Plasma XPS: a New Operando Metrology for Semiconductor Process Development and Control

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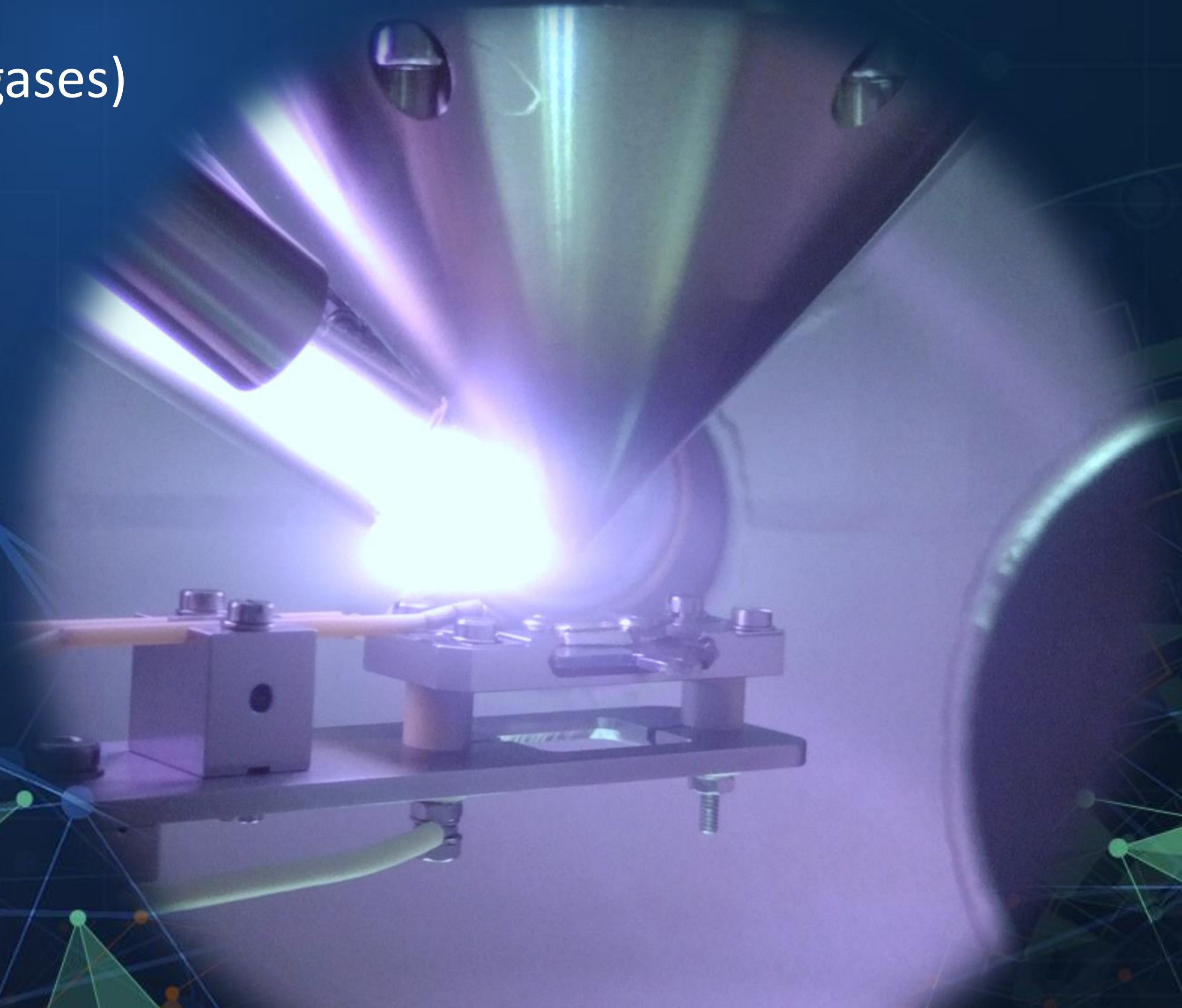
- XPS of solids (in UHV)
- XPS of gases (and solids in gases)
- XPS in liquids
- **XPS in plasmas**



Outline

- Motivation: NIST CHIPS R&D Metrology program and beyond
- Prior efforts and current state
- Experimental
- Application Examples
- Plasma diagnostics
- Summary

Disclaimer

This work was performed with funding from the CHIPS Metrology Program, part of CHIPS for America, National Institute of Standards and Technology, U.S. Department of Commerce.

- Statements and responses to questions about advanced microelectronics research and development programs in this presentation:
    - Are informational, pre-decisional, and preliminary in nature.
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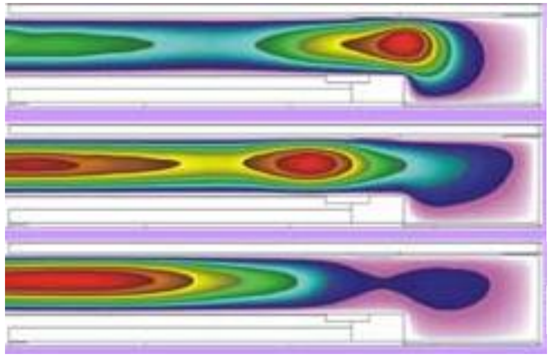
    - Are subject in their entirety to any final action by NIST or the Department of Commerce.
- Nothing in this presentation is intended to contradict or supersede the requirements published in any future policy documents or Notices of Funding Opportunity.

Motivation

The need for *in situ* (nanoscale) characterization of surface/interface morphologies *during* plasma treatments



Plasma-liquid-solid interactions, chemistry and (nano-)materials synthesis

Image credit: M. Kushner. Uni. Michigan

Plasma catalysis

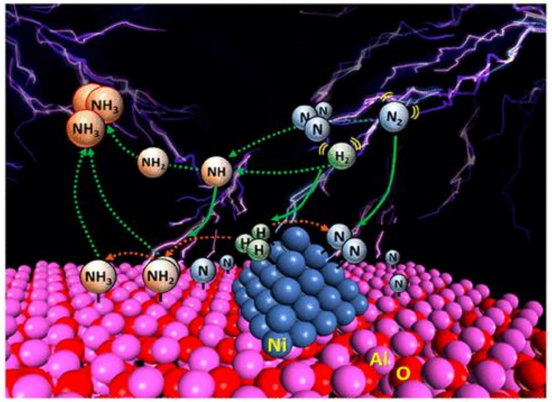
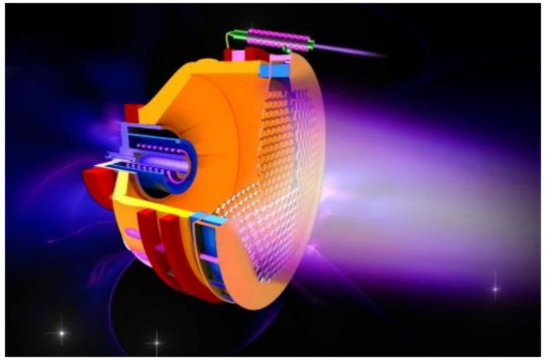


Image credit: Xin Tu, ACS Catalysis

Aerospace



https://iopscience.iop.org/

Semiconductor processing

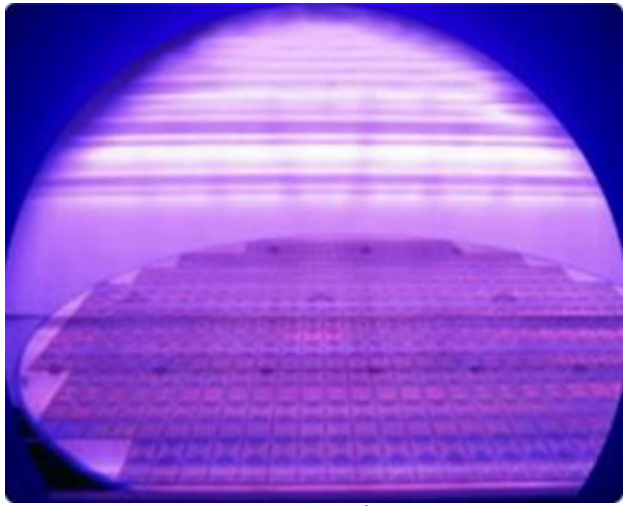


Image: Picotech.com

Biomedical

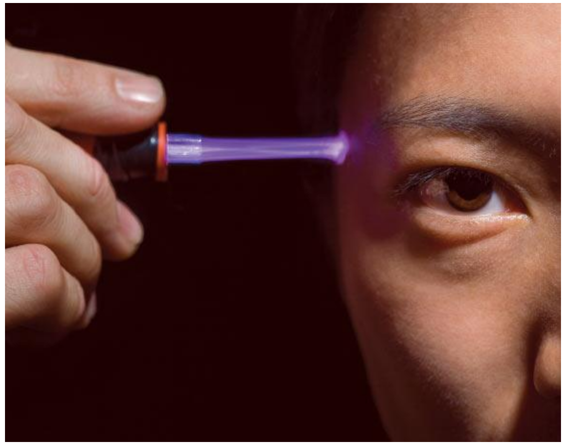
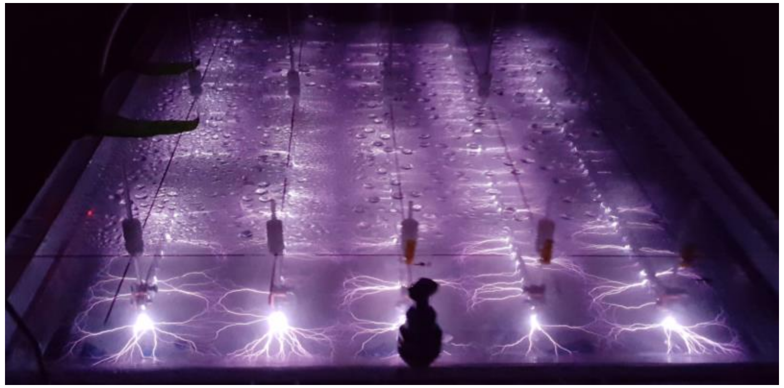


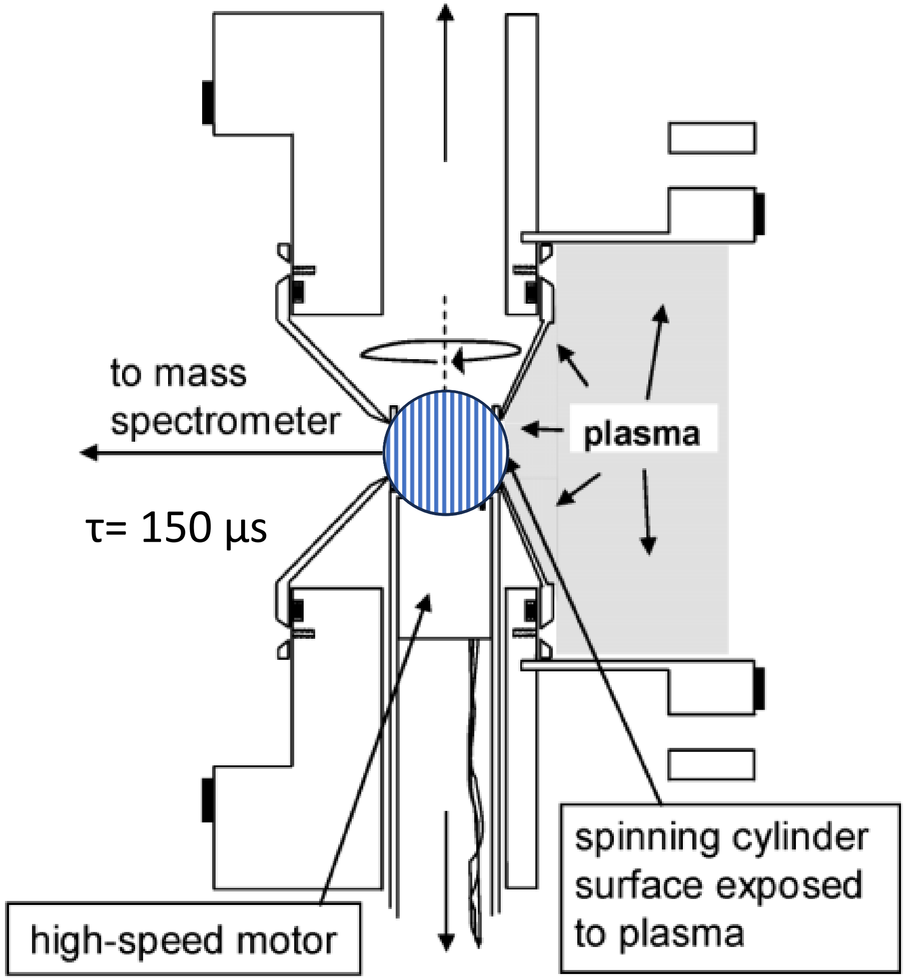
Image credit: Texas A&M University

Remediation technologies



Courtesy photo/Clarkson University

Prior efforts: spinning wall approach



τ= 150 µs

200 000 rpm

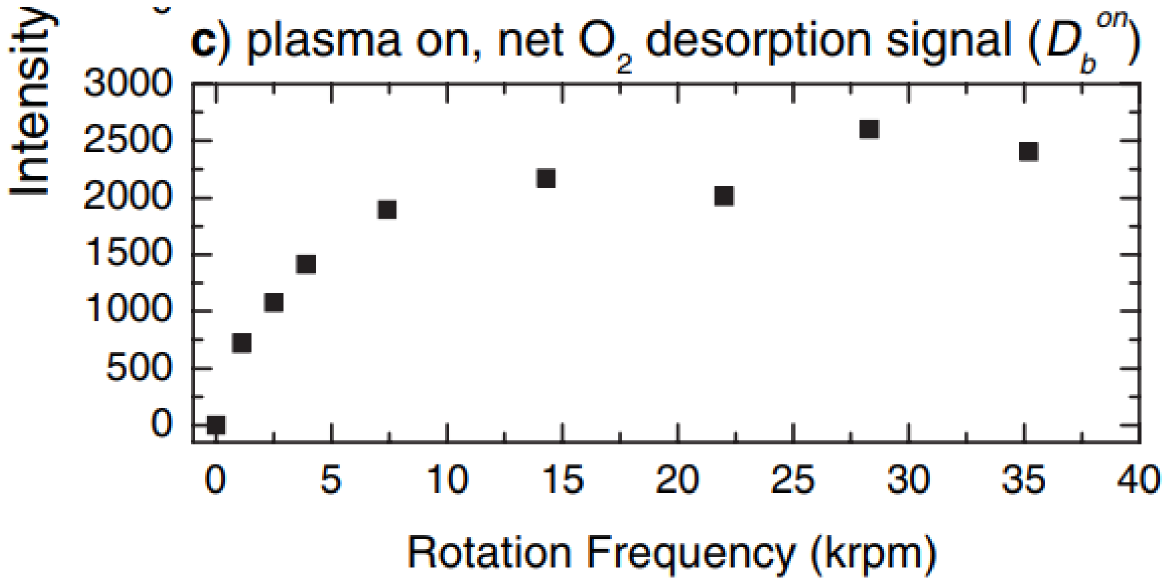
PRL **96,** 018306 (2006) PHYSICAL REVIEW LETTERS

Plasma-Surface Reactions at a Spinning Wall

P. F. Kurunczi, J. Guha, and V. M. Donnelly
Department of Chemical Engineering University of Houston, Houston, Texas 77204, USA
(Received 18 July 2005; published 13 January 2006)

$$O_{(g)} + S \rightarrow O_{(ads)}$$

$$2O_{(ads)} \xrightarrow{k_r} O_{2(g)} + 2S,$$



Plasma XPS: current state

The Journal of Physical Chemistry C
pubs.acs.org/JPCC — Article

Operando XPS for Plasma Process Monitoring: A Case Study on the Hydrogenation of Copper Oxide Confined under h-BN

J. Trey Diulus,* Andrew E. Naclerio, Jorge Anibal Boscoboinik, Ashley R. Head, Evgheni Strelcov, ...ran R. Kidambi, and Andrei Kolmakov*

JVST A — LETTER — pubs.aip.org/avs/jva

***Operando* XPS in reactive plasmas: The importance of the wall reactions**

Cite as: J. Vac. Sci. Technol. A 43, 040401 (2025); doi: 10.1116/6.0004569
Submitted: 14 March 2025 · Accepted: 24 April 2025 ·
Published Online: 15 May 2025

J. Trey Diulus,[1,a)] Ashley R. Head,[2] Jorge Anibal Boscoboinik,[2] and Andrei Kolmakov[1,a)]

JVST A — LETTER — pubs.aip.org/avs/jva

Toward the origins of binding energy shifts and "satellites" formation during plasma-XPS measurements

Cite as: J. Vac. Sci. Technol. A 44, 020405 (2026); doi: 10.1116/6.0005249
Submitted: 18 December 2025 · Accepted: 26 January 2026 ·
Published Online: 17 February 2026

J. Trey Diulus,[1] Ashley R. Head,[2] Jorge Anibal Boscoboinik,[2] Carles Corbella,[3] Alexander Tselev,[4] and Andrei Kolmakov[3,a)]

LANGMUIR
pubs.acs.org/Langmuir — Article — Open Access

In Situ Ambient Pressure Photoelectron Spectroscopy Study of the Plasma–Surface Interaction on Metal Foils

Sam Taylor,* Filip Hallböök, Robert H. Temperton, Jinguo Sun, Lisa Rämisch, Sabrina Maria Gericke, Andreas Ehn, Johan Zetterberg, and Sara Blomberg*

Cite This: Langmuir 2024, 40, 13950–13956 — Read Online

Review of Scientific Instruments — ARTICLE — pubs.aip.org/aip/rsi

Extending ambient pressure x-ray photoelectron spectroscopy to plasma studies: A custom-built plasma source apparatus

Cite as: Rev. Sci. Instrum. 96, 065203 (2025); doi: 10.1063/5.0249456
Submitted: 18 November 2024 • Accepted: 13 May 2025 •
Published Online: 5 June 2025

Yang Gu,[1,2] Zhehao Qiu,[1] Shui Lin,[1,2] Yong Han,[2] Hui Zhang,[3] Zhi Liu,[1,2,a)] and Jun Cai[1,2,a)]

SSS Surface Science Spectra — ARTICLE — pubs.aip.org/avs/sss

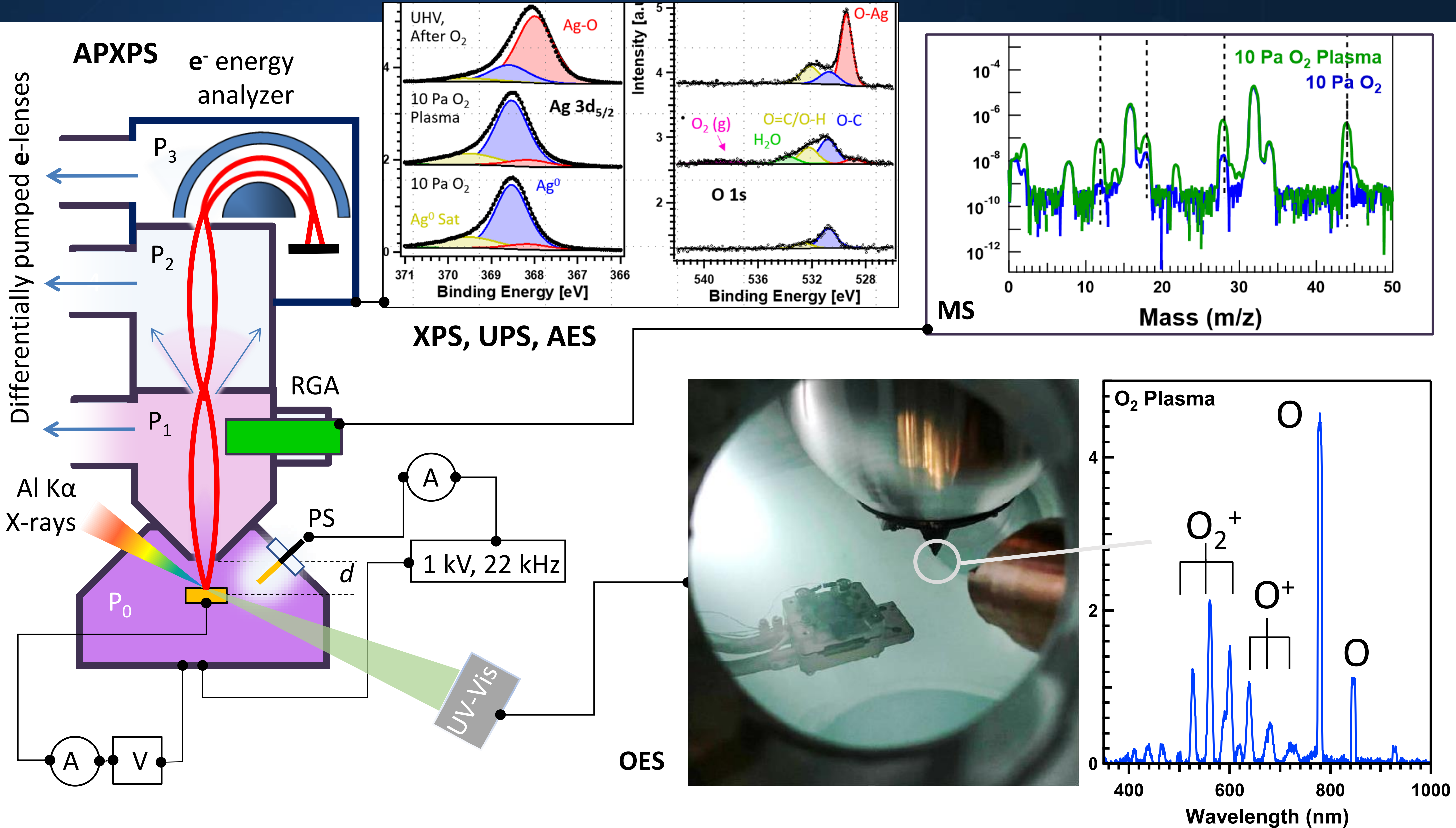
***In situ* NAP-XPS study of plasma-enhanced silver oxidation and reduction reactions**

Cite as: Surf. Sci. Spectra 32, 014005 (2025); doi: 10.1116/6.0004223
Submitted: 22 November 2024 · Accepted: 12 March 2025 ·
Published Online: 27 March 2025

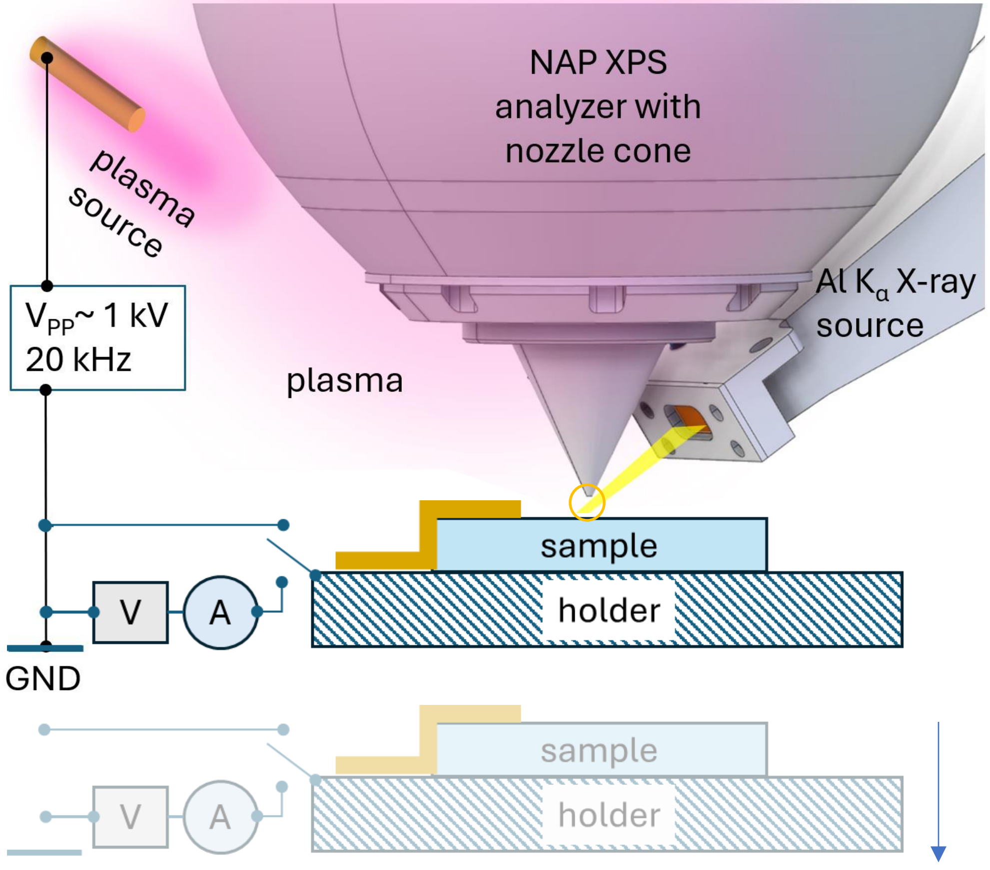
Paul M. Dietrich[a)] and Andreas Thissen

Experimental setup

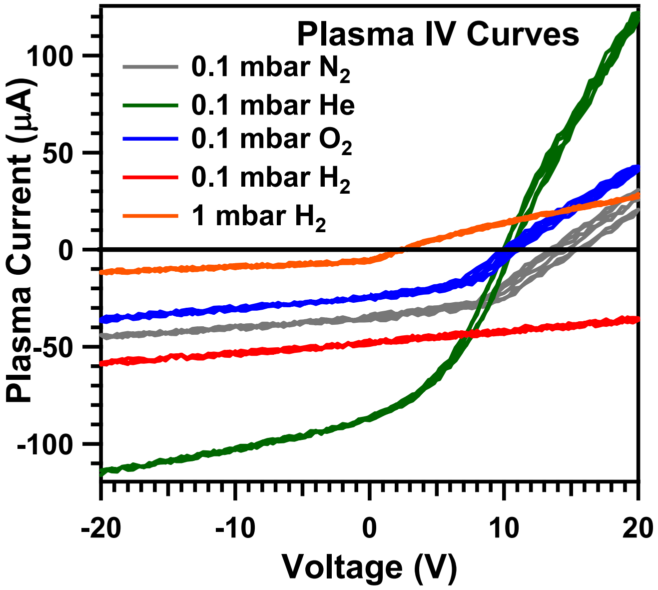
BNL/CNF



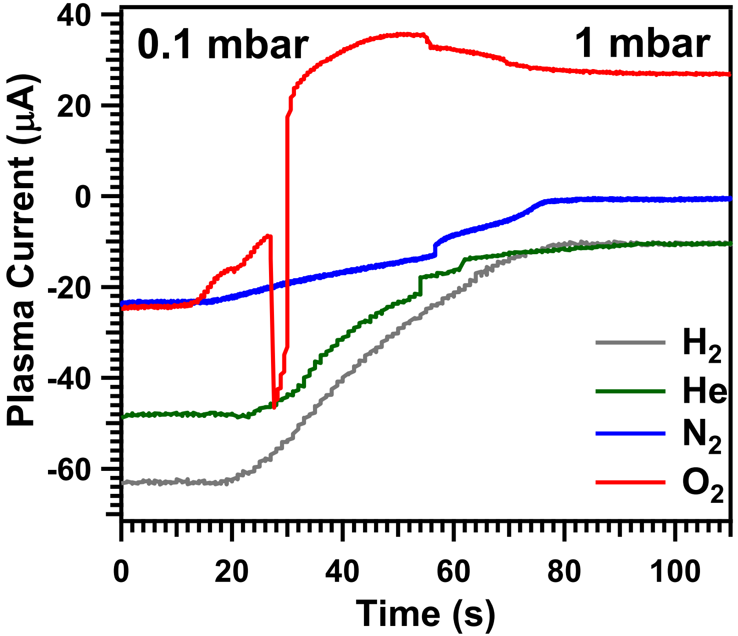
Experimental setup



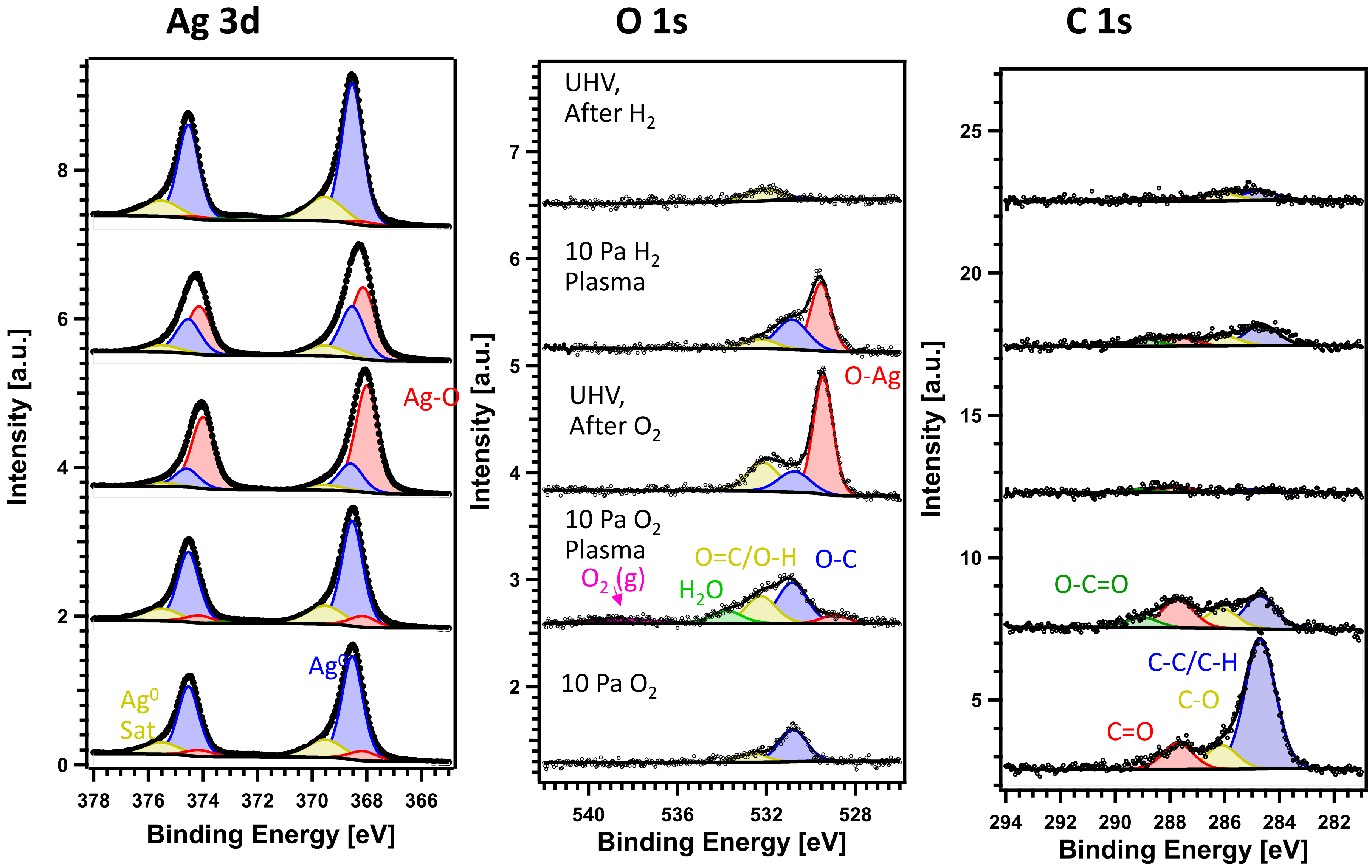
moved out of focus for the gas phase analysis



Complementary Langmuir probe-like electrical measurements for plasma characterization



Application Example: Cleaning/Oxidation/Reduction/Wall reactions



AgOx is reduced by H2 plasma

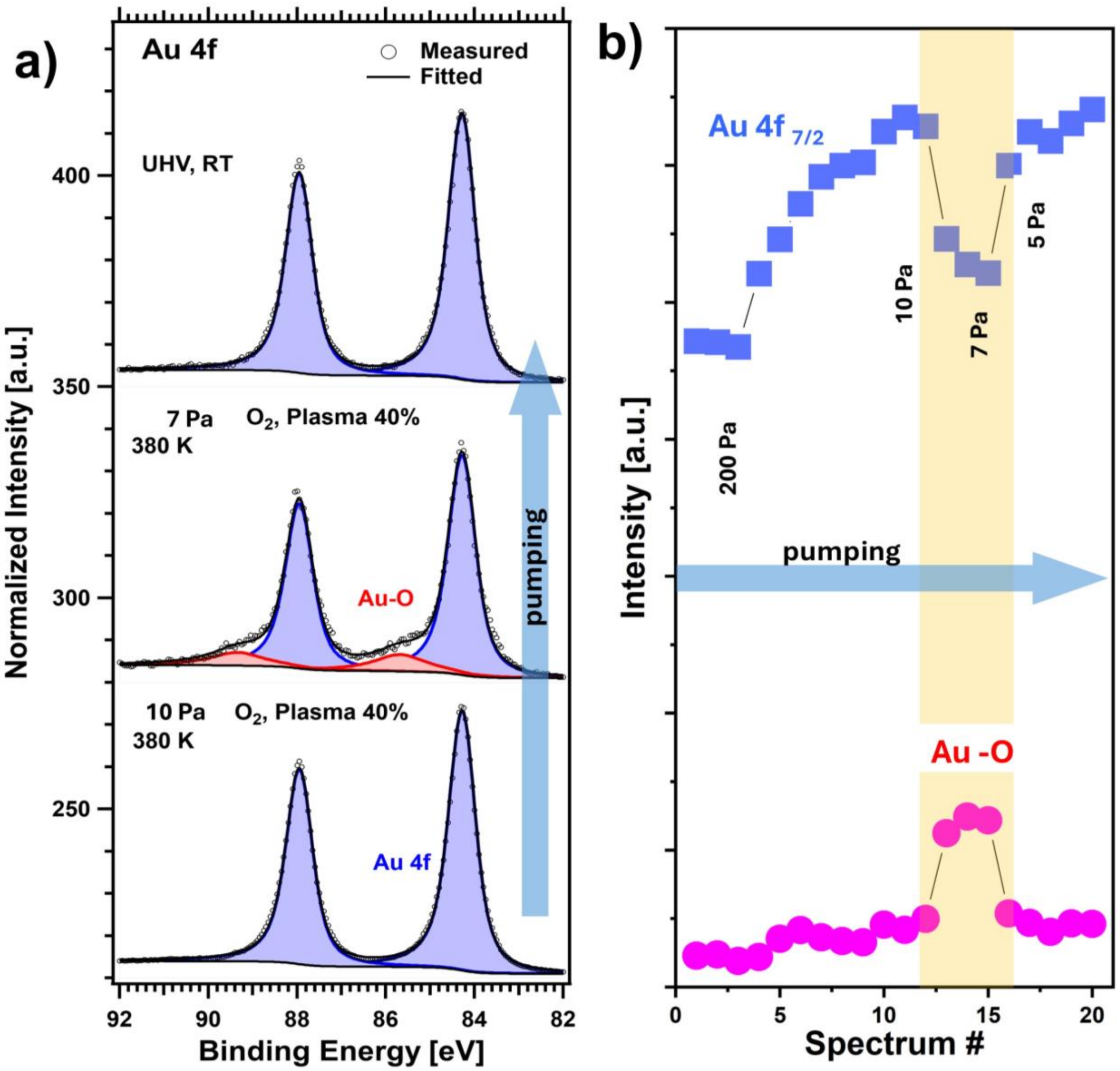
H_2 plasma induces some contamination again due to the parasitic plasma-induced wall reactions

C-contaminations are completely removed by O_2 plasma

O_2 plasma cleans and then oxidizes Ag to AgO_x

Initial contaminated and partially oxidized Ag.

Application Example: Detection of unstable "states"



Au oxide is **unstable in UHV and at elevated** temperatures

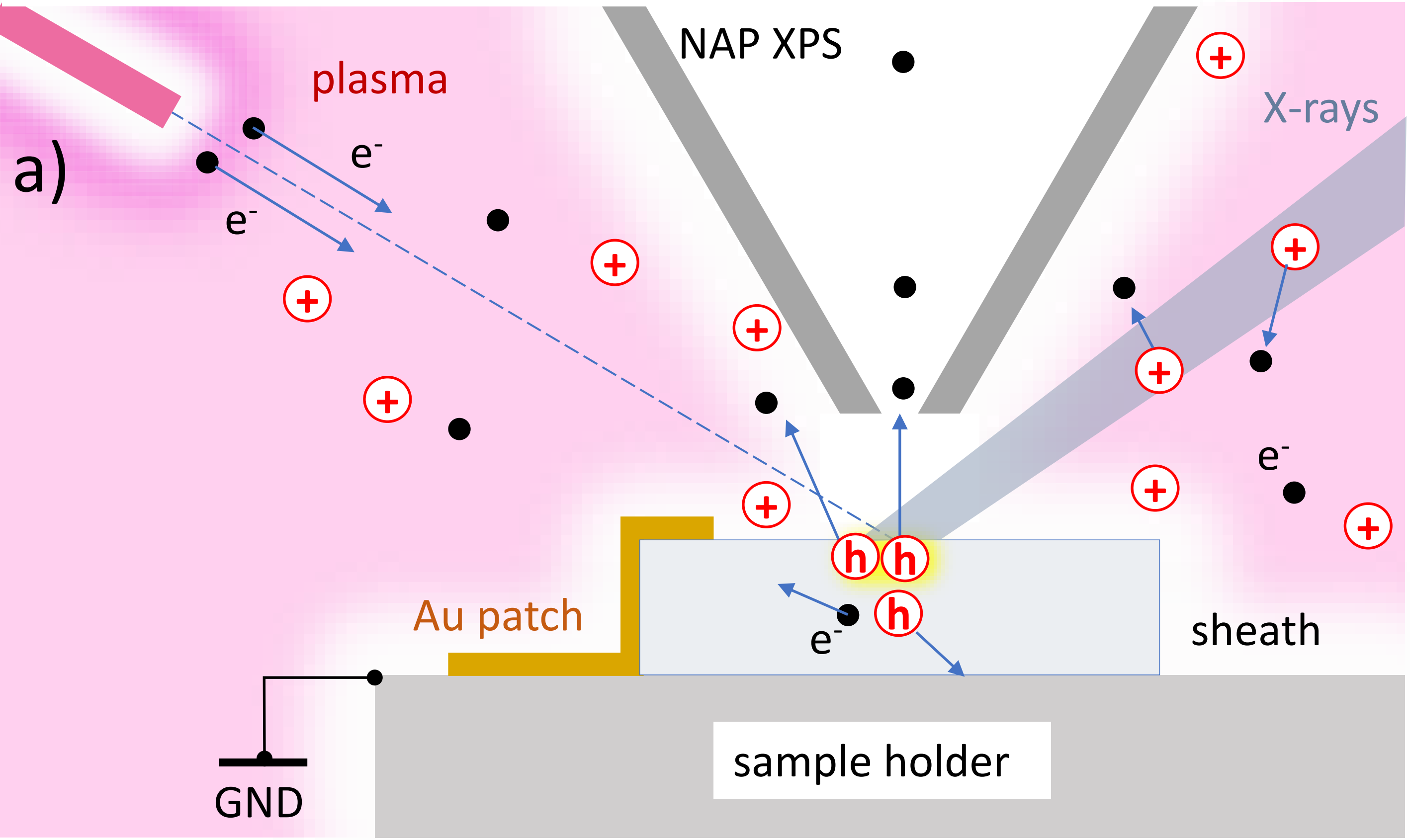
The dynamic equilibrium between incoming oxygen radicals reacting with Au and the desorption of O_2 results in the metastable Au-oxide that can be detected at the surface by Plasma–XPS.

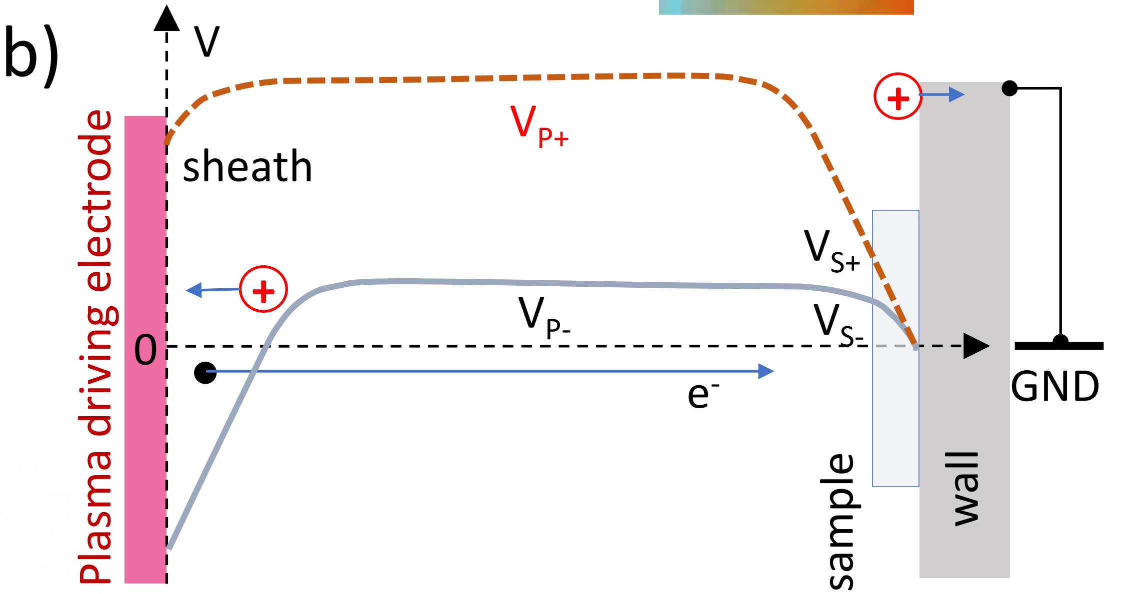
Plasma potentials & sample charging

Surface charge depends on:

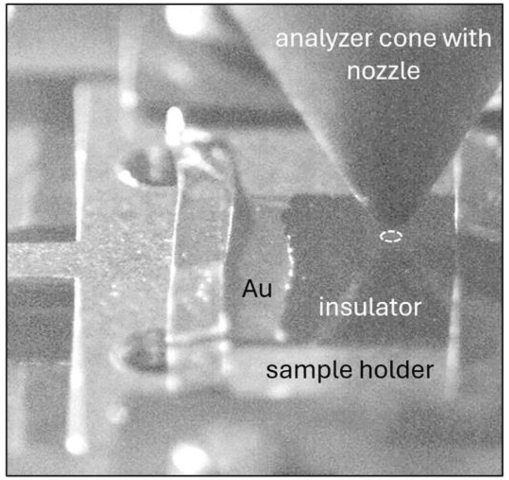
- Electrons/ions, secondary electrons, photoelectrons
- UV-Vis photons
- EM field
- Reactive radicals
- Surface temperature

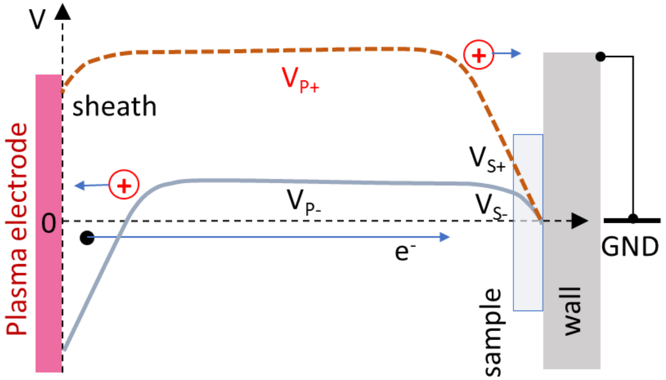
Importance:

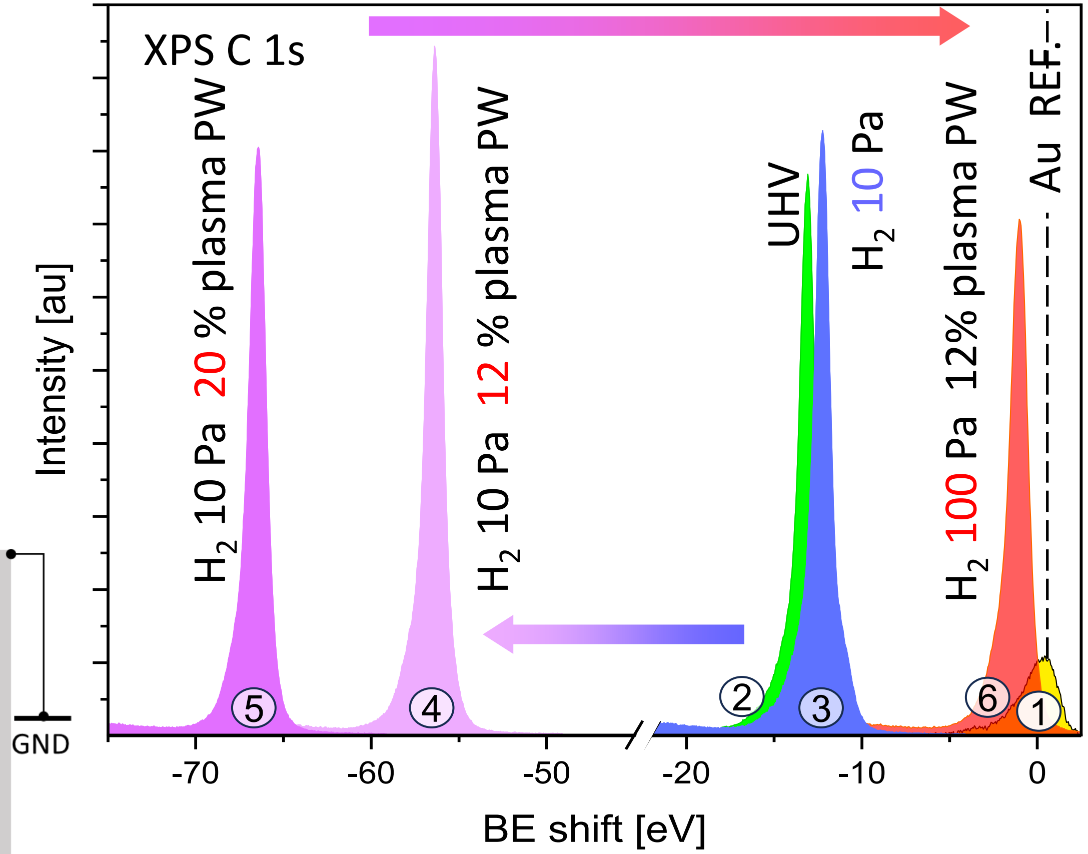


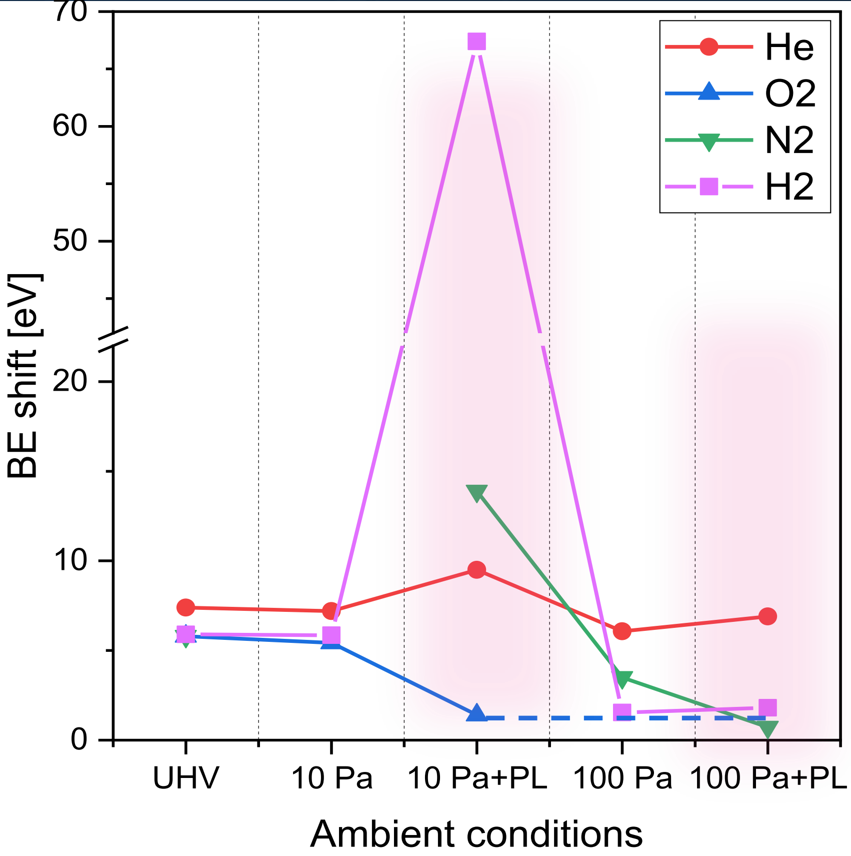


Application Example: Diagnostics of the sample charge







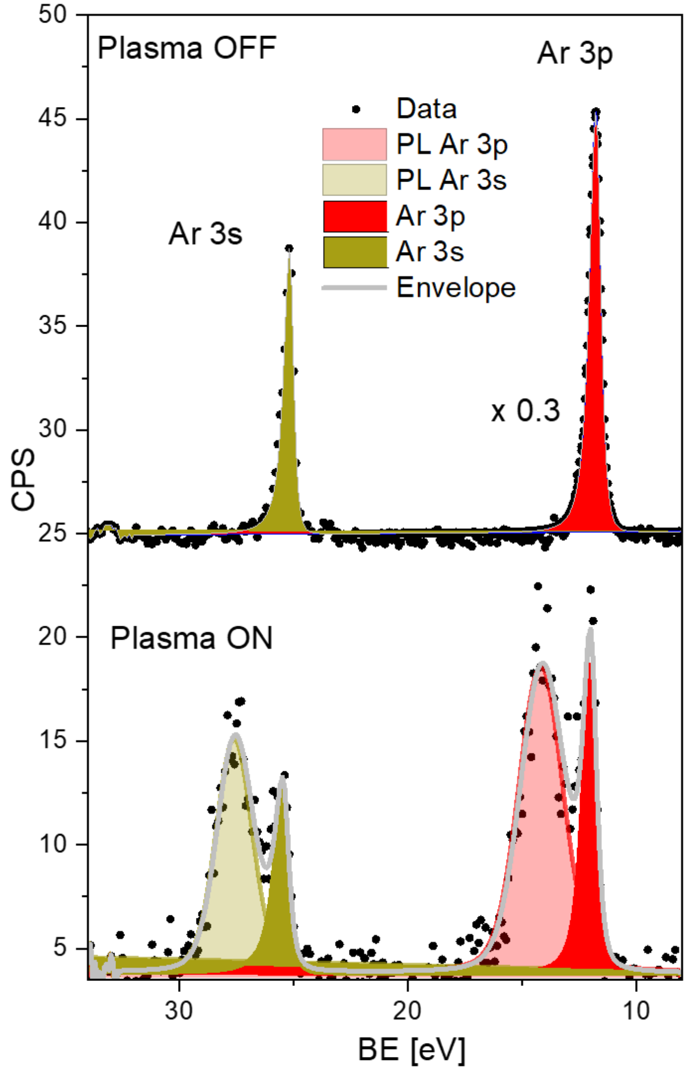


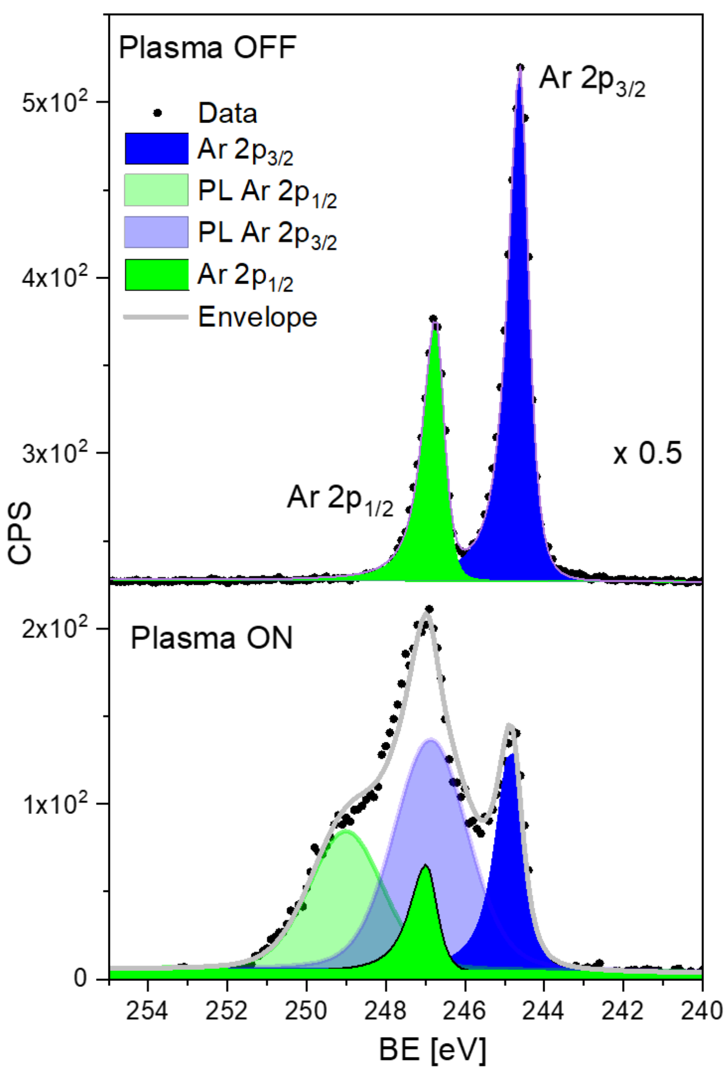
UV light ❌
Cycle-averaged plasma potential ✅
Ballistic electrons from the cathode at the cathode cycle ✅
Reduced recapture of the photoemitted electrons at low pressure ✅
At high pressure, the increased electron scattering and near-surface gas ionization, results in charge neutralization.

In electronegative plasma-electrons are effectively captured

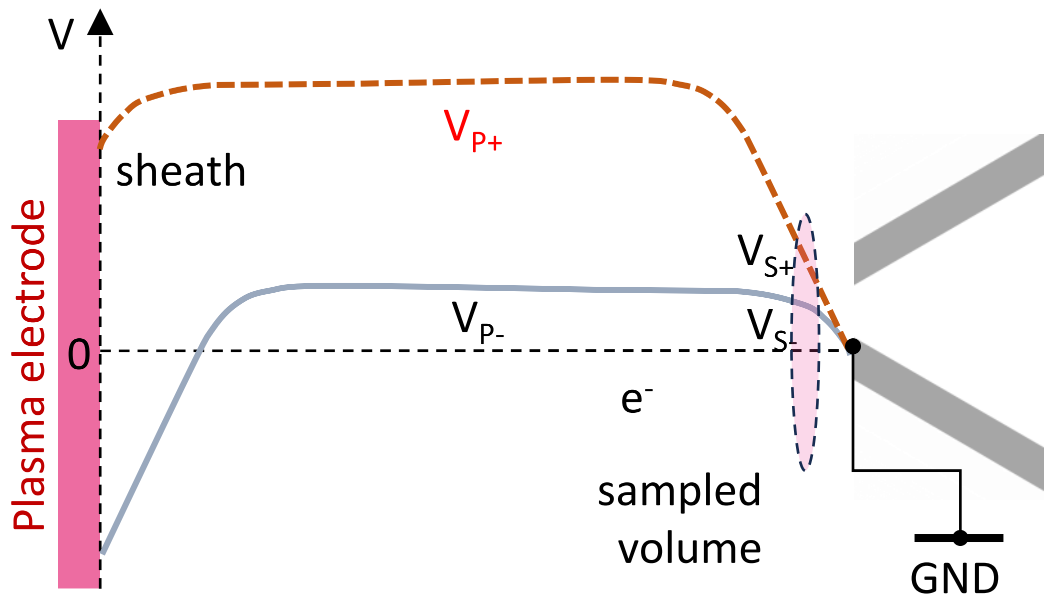
Plasma diagnostics: Gas phase XPS & plasma potential

Ar 500 Pa, Plasma: AC 22 kHz , 1 kV pk-pk

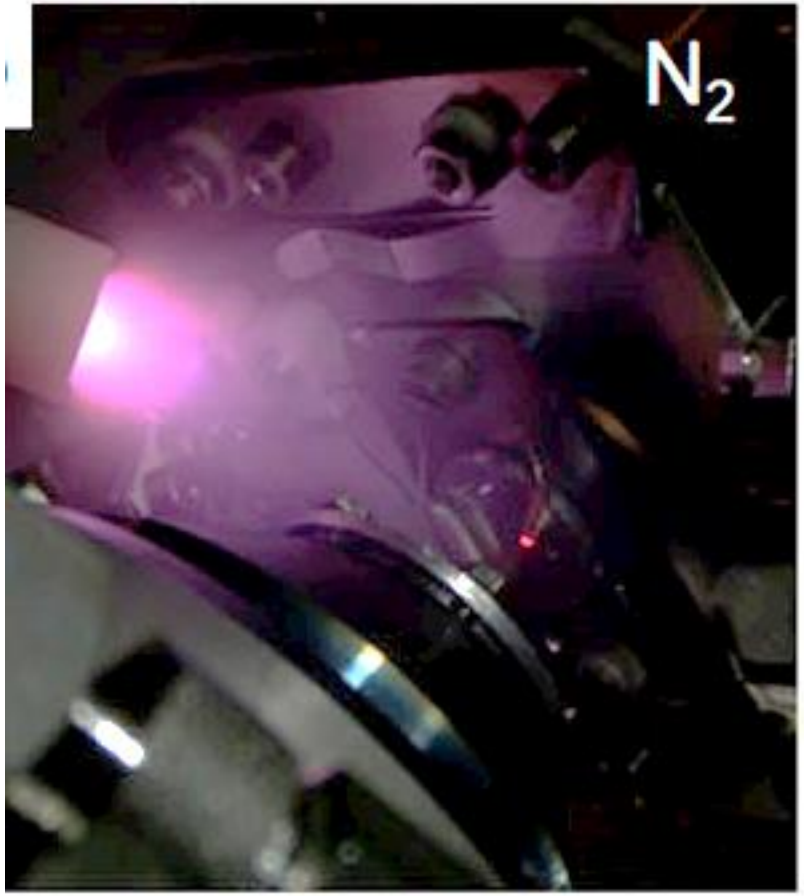


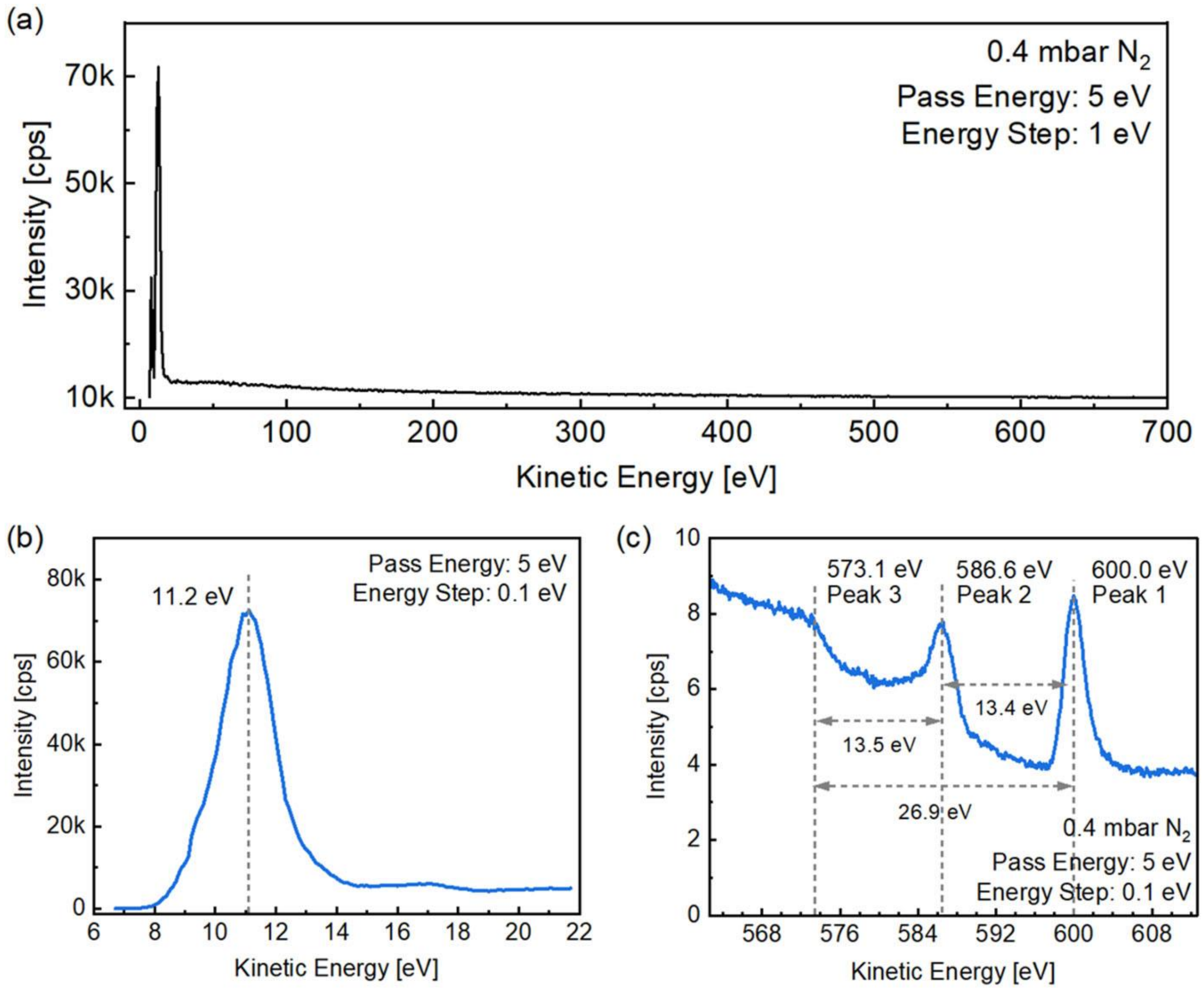


- Appreciable reduction of the intensity of the main peaks while the integrated area stays the same
- Slight shift of the main peaks position toward the higher BE
- Slight broadening of the main peaks and
- The most pronounced effect is the appearance of prominent, broad satellite peaks at higher binding energies (Δ~ 2eV)



Plasma Diagnostics: Electron Energy Distribution ?





Zhi Liu group, Shanghai Tech University

Summary

- Plasma-XPS metrology-the unique capability to detect **real-time chemical state** (e.g., due to short-living transients) not accessible in conventional “before & after” XPS

- **XPS peaks shifts,** and broadening can be used for **plasma-induced surface charge** analysis

- **Gas phase Plasma XPS** can be used as a **plasma diagnostic tool**: chemical composition, plasma potential, electron energy distribution (to be proved), and ion energy distribution (to be tested)

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