performance. Therefore, hybrid materials combining advantages of organic and inorganic materials are of much research interest. Molecular layer deposition (MLD) is a promising technology for deposition of organic and inorganic hybrid thin films for conformity and excellent thickness controllability.[2] In this work, indocine thin films containing indium and organic diol linkage are deposited by MLD. [1,1,1-trimethyl-N-(trimethylsilyl)-silanaminato]-indium (InCA-1) and hydroquinone (HQ) are used as the indium and the organic precursor, respectively, at deposition temperature between 100-250°C. The MLD properties are demonstrated from growth behavior; Fourier transform infrared (FTIR) spectroscopy and X-ray photoelectron spectroscopy (XPS) are used to analyze the chemical characteristics in the material. Density functional theory (DFT) calculations are utilized to investigate the chemical mechanism of the deposition reaction. Indium-based hybrid films are grown by supercycles of indium oxide atomic layer deposition (ALD) and indocene MLD. Structural, optical and electrical properties with respect to the super-cycle ratio are investigated. As the fraction of indocene incorporated in the hybrid films increases, crystallinity decreases while electrical resistivity increases. The hybrid film, which has 99.1% indium oxide and indocene ratio, shows slightly increased resistivity, but shows enhanced resistance toward mechanical deformation compared to pure ALD indium oxide thin films. The hybrid film has superior mechanical property for future flexible devices.

Molecular layer deposition (MLD) is fundamentally a modified Atomic Layer Deposition (ALD) principle, where conformal thin films are fabricated with self-limiting surface reaction chemistry. The ALD/MLD hybrid process makes it possible to deposit thin film by in-situ process only by changing the precursor and to manufacture excellent organic-inorganic hybrid thin films. Many researcher groups reported “metalcone” films using various metal and organic precursors but there are not many studies on hetero bifunctional group organic precursors. [1] Because of its two different functional groups, it has different thin film properties, and this reinforces the moisture-sensitive problems of most MLD films. Therefore, it will be very useful in the application field of the organic thin film.

In this work, we fabricated alucone thin films using Trimeethylaluminum (TMA) and 4-mercaptophenol(4MP) by MLD and the properties of the thin films were analyzed as annealing progressed with increasing temperature. In particular, we observed the alucone film characteristics from 4MP with different functional groups of -OH and -SH group. Growth per cycle tends to decrease due to the difference in reactivity between the -OH and the -SH group but it forms a denser thin film due to the bonding angle close to 90°
when bonded to the -SH group. XPS analysis confirmed that some elements including S were reduced during the annealing and SE analysis indirectly confirmed that the film was dense by increasing the refractive index. Annealed alucone film was occurred thermal polymerization in the high temperature region and carbon ring structure trans the graphene flake by graphitization. Raman and XPS analysis carried out various characterization related to carbon. At the annealing temperature of 750°C, the resistance can be measured while changing from insulator to conductor. Annealed MLD alucone thin film as a hybrid semiconductor material has various potential applications such as electronic, capacitor or thermoelectric devices.

reference


9:30am EM1-WeM7 Molecular Layer Deposition of “Magnesicone”, a Magnesium-based Hybrid Material, as a Matrix Material for Solid Composite Electrolytes, Jeroen Kint, F. Mattelaer, M. Minjauw, Ghent University, Belgium; P. Vereeken, IMEC, Belgium; J. Dendooven, C. Detavernier, Ghent University, Belgium

Porous thin films are a very versatile class of materials for a wide range of applications due to their high (reactive) surface area. Numerous deposition methods are available, yet when conformity on complex 3D structures and sub-nm uniformity and thickness control and are requirements for the envisioned applications, these deposition methods often don’t meet these demands. Atomic and molecular layer deposition (ALD/MLD) are generally accepted as the go-to methods when conformity, uniformity and sub-nm thickness control are necessary conditions. When the application requires porous films, organic/inorganic hybrids (metalcones) can be deposited using MLD, and with a post-treatment, they can be made porous. This has already been shown for alucones. A wide variety of these metalcones exist, yet no Mg-based flavours are available. In this work, MLD and a post-deposition anneal were used to obtain porous MgO thin films.

A novel magnesium-based organic-inorganic hybrid process was developed using magnesium bis-(methylcyclopentadienyl) and ethylene glycol or glycerol. The growth characteristics of both processes were characterized using in-situ ellipsometry. For both flavours of the magnesicone, saturated growth could be achieved in a broad temperature window (100-250°C). The hybrid nature of these films was confirmed using FTIR and EDX. Exposure of these “magnesicone” films to ambient atmosphere was investigated using FTIR. Both flavours reacted with ambient air, absorbing water.

As deposited magnesicone films were annealed in oxidizing ambient at different heating/cooling rates, while being monitored using real-time spectroscopic ellipsometry (RTSE). The influence of the heating/cooling rates on pore formation was extracted from the changes in refractive index (linked to the density) and the film thickness. Three regimes could be discerned. Firstly, moderate heating/cooling rates lead to porous films (corresponding to a sudden drop in density and increase in porosity). Secondly, it was observed that pores collapse when a rapid cool-down takes place, as seen from an increase in density and a decrease in thickness. Finally, heating at high ramp rates causes no pore formation. These findings were backed up by subsequent ellipsometric porosimetry measurements. For high ramp rates (>400°C/h), no pores were formed, whereas at lower ramp rates (<200°C/h) pore formation was confirmed.

A novel process for the deposition of a magnesium-based hybrid organic-inorganic material, “magnesicone” was developed. It’s response to different annealing conditions was investigated using RTSE and EP. By doing so, porous MgO films with porosities up to 45% could be achieved.

9:45am EM1-WeM8 Molecular Layer Deposition of Polyamide Films on Particles Using a Rotating Cylinder Reactor, Tyler Myers, S.M. George, University of Colorado – Boulder

Molecular layer deposition (MLD) utilizes sequential, self-limiting surfaces reactions to deposit polymeric thin films. Depending on the precursors, the MLD polymeric film can be all-organic or a mixed organic-inorganic hybrid film. In this study, all-organic polyamide MLD films are deposited on particles using adipoyl chloride and ethylene diamine as precursors. This polyamide MLD film is designated as Nylon 6,2. The MLD is performed in a rotating cylinder reactor to agitate the particles. The rotating cylinder reactor is also located inside an isothermal enclosure to eliminate cold spots that cause difficulties when using low vapor pressure precursors. The polyamide MLD was performed at low temperatures ranging from 37°C to 80°C. These low temperatures allow the polyamide MLD film to be deposited on thermally sensitive organic particles such as pharmaceutical particles. Using witness wafers in the reactor, the sequential adipoyl chloride and ethylene diamine exposures led to a growth rate of 4 Å/cycle at 67 °C for the Nylon 6,2 MLD film as determined by x-ray reflectivity (XRR) measurements. These growth rates were in good agreement with the film thicknesses measured by transmission electron microscopy (TEM) on inorganic particles (ZrO₂ and TiO₂) and organic particles (cellulose and active charring from liquid ingredients) (See Supplemental Figure 1). The polyamide MLD growth rates were inversely dependent on temperature as observed earlier for previous polyamide MLD and alucone MLD film growth.

The TEM images revealed that the polyamide MLD films were smooth and conformal on the various particle substrates (See Supplemental Figure 1). Fourier Transform Infrared (FTIR) vibrational analysis of the polyamide MLD films revealed the presence of N-H, C-H, C-N, and C=O stretching vibrations and CO-N-H bending modes. X-ray photoelectron spectroscopy (XPS) analysis on witness wafers yielded peaks corresponding to C, N, O, and a small amount of Cl. Energy Dispersive Spectroscopy (EDS) mapping of the polyamide MLD film grown on cellulose particles observed N and Cl in the polyamide coating. The deposition of all-organic polymer MLD films on particles may have many interesting applications because of their high elasticity and chemical stability.

Emerging Materials

Grand Ballroom A-C - Session EM2-WeM

Organic-Inorganic Hybrid Materials

Moderators: Gregory N. Parsons, North Carolina State University, Jonas Sundquist, Fraunhofer Institute for Ceramic Technologies and Systems IKTS

10:45am EM2-WeM12 Vapor Phase Infiltration: A Route for Making Insulating Polymer Fibers Conductive, Mato Knez, CIC nanoGUNE, Spain; I. Azpitarte, CTechNano, Spain

Future technological devices rely in large parts on flexible functional materials. Polymers play an important role for this approach as the combination of low weight and mechanical flexibility makes them unavoidable within this technological concept. However, for a variety of technological approaches, not only the mechanical properties, but also electronic properties of polymers need to satisfy the technological needs.

A promising strategy to implement conductivity into polymer fibers is based on vapor phase infiltration (VPI), if it was successfully applied for an infiltration of a conductive or semiconducting material. VPI is a modification of Atomic Layer Deposition (ALD) which allows synthesis of hybrid materials by infiltration of inorganic materials into organic substrate. With this technique diffusion of precursors into polymeric materials from the gas phase is enforced and yields new composites with inorganic moieties coordinated or covalently linked with the polymeric matrix.

Fibers of poly(p-benzamides), for example Kevlar®, are known since decades and are of great commercial importance primarily because of their exceptional mechanical strength and flexibility as well as an established industrial fabrication process. The polymer gains its mechanical properties through the high molecular order and the intermolecular hydrogen bonds, which in turn makes it very complex to introduce further functionalities into the material. This seriously limits the application range. For example, Kevlar is an electrical insulator and as such by default not suitable as active component in wearable electronic applications.

The present work shows a VPI-based approach towards functionalization of Kevlar fibers in two aspects. In the first instance, electrical conductivity of the intrinsically insulating fibers was induced. This was performed by infiltration of conductive metal oxides. In the second instance the resulting hybrid polymer-inorganic fibers became photocatalytically active upon irradiation with visible light. The photocatalytic effect relies on the insertion of ZnO into the fiber matrix and the chemical interaction between the inorganic and polymeric phase, which eventually result in back-doping of the ZnO with nitrogen hand in hand with the alteration of the electronic structure of the polymeric chain.
Membrane-based organic solvent separations promise a low-energy alternative to traditional thermal separations but require advanced materials that operate reliably in chemically aggressive environments. While inorganic membranes can withstand demanding conditions, they are costly and difficult to scale. Polymeric membranes, such as poly(vinylidene fluoride) (PVDF), are easily manufactured into form factors consistent with large-scale separations (e.g., hollow fibers), but perform poorly in aggressive solvents. Here, a new post-fabrication membrane modification technique, vapor phase infiltration (VPI), is reported that infuses polymer of intrinsic microporosity 1 (PIM-1) with inorganic constituents to improve stability while generally maintaining the polymer’s macroscale form factor and microporous internal structure (Figure 1). The atomic-scale metal oxide networks within these hybrid membranes protect PIM-1 from swelling or dissolving in organic solvents including: tetrahydrofuran, dichloromethane, and chloroform (Figure 2a). This atomic-scale metal oxide network further increases the molecular weight cutoff (MWCO: the smallest molecular weight the membrane “successfully” rejects) in n-heptane and toluene from a MWCO of about 600 g/mol for pristine PIM-1 thin film composite membranes to 204 g/mol for hybrid AlOx/PIM-1 membranes (Figure 2b). The hybrid membranes further retain this MWCO and high levels of rejection (>95%) in solvents that traditionally swell or even dissolve pristine PIM-1 (such as ethanol and tetrahydrofuran). The decrease in MWCO and increase in stability of AlOx/PIM-1 hybrid membranes allows them to perform separations not only between solutes and solvents, but also separations of more challenging systems such as those comprising multiple solvents. For example, the hybrid AlOx/PIM-1 membranes are capable of enriching the toluene concentration in a mixture of 90 wt% toluene, 5 wt% 1,3-trisopropylbenzene, and 5 wt% 1,3-diisopropylbenzene from 90.0 wt% to 97.8 ± 0.3 wt%. In this talk, we will discuss the chemical mechanisms of the infiltration process that we believe create the hybrid structures necessary to support this enhanced stability and separation performance.

Organic-inorganic hybrids generated by infiltration synthesis, a hybridization technique derived from atomic layer deposition (ALD), can feature various unique materials properties and functionalities not observed in conventional materials. In this work, we discover that the ZnO-infiltrated polymer hybrid nanocomposite thin film exhibits remarkably enhanced light-activated gravimetric gas sensing properties. The hybrid nanocomposite thin film prepared by infiltrating molecular ZnO in SU-8, a common negative-tone, epoxy-based polymer resist, features up to 20-fold greater gravimetric responses to oxygen and water vapors compared with control ZnO or SU-8 thin films in a dark environment. Additional 50 – 500% enhanced responses are detected under ultraviolet (UV) irradiation. Experimental interrogation shows that the increased gravimetric response of the hybrid film is attributed not only to the higher analyte accessibility to active ZnO sites in the matrix but also to the reversible, light-induced increase in surface potential and adsorption energy. Density function theory calculations suggest that the UV enhancement is caused by the light-induced, reversible generation of hydrophilic fluorooantimonic acid from the photocatalyst generator (PAG) residual in the SU-8 film matrix. A gravimetric sensor based on the ZnO-infiltrated SU-8 hybrid nanocomposite film effectively classifies water and oxygen environments with sub-10 mTorr detection limits. The results highlight the utility of infiltration synthesis for advancing sensor technologies.

Emerging Materials

Grand Ballroom E-G - Session EM3-WeM

Epitaxial Growth and III-V Materials

Moderator: John Ekerdt, University of Texas at Austin

A challenge to atomic layer epitaxy (ALEp) is the mismatch between low-temperature windows for certain ALD precursors and the higher thermal budgets required for epitaxial growth. A common solution is to use precursors with higher ALD temperature windows, but these do not necessarily exist for all desired chemistries. Therefore, ALEp is limited to material combinations having low lattice mismatch and high temperature precursor stability. To circumvent this challenge, we are exploring a new technique called pulsed-heating ALD (PH-ALD) that interleaves individual ALD growth cycles with a fast, high-temperature heat pulse using a high-
power resistive heater. As proof-of-concept, we study epitaxial growth of ZnO on c-plane sapphire using a diethylzinc (DEZ) / water chemistry. DEZ is known to decompose above about 180°C, and the DEZ:H2O system cannot be grown epitaxially on c-sapphire with traditional thermal ALD approaches. Here, we explore the use of pulse heating to temperatures of up to 900°C and for various ALD cycle ratios. X-ray diffraction shows the best epitaxial alignment and ZnO rocking curve, with a FWHM of <0.5˚, at a pulse heating temperature of 900°C and a 1:1 ALD pulse ratio. Crystal quality and intensity drop significantly with pulse temperatures less than 800°C. Reducing the ALD cycles:heat pulse ratio also lowers crystal quality, but epitaxial growth is retained down to 5 ALD cycles per heat pulse. Photoluminescence spectroscopy of the D0x band shows that the 1:1 PH-ALD samples have 1.3x the intensity of post-deposited ZnO ALD and 10x the intensity of as-deposited ZnO ALD. Finally, we study growing a few layers of PH-ALD ZnO followed by standard thermal ALD with no pulse heating. We find that a template layer of only 20 PH-ALD cycles is sufficient to template ZnO epitaxial films up to 100 nm thick.

11:00am EM3-WeM13 Growth of AIN Barriers in Al/AIN/Al SIS Josephson Junctions by Low Temperature Atomic Layer Epitaxy, Charles Eddy, Jr., U.S. Naval Research Laboratory; D.J. Pennachio, J. Lee, A. McFadden, University of California, Santa Barbara; S.G. Rosenberg, U.S. Naval Research Laboratory; Y.H. Chang, C.J. Palmstrom, University of California, Santa Barbara
Superconductor-Insulator-Superconductor (SIS) structures are of increasing interest for the creation of Josephson junctions that can serve as the basis for quantum qubit transmons, which hold significant promise for quantum computing technologies. Traditionally, these devices have been developed using amorphous AlOx in Al/AlOx/Al structures and have enabled fundamental demonstrations of transmon performance. However, improved performance may be expected with an epitaxial insulator. Even in these structures, the nature of the superconductor/substrate interface and the superconductor/ambient interface limits coherence and, consequently, qubit performance.

In an effort to address this challenge, we employ low temperature atomic layer epitaxy (ALEp) to grow crystalline AIN insulators on crystalline aluminum films. Smooth epitaxial aluminum films are grown by evaporation on cryogenically-cooled, buffered GaAs(001) substrates [1]. These epitaxial surfaces are "frozen" using a low temperature nitridation atomic layer process (ALP) before the samples are ramped to 300°C for low temperature ALE of AIN using semiconductor grade trimethylaluminum and UHP argon and nitride gas for 900°C and a 1:1 ALD pulse ratio. Crystals with high quality ALD grown insure good interface quality and enable fundamental demonstrations of transistor performance. However, improved performance may be expected with an epitaxial insulator. Even in these structures, the nature of the superconductor/substrate interface and the superconductor/ambient interface limits coherence and, consequently, qubit performance.


11:15am EM3-WeM14 Investigating Plasma Parameters and Influence of Argon to the Crystallinity of GaN Films Grown by Plasma-Assisted ALD, Deepa Shukla, I. Saidjafarzoda, A. Mohammad, B. Brian Willis, N. Biyikli, University of Connecticut
Gallium nitride has attracted significant attention in (opto)electronic and RF-chip industry mainly due to its wide bandgap of about 3.4 eV, which revolutionized lighting as well as high-power and high-frequency electronic devices. However, conventional crystal growth methods employ substrate temperatures typically around ~1000°C, which is incompatible with post-CMOS integration and other temperature-sensitive substrates. To broaden the application spectrum of GaN, lower temperature growth methods are highly needed. Plasma-assisted ALD (PA-ALD) is a strong candidate which also provides unmatched conformity and uniformity performance. In this work, GaN thin films were grown on Si (100) substrates using PA-ALD. Trimethylgallium (TMG) and N2 /H2/Ar plasma were used as metal precursor and co-reactants. GaN deposition experiments were performed with and without Ar plasma at different plasma powers (150W, 175W, 200W) and different temperatures ranging within 120-240°C. An optimal growth per cycle (GPC) of ~0.7Å was observed at 150°C using in-situ ellipsometer and was confirmed by ex-situ x-ray reflectivity (XRR) analysis. The hexagonal wurtzite crystal peaks were observed in the grazing-incidence x-ray diffraction (GI-XRD) analysis. Among the films deposited, GaN samples grown at 240°C showed crystalline character with a preferred orientation along the (002) plane signifying GaN crystal formation temperature above 200°C. Moreover, the absence of Ar gas in the plasma showed a notable reduction in the peak intensities of (100) and (101) crystal domains, resulting in a predominantly preferred (002) orientation. Effect of plasma power and plasma duration on the quality of GaN was evaluated with N2/H2-plasma during deposition cycles. No considerable change in crystal orientation was observed with change in plasma power, however increase in plasma duration from 10 to 40 sec suppressed the formation of (100) and (101) domains, resulting in a dominant (002) diffraction peak.

11:30am EM3-WeM15 Ultrathin GaN Epilayer by Low-temperature Atomic Layer Annealing and Epitaxy, Wei-Chung Kao, W.-H. Lee, Y.-T. Yin, National Taiwan University, Republic of China; J.-S. Shyu, Academia Sinica; H.-C. Lin, M.J. Chen, National Taiwan University, Republic of China
Conventionally, GaN epilayers have been grown by metal-organic chemical vapor deposition (MOCVD) at very high growth temperatures (>1000°C) in order to achieve high crystal quality. However, the high-temperature growth technique is challenged by thermal stress and cracking due to the large difference in thermal expansion coefficients between GaN and the substrate. In this research, high-quality GaN heteroepitaxys has been achieved by atomic layer annealing and epitaxy (ALAE) at a low growth temperature of 300°C. By introducing a layer-by-layer, in-situ He/Ar plasma treatment at a low plasma power in each cycle of atomic layer deposition, the crystal quality of the GaN is significantly enhanced. The significant improvement of the GaN crystal quality is attributed to the effective annealing effect due to ion bombardment from the He/Ar plasma to each as-deposited layer. The nano-beam electron diffraction, high-resolution transmission electron microscopy, and atomic force microscopy reveal a high-quality nanoscale single-crystal GaN epilayer with a very smooth surface. The full width at half-maximum of the X-ray rocking curve of the GaN epilayer is as low as 168 arcsec. This research demonstrates the impact of the low-temperature ALAE technique for growing high-quality nanoscale GaN epilayers for high-performance solid-state lighting, solar cells, and high-power electronics.

11:45am EM3-WeM16 High Quality ALD Formation of Group-III Nitrides and their Applications in ETO-based Thin Film Solar Cells, Xinke Cheng, H. Wei, P. Qiu, M. Peng, S. Liu, Y. He, Y. Song, Y. An, University of Science and Technology Beijing, China
Group-III nitrides semiconductors (GaN, AlN, InN), grown by high-temperature MOCVD or MBE methods, have been widely utilized in optoelectronic and microelectronic devices. However, due to some benefits such as low deposition temperature, precise thickness control and good conformality, ALD has attracted much attention in the fabrication of group-III nitrides materials. Here, we report high-quality growth of nitrides using plasma-enhanced ALD (PEALD). By optimizing the ALD window parameters, single-crystal AlN nitride thin films can be achieved. Their optical, electrical, structural properties and impurities content are in detail characterized.

For some thin film solar cells using ETO glass substrates, interface modification and/or carrier transportation have been mainly focused for the improvement of device performance. So far, various metal oxides (TiO2, Al2O3, ZnO, SiO2, etc) deposited by ALD have been used in the CIS and perovskite solar cells. However, there are still no reports about the application of group-III nitrides in ETO-based thin film solar cells using quantum dots (QDs) and perovskite composites as solar energy materials. In this study, we successfully fabricated high quality GaN and AlN onto the ETO glass substrates at a very low temperature by PEALD. It was found that the existence of ultrathin AlN coating can efficiently reduce quantum loss in the interface between TiO2 and CdS/CdTe QDs. An enhancement of open-circuit voltage from 0.642 V to 0.673 V, corresponding to an increase of conversion efficiency from 8.51% to 9.31% under AM 1.5G irradiation, is achieved for an insertion of AlN. The results show that the ultrathin-AlN layer works...
TiO₂/QDs surfaces can create an energy barrier for electron injection from QDs into the electrolyte and the injected electron from TiO₂ into the electrolyte, thus effectively inhibiting photo-generated electron recombination. The ALD GaN thin film on FTO glass here could serve electron transport layer for perovskite solar cells. The results indicate that GaN thin-film thickness has a significant effect on the electron transport and collection of the photovoltaic cells. It is found that the devices based on the 50-cycle GaN thin-film (~4 nm) show the best cell performance with efficiency of 15.2%. The introduction of group-III nitrides has shown promise for improving solar cell performance and could open up a way in designing novel thin film solar cells.

References
The intensity of the raw powders also appears to increase with Al₂O₃ ALD. Interestingly, the photoluminescence emergence of secondary phases and photoluminescence properties are powder for up to 2 weeks in direct water exposure. XRD confirms no decomposition to SrO, Al(OH)₃, and Al₂O₃ within 3 hours of water exposure. 10 nm coatings are found to protect the phosphor; M. Uyaner, M. Losego, Georgia Institute of Technology.

The metal oxide-metal heterostructure is reported to be effective for improving the performance of photocatalysts. Zinc oxide (ZnO) is widely used as a photocatalyst due to its proper band gap (3.3 eV) that enables outstanding semiconducting characteristics. Also, ZnO has been fabricated in a variety of forms including thin film, particles or nanowires, that are useful for catalysis with high surface area. Palladium (Pd) is considered as a well-matching metal with ZnO to synergistically improve photocatalytic performance with an appropriate Fermi level. Recombination of generated charges is prohibited since Pd catches excited charges from ZnO leading to highly improved photocatalytic efficiency.

In this study, ZnO nanorods coated with Pd nanoparticles is evaluated as photocatalysts. The ZnO nanorods are prepared by hydrothermal growth on silicon wafers. The Pd nanoparticles are fabricated by atomic layer deposition (ALD). ALD Pd is conducted using Pd(II) hexafluoroacetylectonate (Pd(Hfac)₂) precursor with forminal in a customized ALD chamber (ICOT Inc.). The growth temperature is 90ºC. To evaluate the photocatalytic performance, the degradation rate of methylene blue is measured under the ultraviolet radiating condition. As a result, it is confirmed that the degradation rates are accelerated with the ZnO-ALD Pd catalysts compared to bare ZnO nanorods. This result will be discussed in more details at the presentation.

The proof-of-concept devices demonstrated include: 1) Generation and switch between two arbitrary ALBs that follow different caustic trajectories; 2) simultaneously achieving efficient and broadband generation and dynamic control of ALBs across the visible region. Our study opens up the possibility of creating ultra-compact, fine-spatial-resolution, and flat-profile structured light beams. The two ALD samples and two control samples were tested at the same level of humidity. Furthermore, we observed stress-corrosion cracking of the ALD-polymer interfaces. By conducting wedge tests in different levels of humidity, we found that although ALD increased equilibrium interfacial fracture toughness at all humidity, the effect decreased as humidity increased. Scanning-electron microscopy (SEM) of samples after testing provided additional evidence of corrosion cracking of the ALD-polymer interface. These results suggest a new application of ALD for engineering the mechanical properties of chemically inert surfaces.

Epoxy Interfaces using ALD Surface Treatments, W. LePage, E. Kazyak, A. Gayle, J. Wang, M.D. Thouless, N.P. Dasgupta, University of Michigan

Polymer interfaces play a critical role in a variety of applications, including consumer products, structural components, biomedical devices, and flexible electronics. In many cases, polymers need to be bonded with adhesives to create structural joints or multi-layer structures. For adhesives to efficiently wet and bond to a substrate, the surface free energy of the substrate must be equal or higher than the surface free energy of the adhesive. However, the surface energy of most polymers is low, which makes adhesion difficult. Thus, there often is a need to increase the surface energy of a polymer without changing the bulk mechanical and chemical properties.

In this work, we demonstrate that atomic layer deposition (ALD) can be applied on poly(methyl methacrylate) (PMMA) and fluorinated ethylene propylene (FEP) to increase their surface energies and, hence, to increase the interfacial fracture toughness when bonded to an epoxy adhesive. ALD alumina films were deposited on each type of polymer to modify the surfaces towards high energy surfaces of metal oxide. Transmission-electron microscopy (TEM) and atomic-force microscopy (AFM) were used to study the film morphology on the polymers. These indicated that the ALD treatment increased the surface roughness and changed the surface chemistry by vapor-phase infiltration (VPI). The increase in surface energy after ALD was measured by the sessile-drop test with water, ethylene glycol and glycerol.

The interfacial fracture toughness of each polymer-epoxy interface was measured using a customized motor-controlled wedge tester. After ALD film growth, the interfacial fracture toughness of the PMMA-epoxy and FEP-epoxy interfaces increased by factors of up to 7 and 60, respectively. The two ALD samples and two control samples were tested at the same level of humidity. Furthermore, we observed stress-corrosion cracking of the ALD-polymer interfaces. By conducting wedge tests in different levels of humidity, we found that although ALD increased equilibrium interfacial fracture toughness at all humidity, the effect decreased as humidity increased. Scanning-electron microscopy (SEM) of samples after testing provided additional evidence of corrosion cracking of the ALD-polymer interface. These results suggest a new application of ALD for engineering the mechanical properties of chemically inert surfaces.
2:30pm AAI-WeA5 Tunable Plasmonic Colours Preserved and Modified by Atomic Layer Deposition of Alumina, J-M. Guay, A. Lesina, G. Killaire, University of Ottawa, Canada; Peter Gordon, Carleton University, Canada; C. Hahn, University of Ottawa, Canada; S. Barry, Carleton University, Canada; L. Ramunno, P. Berini, A. Weck, University of Ottawa, Canada

Decorative colouring of pure silver and gold surfaces is an important application for jewelry and coinage, particularly collector's coins. In order to preserve the purity of these substrates, colours created by adding materials like inks or patinas should be avoided. A novel colouring method that uses careful laser treatment to create a surface with nanoscale, plasmonic features has been developed but the bare surface features undergo dynamic coalescence that dulls and shifts the available colour palette. This work demonstrates that colours generated by nanostructured plasmonic silver surfaces can be preserved and tuned by overcoating with alumina films by ALD. These colours were observed to shift with increasing alumina film thickness.

Two types of laser treatment were used to create surface features on silver that gave rise to colours in the visible spectrum: burst and nonburst. For burst surfaces, the colours first degrade with increasing alumina film thickness but recover at larger thicknesses with an expanded colour range. For nonburst surfaces the colours degraded with increasing thickness without any recovery. Underlying periodic structures specific to the burst method are responsible for this behavior. FDTD modeling of representative surfaces, including the conformal alumina layer, helps explain these colour changes. For alumina thicknesses smaller than the nanoparticle gaps, the changes in the perceived colours are due to the perturbation of plasmonic resonances. For alumina thicknesses larger than the nanoparticle gap, the change in colours originates primarily from the complex reflectance response of the alumina coated structures and modification of the refractive index of the resulting complex surface.

The coloured surfaces were evaluated for applications in colourimetric and radiometric sensing showing large sensitivities of up to 3.06/nm and 3.19 nm/nm, respectively. The colourimetric and radiometric sensitivities are observed to be colour dependent.

2:45pm AAI-WeA6 TFE of OLED Displays by Time-Space-Divided (TSD) PE-ALD and PE-CVD Hybrid System, Bongsik Kim, JUSUNG Engineering, Republic of Korea

In this paper we introduce a time space divided (TSD) plasma assisted deposition equipment available to in-situ atomic layer deposition (ALD) and chemical vapor deposition (CVD) process and a thin film encapsulation (TFE) of organic light emitting diodes (OLEDs) deposited by the above mentioned equipment, TSD hybrid system. Figure 1 represents a structure of the TSD hybrid system. The 1st electrode, included protruding rod-like metal bars, is composed of two types of gas injection systems and the protruded parts are inserted into holes of the 2nd electrode. Each electrode is rigorously designed considering the hollow cathode effect (HCE), the plasma sheaths and the surface area for optimizing RF power efficiency. The remote plasma source cleaning (RPSC) system enables an in-situ cleaning to etch away the film residue in the chamber.

Figure 2 show cross-sectional views of two kinds of TFEs in particle environments. Figure 2-1 represents seam defect of general SiO film, deposited by using the hexamethyldisiloxane (HMDSO), and figure 2-2 represents the cross-sectional view of the coated particle by flowable SiO, named pp-HMDSO. Because deposited films generally grow to the direction from which the gas is flowing, almost films which are deposited by the general CVD process cannot avoid to growth of the defect from the blind spot. So, we, by controlling process conditions, fabricated the TFE which includes flowable SiO film in order to fill the blind spot and hardened the film to reinforce the adhesion to neighboring layers.

Figure 3 showed the characteristics of the TFE structure of the figure 2-2, deposited by the TSD hybrid system at low substrate temperature (<100°C). In order to suppress film defects, induced by particles, first, we coated particles with the pp-HMDSO and then, the ALD SiO layer is deposited as a second barrier and a buffer layer between the SiO and the SiN. Even if the film coats conformally without any defect, the permeation of water and oxygen through the film bulk direction would be occurred. So, finally, we coated with the CVD SiN layer for an ultra-low water vapor transmission rate (WVTR). As shown in figure 3, the WVTR of <5×10⁻⁸ g/m²/day at 40 °C/100%RH conditions is measured by MOCON Aquitran2 and also we get the optical transmittance (>95%) and the low film stress (<100Mpa) data.

The TSD hybrid system can make various kinds of thin films, such as CVD SiN, SiON, SiO, ALD SiO, SiN, etc. by in-situ ALD or CVD process and also can control characteristics of thin films widely by changing the process conditions. By TSD hybrid system, manufactured by JUSUNG engineering, we expect to contribute the OLED industry development.

3:00pm AAI-WeA7 Tailoring the Ferroelectricity of ZrO2 Thin Films using Ultrathin Interfacial Layers Prepared by Plasma-Enhanced Atomic Layer Deposition, Sheng-Han Yi, B.-T. Lin, T.-Y. Hsu, J. Shieh, M.J. Chen, National Taiwan University, Republic of China

In recent years, HfO2/ZrO2-based ferroelectric thin films have been recognized as promising candidates for memory devices and negative-capacitance field-effect-transistors to achieve a further improvement of device performance. The ferroelectricity(PE) and antiferroelectric(AF) properties of these CMOS-compatible oxides have been confirmed to originate from the polar orthorhombic phase and non-polar tetragonal phase, respectively. In this work, we report the significant impact of ALD-deposited interfacial layers on the microstructures and FE/AF properties of ZrO2 thin films. Sub-nanometer interfacial layers deposited by plasma-enhanced atomic layer deposition are intentionally introduced between the ZrO2 thin film and the electrodes of metal-insulator-metal structures to tailor the crystalline phase and ferroelectricity of the ZrO2. The interfacial layers boost the formation of orthorhombic ZrO2, leading to significant enhancement of the ferroelectricity with a significant increment of the remanent polarization. On the other hand, another interfacial layers contribute to the formation of tetragonal ZrO2, giving rise to the dramatic transformation of ZrO2: from ferroelectricity to antiferroelectricity. The findings indicate that interface engineering by ALD is an effective and advantageous approach to tailor the PE/AF characteristics of materials.

3:15pm AAI-WeA8 Spin-Hall-Active Platinum Thin Films Grown Via Atomic Layer Deposition, Michaela Lammel, IFW Dresden, Germany; R. Schlitz, Technische Universität Dresden, Germany; A.A. Amuson, IFW Dresden, Germany; S. Schlcht, FAU Erlangen, Germany; T. Tynell, IFW Dresden, Germany; J. Bachmann, FAU Erlangen, Germany; G. Woltersdorf, Martin-Luther-Universität Halle-Wittenberg, Germany; K. Nielsch, IFW Dresden, Germany; S.T.B. Goennenwein, Technische Universität Dresden, Germany; A. Thomas, IFW Dresden, Germany

Due to its strong spin orbit coupling platinum (Pt) is often used as a spin injector/detector in spintronics. We used atomic layer deposition (ALD) to fabricate platinum thin films on a substrate consisting of liquid phase epitaxy grown yttrium iron garnet (YFeO3; YIG) on gadolinium gallium garnet (Gd:GaO2). Magnetotransport experiments were performed on the YIG/Pt heterostructures in three mutually orthogonal rotation planes, revealing the fingerprint of spin Hall magnetoresistance. Samples with different platinum thicknesses were used to estimate the spin transport parameters of the Pt thin films. Comparing the values for the spin Hall angle as well as the spin diffusion length with literature we found the spin diffusion length in the ALD Pt thin films agrees well with results reported for high-quality sputtered platinum. The spin Hall magnetoresistance however is smaller by approximately a factor of 20. Clearly, further experiments will be required to optimize the interface quality in such ALD-based heterostructures. Nevertheless, our results show that spin Hall active Pt thin films can be fabricated by ALD featuring an appropriate quality for spin transport.

The reported results build the framework for establishing conformal coatings for non-planar surface geometries with spin Hall active metals via ALD which in the future can provide the basis for developing 3D spintronic devices [1].

In this work, we investigate the performance of TiN TSV interconnects. We etch arrays of 60 μm diameter TSVs in 495 μm thick 6-inch silicon wafers by deep reactive ion etching using the Bosch process (Omega I2L, Aviza Technology). We use 2 μm thick oxide layers both as a mask (top side) as well as an etch stop layer (back side). We coat the TSVs with a TiN layer by ALD (SUNALE R-150B, Picosun), performing 2,500 cycles at 450°C, using TiCl₄ and ammonia as precursors and nitrogen as a carrier gas. The superconducting behaviour of this TiN layer has been previously investigated for layers deposited by plasma-ALD [3], but this technique is not applicable for coating high-aspect-ratio trenches (the aspect ratio of our TSVs is about 8:1). Therefore, we use thermal ALD in this work.

Initially, the deposited layers did not become superconducting even at 0.1 K. Optimization of the ALD process by tuning precursor pulse/purge times finally led to superconducting TiN layers with a Tc of approximately 0.85 K. The room temperature sheet resistance for a 47 nm thick layer is approximately 60 Ω/sq, as measured on the flat area of the samples. We confirm the conformality of the TiN inside vias using scanning electron microscopy. Future plans include increasing the Tc as well as integrating TSVs on chips with other structures (resonators, qubits).

advanced 3D-transistor structures in VLSI manufacturing. Targeting this application, we evaluated three non-halogenated boron compounds for their suitability as ALD precursors: boric acid (B(OH)3), trimethyl borate (B(OCH3)3), and hafnium borohydride Hf(BH4). The B(OH)3, Hf(BH4), and B(OCH3)3 were used in combination with trimethyl aluminum to deposit BAl2-xO3 ALD films, and the Hf(BH4) was used with H2O to deposit HfB2O4 films. We evaluated the ALD surface chemistries for these processes using in-situ quartz crystal microbalance (QCM) and Fourier transform infrared spectroscopy (FTIR) studies. The QCM measurements also confirmed self-limiting behavior and helped to optimize the ALD timing. The resultant boron containing nanocomposite films were analyzed using X-ray photoelectron spectroscopy (XPS), secondary ion mass spectrometry (SIMS), ellipsometry, and electrical capacitance measurements. The boron content in the BAl2-xO3 and HfB2O4 composite films was controllable by tuning the ALD cycle ratio and the precursor sequence. We performed rapid thermal annealing of composite films as a function of temperature and determined the B-diffusion in silicon as well as changes in the optical properties of the BAl2-xO3 and HfB2O4 layers. Here we will present a detailed investigation of ALD methods for creating B-containing layer for shallow dopant application.

3:00pm AA2-WeA7 Impact of Medium Energy Ions on the Microstructure and Physical Properties of TiN Thin Layers Grown by Plasma Enhanced Atomic Layer Deposition (PE-ALD).

S. Belachew, C. Vallette, A. Bisey, Marceline Bonvalot, LTM-UGA, France

Titanium nitride TiN has been extensively used in common microelectronic devices as an electrode material, where it serves as an interfacial connection material between a device and the metallic contacts used to drive it, while simultaneously preventing any diffusion of the metal into silicon. TiN is also involved in biological Micro-Electro-Mechanical Systems (bioMEMS) as an electrode material, for instance in cardiac pacemakers or neural stimulation applications, thanks to its unequalled conducting properties at reduced dimensions, as compared to traditional noble metals, and also thanks to its high corrosion resistance to human body fluids. For such applications, a deep knowledge of the microstructural properties of TiN are of utmost importance.

In this work, the impact of processing parameters on the physical properties of TiN has been investigated in details. TiN thin layers (20 nm) have been prepared on SiO2 (100 nm)/Si substrates by Plasma Enhanced ALD (PE-ALD), using TDMAT as a precursor and N2 as a plasma gas. The PE-ALD setup used for this purpose has been equipped with an original Atomic Layer Etching (ALE) kit positioned at the back-face of the substrate holder, which allows medium energy ions to be extracted from the plasma during the ALD growth. Several bias values ranging from 0 W to 90 W have thus been tested during the plasma step to investigate the impact of ions with varying kinetic energies on the morphological properties of TiN.

The rugosity of as deposited TiN layers has been obtained from AFM measurements. XRD and XRR analyses have been systematically carried out in order to evaluate the texturation, crystallinity and mechanical stress in the layer. The impact of medium energy ions during TiN growth has been correlated to the rugosity, density and residual stress. These results will be discussed in view of potential applications of TiN as an electrode material in microelectronic devices.

3:15pm AA2-WeA8 ALD Process Monitoring for 3D Device Structures, Jiangtao Hu, Lam Research Corp.

Semiconductor device structures have become increasingly complex, requiring new measurement techniques to support manufacturing. Measurement of high aspect ratio (HAR) structures requires a response signal to depth and profile, and the bottom may be invisible to top-down optical signals. Likewise, certain thick films are opaque to optical thickness measurement. Lateral processing steps occur too deeply in a structure to be visible, and thin conformal deposition films need to be characterized inside the feature.

For ALD applications, a critical requirement is to have complete and uniform coverage from the top to the bottom of a 3D device. A thinner or incomplete deposition at the bottom of a device can often lead to high leakage and high failure rates. Conventional optical thickness measurements of ALD films can identify thickness variations at the top of a high aspect ratio (HAR) device but may not identify process deviations at the bottom of this type of device.

Monitoring ALD using mass metrology is a potential solution to this issue. The direct measurement of mass change due to process enables detection of process excursions. Measurement of the wafer mass before and after a process is a simple and direct means of monitoring and control. This is particularly true for ultra-opaque films and complex stacks, film density monitoring, and conformal and ALD/sidewall deposition, where traditional optical metrology techniques may not be effective.

More importantly, mass metrology directly monitors the amount of material change in a device across the entire HAR structure while conventional optical film metrology typically measures these changes on a test pad or blanket test wafer. Mass metrology instrumentation can detect low coverage of ALD films at the bottom of a HAR device which otherwise would be missed using optical measurement. For example, we can compare mass change induced by flow rate reduction on blanket or patterned wafers (Fig 2). Significant mass change occurs on patterned wafers after a 3% of flow rate reduction, while on patterned wafers this deviation is pronounced after a 1% reduction.

In this discussion, we will discuss how Mass Metrology can be used to monitor ALD process variations in 3D semiconductor devices, along with the applications and benefits of this technology in ALD.

Emerging Materials
Regency Ballroom A-C - Session EM1-WeA

Ternary and Quaternary Oxide Materials
Moderator: Bart Macco, Eindhoven University of Technology

1:30pm EM1-WeA1 Rhenium(III)-based Ternary Oxides: Novel Materials from Straightforward Synthesis via ALD Comprising Uncommon Reaction Pathways, Max Gebhard, S. Letourneau, D. Mandia, D. Chaudhury, A. Vangvas-Gil, A. Mane, A. Sattelberger, J.W. Elam, Argonne National Lab Oxides of rhenium, such as ReO and ReO2, exhibit high conductivity in the order a 10–10 (Ωcm), close to that of metals. This property is of high importance regarding applications with high demands on tailored electrical properties. An example of such an application are microchannel plates (MCPs), which are used as signal amplifiers in advanced detector units for UV-light (space aviation) and photoelectronics (XPS). Also, MCPs play a crucial role in the development of large area photodetectors. MCPs are comprised of a glass capillary array. By applying a material with high secondary electron emission (SEE) yield, an incident electron/photon can create an electron avalanche that eventually increases the signal-to-noise ratio and thereby allows the detection of event starters. Below the SEE layer, a resistive coating must be applied, exhibiting the right range of resistivity to avoid electrons from being drained and to act as electron supplier. This material must be operable at elevated temperatures, i.e. it must have a low temperature-coefficient of resistance (TCR) to avoid decreased device performance at higher temperatures. Metal nanoparticles embedded in an AlOx-matrix have been shown to provide the right resistivity for MCP application. However, their TCR values demand for the development of materials with improved properties.

In this context, the development of ternary oxides, comprising ReO, units with electrical conductivity and other components with dielectric character, provide a good opportunity to overcome the limitations of existing coatings.

Herein, we present two new materials, namely ReAl2O3 and ReSiO3. These materials, where ReSiO3 is reported for the first time, have been deposited using ALD and detailed mechanistic studies revealed that during the growth, reductive elimination reactions cause the formation of uncommon but stable Re(III) oxide species. Furthermore, fascinating mechanisms allowing the formation of unsaturated hydrocarbons and hydrogen, were identified during the growth. The processes were explored in detail employing in-situ tools such as QCM, QMS and FTIR. Furthermore, the materials were fully characterized in terms of composition, structure, and electrical properties using XPS, RBS/HFS, XRD, XRR and XAS.
this work, ALD of NiAl_yO_x was studied using the nickelocene (NiCp_2)/O_3 and trimethyl aluminum (TMA)/H_2O precursor systems for nickel oxide and aluminum oxide respectively. Deposition of NiAl_yO_x was performed using ALD by alternating the cycle ratio of nickel oxide to aluminum oxide ALD on 200mm substrates. The process does not involve BEOL thermal budget or partial reactions associated with plasma oxidation and can therefore be applied to areas close to nanostructures. Moreover, the ALD process allows for films to be ~6x thinner than the commercial TiN film, which forms Mg-B-O* surface species that undergoes further reaction to stabilize B_2O_3 by dosing Mg(Cp)_2 after the B(OCH_3)_3 pulse which forms Mg-B-O* surface species that undergoes further reaction to stabilize B_2O_3 occurring by dosing Mg(Cp). The incorporation of Zr(OTBu)_4 and Zr(TiBu)_4 led to improved tunability of the zirconium concentration but also resulted in lower thicknesses by other well-accepted processing methods. Several other zirconium precursors were investigated for inclusion into ALD PZT including zirconium tert-butoxide [Zr(OTBu)_4] and zirconium ethylmethylzirconium tetramethylzirconium [TMAZ]. The incorporation of Zr(OTBu)_4 and Zr(TiBu)_4 led to improved tunability of the zirconium concentration but also resulted in a lower overall growth rate of PZT.

References

2:00pm EM1-WeA3 Understanding Growth Characteristics of ALD NiAlO_x: The Role of Ozone, Jonathan Baker, J. Schneider, S.F. Bent, Stanford University

ALD of ternary films has grown in interest as applications requiring the advantages of ALD (including sub-nanometer thickness control, uniformity, compositional control and conformality) have demanded more complex materials. However, depositing ternary materials by ALD is typically more complicated than the binary ALD systems from which the ternary ALD systems are derived. As a result, the growth of a ternary material by ALD often deviates from ideal growth behavior described by the “rule of mixtures.” In this work, ALD of NiAlO_x was studied using the nickelocene (NiCp_2)/O_3 and trimethyl aluminum (TMA)/H_2O precursor systems for nickel oxide and aluminum oxide respectively. Depositions of NiAlO_x were performed using the supercycle method, allowing a wide range of compositions to be achieved by altering the cycle ratio of nickel oxide to aluminum oxide ALD cycles. However, composition as a function of cycle ratio was found to be nickel deficient compared to the ideal rule of mixtures. The cause of the observed non-ideality was explored to help elucidate the ALD reaction mechanisms. Characterization of the films revealed that the growth rate of aluminum oxide was significantly enhanced following a NiCp_2/O_3 cycle. Modification of the rule of mixtures to account for the enhanced growth rate of Al_2O_3 resulted in a model which fits observed properties well, accounting for both the observed compositions and growth rates. In addition, NiAlO_x has shown to be an interesting case study for understanding the deposition of ternary materials of first-row transition elements grown with O_3. Similar to ALD of FeO_x and MnO_x, which utilize metalloocene-derivatives and O_3, NIO ALD requires long precursors and O_3 exposures to achieve fully self-limiting growth. The root cause for this behavior is hypothesized to stem from the use of the strong oxidizer O_3, which may oxidize the metal centers to higher oxidation states or otherwise introduce extra oxygen into the film. For the deposition of NiAlO_x, low O_3 exposures were used to develop the initial NiAlO_x system. To understand the effect of O_3 exposure on the deposition of the ternary ALD film and binary NiO-x system, growth of NiAlO_x as a function of O_3 exposure was explored with an aim to understand the ALD reaction mechanisms at play when using O_3 as an oxidizer. The effect of high O_3 exposures will be discussed.

2:15pm EM1-WeA4 Atomic Layer Deposition of B_xMg_{1-x}O Films: Progress Towards Shallow Boron Doping - David Mandia, D. Choudhury, M. Gebhard, Argonne National Laboratory; (U, Northwestern University; A. Mirollo, D. J. Ulman, Argonne National Laboratory; Argoje National Laboratory)

Preparation of B_xMg_{1-x}O films through an ABC-type ALD program employing bis(cyclopentadienyl)magnesium (Mg(Cp)_2), trimethyl borate (B(OCH_3)_3), and water as precursors is presented herein. Thin film properties are extensively characterized by X-ray photoelectron spectroscopy (XPS), diffraction (XRD), and reflectivity (XRR). Moreover, optical properties of the as-grown and post-deposition annealed films are assessed through spectroscopic ellipsometry measurements with a particular focus on the effective optical properties of the B_xMg_{1-x}O film, which is an attractive shallow-boron dopant source material. Instead of using the highly toxic diborane (B_2H_6) as a boron doping source, the present work employs ALD to generate MgO-stabilized B-O_x in a more environmentally friendly manner. In situ neutron diffraction analysis of the B_xMg_{1-x}O thin films shows that the film thickness increases with increasing Mg concentration. The growth of B_xMg_{1-x}O films on silicon in concert with post-deposition annealing treatments along with follow-up spectroscopic ellipsometry and high resolution XPS/depth profiling measurements were performed to characterize the composite films’ optical and electronic structural properties, respectively. The thermal ALD synthesis of B_xMg_{1-x}O composite films on silicon in concert with post-deposition annealing is a potentially viable approach towards shallow-boron dopant layer or junction formation through the stable B-O_x component and could find use in solid state electronics applications.

2:30pm EM1-WeA5 Enhanced Doping Control of Metal Oxide Thin Films Using a Modified ALD Process - E. Levrin, IBM TJ Watson Research Center; Yohei Ogawa, ULVAC, Japan; M. Frank, M. Hopstaken, E. Cartier, IBM T.J. Watson Research Center; J. Rozen, IBM Research - Almaden; M. Hatanaka, ULVAC, Japan; J. Rozen, IBM T.J. Watson Research Center

The introduction of controlled amounts of dopants into logic and memory devices has been extensively used in nanoelectronics. In order to alter the properties of a material and make it suitable for a specific application, Doping thin films can be complicated because of the difficulty to control thickness and dopant gradient distribution. Atomic Layer Deposition allows for excellent thickness control and doping is usually achieved by varying the cycle ratio of two metal oxides during deposition, M1O and M2O, in what are called super-cycles. We refer to this as ‘modified ALD’ and will provide examples for the synthesis of B_{2x}Mg_{1-x}O composite films on silicon in concert with post-deposition annealing treatments along with follow-up spectroscopic ellipsometry and high resolution XPS/depth profiling measurements.

In figure 1, a comparison of the film properties is presented. Here, HfZrO thin films with varying dopant levels of Zr are synthesized with Mg dopants. The thermal ALD synthesis of B_{2x}Mg_{1-x}O composite films on silicon in concert with post-deposition annealing is a potentially viable approach towards shallow-boron dopant layer or junction formation through the stable B-O_x component and could find use in solid state electronics applications.
analyzed with spectroscopic ellipsometry and XPS. Thin-film HfO2-based ferroelectric devices with different dopants will be evaluated.


2:45pm EM1-WeA6 As Deposited Epitaxial LaNiO3 and La[Ni,Cu]O3 with Controllable Electric Properties. Henrik Hovde Sønstebry, University of Oslo / Argonne Natl. Labs, Norway; O. Nilsen, H. Fjellvåg, University of Oslo, Norway.

Depositing complex oxides by ALD is a rapidly emerging field, with new materials with excellent properties published every month. LaNiO3 is a perovskite-type oxide with metallic behavior, thought to play a major role in functional multilayer stacks and integrated electronics. Although routes for depositing LaNiO3 has been reported in literature, an annealing step has always been necessary to obtain epitaxial films. In many applications this hinders monolithic device integration, and can cause unwanted strain effects and cracking.

In this presentation we show a facile route for direct epitaxial growth of LaNiO3 by thermal ALD at temperatures as low as 250 °C. The films show excellent conductive properties as deposited, with specific resistivity as low as 10^4 Ohm cm. The functional properties of the films are slightly improved upon annealing, reaching specific resistivities in the 10^3 Ohm cm order of magnitude. Furthermore, we show that the order of precursor pulses plays a fundamental role in obtaining high quality as deposited epitaxial films.

LaNiO3 is a remarkable member of the RENiO3 series of materials (RE = La, Pr, Nd, Sm, Eu, Gd, Dy, Ho, Er, Y, Lu), as it is the only member that remains metallic to 0 K. All other members observe a metal-insulator-transition (MIT) temperature varying from ~100 K (Pr) to ~600 K (Lu). Controllably tuning the MIT is highly awaited by the community.

In this presentation we also show how substitution by Cu on the Ni-site alters the electronic properties and MIT temperature of LaNiO3. We show that a full range of compositions is attainable, from LaCuOx to LaNiO3, and that the electronic properties vary smoothly over this composition range. ALD can be used to obtain a remarkable cation composition control. Furthermore, we hypothesize on the reason behind the varying properties of this material system, and try to explain it by showing how oxygen vacancies are introduced by copper substitution. This may help shed light on the surprising properties of LaNiO3 itself, but more importantly the films can be directly used in applications where a tunable MIT is necessary.

This presentation highlights the use of complex oxide ALD as a real alternative to MBE, with several key advantages such as conformality and low temperature deposition.

3:00pm EM1-WeA7 Time Dependence of Pyroelectric Response in Ferroelectric Hf0.58Zr0.42O2 Films, Sean Smith, M.D. Henny, M. Rodriguez, Sandia National Laboratories; J. Ihlefeld, University of Virginia.

HfO2 based ferroelectrics are a promising family of ferroelectrics stable as thin films. The ferroelectric response in HfO2 thin films is associated with a metastable orthorhombic phase, typically seen in films < 30 nm thick, stabilized by doping, electrode material, deposition conditions and annealing. Thin HfO2 based ferroelectrics are attractive for use in memory, energy harvesting, and sensing applications, however the polarization response of the thinnest of these films, ~5 nm, has been reported to be unstable over time. In this work we show that the pyroelectric response of 5 nm Hf0.58Zr0.42O2 with TaN electrodes decreases logarithmically after biasing, decreasing from an initial value of ~5.8 µCm-2K-1 to ~40 µCm-2K-1 in the first 24 hours. While films 10 nm and thicker have a pyroelectric response that is constant on the same timescale.

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3:15pm EM1-WeA8 Tailoring Nickel Oxide Conductivity by Introducing Transition Metals: From First-principles to Experimental Demonstration, Md. Anower Hossain, T. Zhang, D. Lombart, University of New South Wales, Australia; Y. Zakaria, Hamad Bin Khalifa University, Qatar; P. Burr, University of New South Wales, Australia; S. Rashkeev, A. Abbaldah, Hamad Bin Khalifa University, Qatar; B. Hoex, University of New South Wales, Australia.

Transition metal oxides, such as MoO3, WO3, V2O5 and NiO have shown potential for application as hole-selective passivating contact for silicon (Si) solar cells. Among them, NiO is a p-type semiconductor which possesses notoriously poor hole-conducting properties. Doping of metal oxides with multivalent metal cations is one of the most effective ways to improve electronic band structure properties of resulting ternary metal oxides because dopants create favorable defect states crucial for charge carrier transport. Therefore, we used first-principles density functional theory (DFT) computations as a predictive tool to identify suitable dopants. The density of states, defect formation energies, and thermodynamic transition levels of various charge states within the band gap of doped NiO were calculated and promising dopants were identified. We synthesized Al-doped NiO (AlNiOx), and Zn-doped NiO (ZnNiOx) films onto 2.0 cm p-Si wafers using atomic layer deposition (ALD). We used a supercycle approach alternating N (10, 25, 50) NiO cycles and 1 Al2O3 cycle. Cross-sectional transmission electron microscopy and energy dispersive x-ray spectroscopy mapping showed conformal films with the elemental distribution of Ni, O, and Al. X-ray photoelectron spectroscopy (XPS) measurements revealed the presence of Ni2+, Ni4+ and Al3+ oxidation state in the films. The Al content was found to scale with the number of AlO, ALD cycles. The density of the Ni2+ and Al3+ oxidation state increased with the increasing number of AlO, ALD cycles, confirming the Al incorporation into the host lattice of NiO. However, a significantly higher Al concentration was found in the AlNiOx film as was expected from the supercycle ratio. This was resulting from a significantly higher growth cycle per cycle of AlO, compared to NiO. While undoped NiO was found to be resistive, the AlNiOx films showed the contact resistivity of 41.6 - 113 mΩcm2 after annealing in a rapid thermal processing furnace at 200-300 °C under N2 for 10 minutes. In addition, the ZnNiOx films deposited by supercycle of NiO and ZnO cycle also showed the Ohmic contact with p-Si. The ZnNiOx films were also thermally stable up to 500 °C with the best contact resistivity of approximately 21.5 mΩcm2. This indicates a significant improvement of contact performance as compared to the undoped NiO counterparts. This work demonstrates that a ternary AlNiOx and ZnNiOx films are suitable hole-selective passivation contact for the p-Si solar cells.
precursors are solids at room temperature, require high temperature vapor. Recently, MoS2 ALD using molybdenum hexafluoride (MoF6) has been reported, providing a high vapor density liquid at room temperature, and hydrogen sulfide (H2S) has been demonstrated. While the nucleation of MoS2 during chemical vapor deposition (CVD) is understood, the nucleation of MoS2 ALD using MoF6 and H2S on dielectric surfaces has yet to be explored. Unlike films grown by high temperature CVD, the ALD process does not require a high growth temperature, allowing for the growth of thin films on a variety of molybdenum and sulfur precursors. However, many of these precursors are solids at room temperature, requiring high temperature vapor transport, and may not be suitable for result in carbon incorporation. Recently, MoS2 ALD using molybdenum hexamfluoride (MoF6), a high vapor pressure liquid at room temperature, and hydrogen sulfide (H2S) has been demonstrated. For device applications, the ALD MoS2 must be integrated with dielectrics. While the nucleation of MoS2 during chemical vapor deposition (CVD) is understood, the nucleation of MoS2 ALD using MoF6 and H2S on dielectric surfaces has yet to be explored. Unlike films grown by high temperature CVD, ALD MoS2 is amorphous and must be annealed to crystallize the film. In this study, we utilized in situ quartz crystal microbalance (QCM) and Fourier transform infrared (FTIR) spectroscopy measurements to investigate the first few cycles of MoS2 ALD on Al2O3 and HFO2 surfaces prepared in situ by ALD. Self-limiting growth of MoS2 was observed on a wide range of dielectric surfaces including alumina, and hafnia. The MoS2 nucleation was found to depend strongly on the substrate. These studies provide insight into the low-temperature ALD process and provide guidance for the integration of MoS2 and other ALD TMDC films.

2.00pm NS-WeA3 Plasma-Enhanced Atomic Layer Deposition of Transition Metal Dichalcogenides: From 2D Monolayers to 3D Vertical Nanofins, Ageeth Bol, Eindhoven University of Technology, Netherlands

Two-dimensional (2D) materials are being studied intensively due to their unique electronic, optical, and catalytic properties and the wide range of potential applications arising from their layered crystal structures. However, the majority of studies focus on only a few of the large group 2D materials, such as the semimetallic graphene, insulating h-BN, and semiconducting MoS2. Semiconducting 2D materials, in particular, are promising for electronic applications including field-effect transistors (FETs), photodetectors, and sensors. HfS2 and ZrS2, members of the transition metal dichalcogenide (TMDC) group, are indirect band gap semiconductors that have recently emerged as potential alternatives to MoS2 and other 2D semiconductors.1 They have an indirect band gap suitable for many semiconductor applications, 1.7–1.8 (ZrS2) or 1.8–2.1 eV (HfS2),2 which can be directly grown on a variety of substrates, including oxides, metals, and sulfides. Single-crystalline substrates, such as sapphire and muscovite mica, enable tailoring the morphology and texture of films and even epitaxial growth. Due to the sensitivity of HfS2 and ZrS2 towards oxidation, we demonstrate encapsulation of the sulfide films “in situ” with an AlGrown oxide layer using an oxidant-free process. We are currently studying the use of HfS2 and ZrS2 films as photodetectors to highlight the potential of the films for electronic applications.

(XPS) and Raman spectroscopy (Figure 2). The quality and the composition of the films were studied using Rutherford back scattering (RBS). It was observed that TMTCs (TiS₃ and NbS₃) can be synthesized using plasma-enhanced ALD using H₂S plasma as co-reactant at low temperatures, while TMDCs (TiS₂ and NbS₂) were synthesized by both plasma-enhanced ALD (at high temperatures) and thermal ALD. The morphology and crystallinity of the synthesized films were investigated using scanning electron microscopy (SEM) and transmission electron microscopy (TEM), which revealed the two-dimensional and nano/poly-crystalline nature of the films. Our experiments show that ALD enables the controlled synthesis of both TMDCs and TMTCs at low temperatures over large scales, which opens up new avenues to include both TMDCs and TMTCs in nano- or optoelectronic applications.

1 W. Hao et al., 2D Mater. 6, 012001 (2018).
2 J.O. Island et al., 2D Mater. 4, 022003 (2017).

3:00pm NS-WeA7 ALD Boron Nitride Coated and Infiltrated Carbon Materials for Environmental Applications, W. Hao, C. Journet, A. Brioude, Université Lyon, France; H. Okuno, Université Grenoble-Alpes, France; Catherine Marichy, Université Lyon, France

Atomic Layer Deposition (ALD) has proven to be an effective approach for surface modification and fabrication of carbon based heterostructures [1]. Nevertheless, ALD BN coating of carbon material has been poorly studied up to date. Our group recently reported a two-step ammonia-free ALD approach for BN allowing the coating of various substrates such as inorganic and polymeric nanostructures [2,3]. While successful deposition of BN layers on carbon nanomaterial has been realized, it has been observed that some BN precursor diffuses into some polymers [4].

Herein various carbon nanostructures (nanoparticles, nanotubes, nanofibers) coated with ALD are discussed. The inertness of highly graphitic carbon inhibiting the initiation of ALD growth, the influence of the crystalline nature of the substrate on the BN coating is investigated in term of growth and structure, using different graphitized/amorphous carbon supports. Nucleation delay and impact on the crystalline quality (amorphous, turbostratic, hexagonal phase) of BN films are observed as a function of the degree of graphitization. Furthermore, obtained from vapor infiltration of polymers, BN-carbon hybrid structures are briefly introduced. The obtained materials are characterized by advanced electron microscopy and related techniques. Finally, the potential of such a coating to improve the oxidation resistance of carbonaceous material is demonstrated.

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