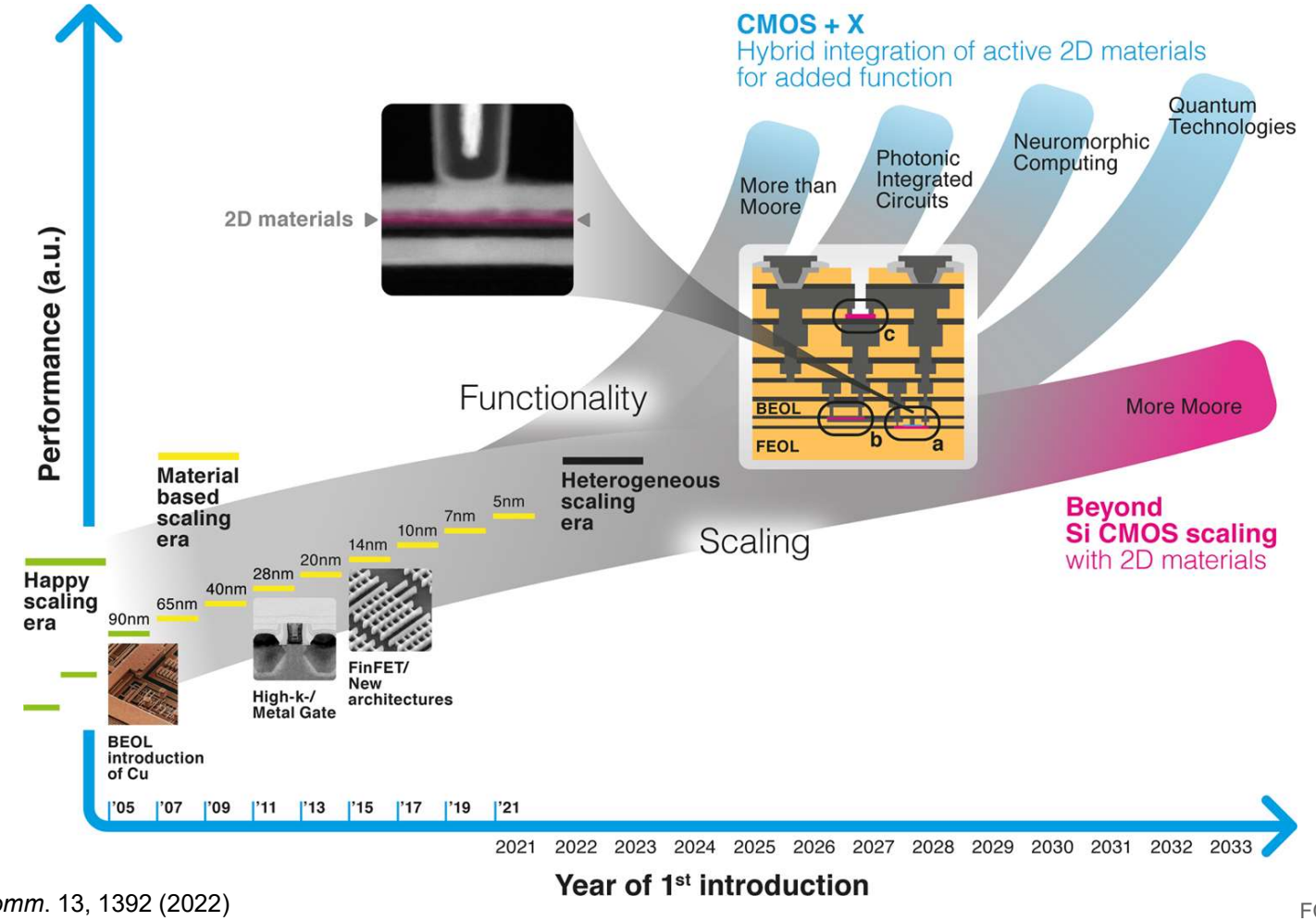



# Photoelectron spectroscopy in device technology: from XPS to HAXPES

FCMN Meeting | June 22nd, 2022

O. Renault, P.-M. Deleuze, N. Gauthier and E. Martinez
Univ. Grenoble-Alpes, CEA, Leti, 38054 Grenoble, France

# **Device technology context:** new materials, critical interfaces

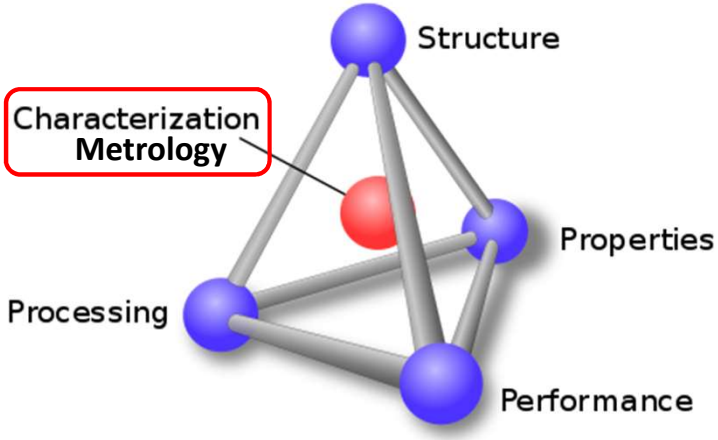


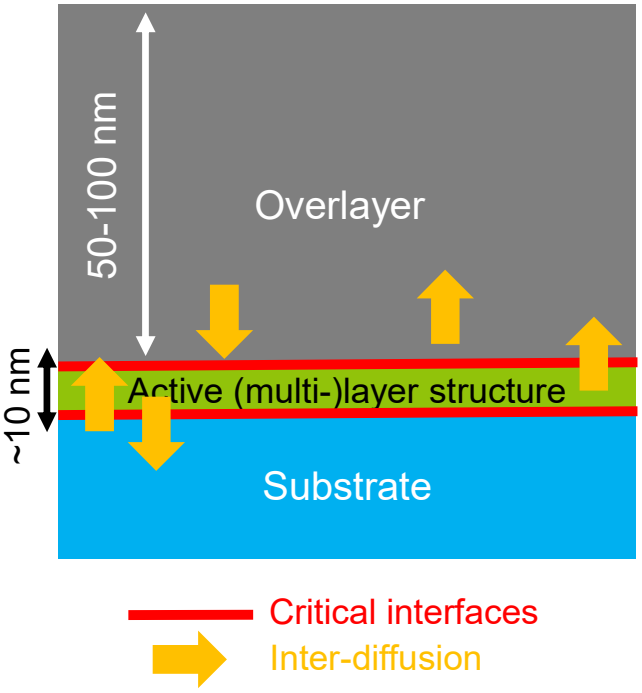

Lemme et al., *Nat. Comm.* 13, 1392 (2022)

# **Device technology context:** new materials, critical interfaces

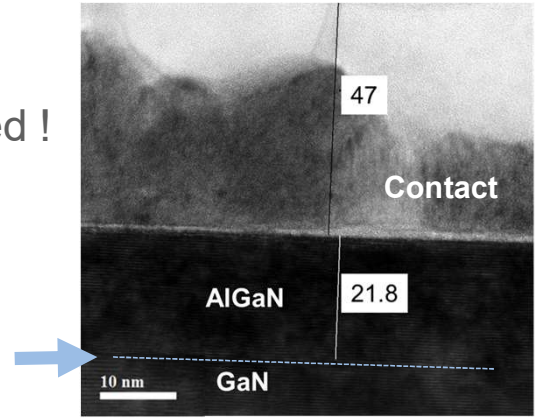
- « The interface is the device » …

*Herbert Kroemer, Nobel Lecture, dec. 8th, 2000*




- … but the interface is ***deeply*** buried !

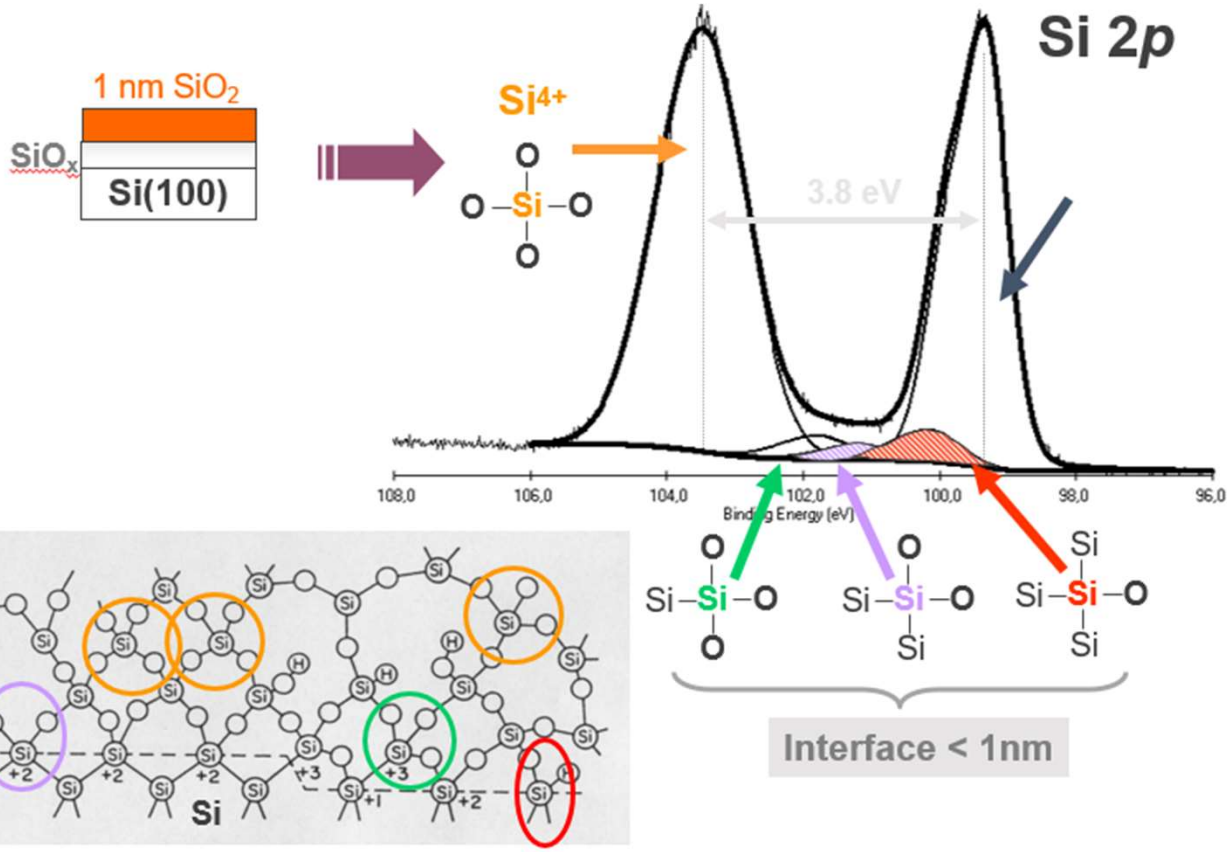


# XPS for interfaces

- **Advantages of XPS:**
  - Non-destructive
  - In-line/fab-compatible
  - Chemical fingerprinting
  - Quantification

- **Downside of XPS:**
  - Trace analysis  1 at.%
  - Depth sensitivity <10 nm

***From XPS to HAXPES***
***From surface to sub-surface and bulk***



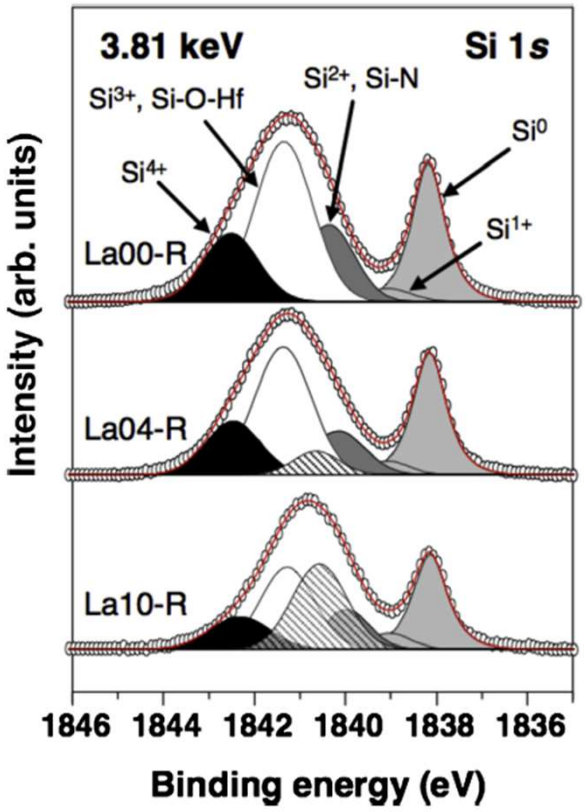

P. J. Grunthaner, *J. Appl. Phys*. **61** (2), 629 (1987)

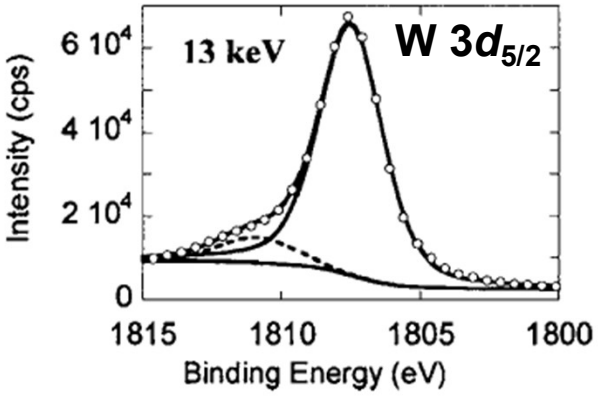
# HAXPES for interfaces at synchrotrons

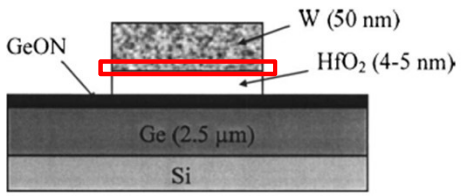
- **Pro's**
  - ✓ Tunable photon energy
  - ✓ Large photon flux
  - ✓ Energy resolution < 0.25 eV
- **Con's**
  - ☹ Limited beam time
  - ☹ Predictability of available beamtime
  - ☹ Quantification often complicated


➡ ***Not suitable for process developments***

Martinez, Renault, et al., Appl. Surf. Sci. 335, 71 (2015)
Boujaama, Martinez, Renault, et al., J. Appl. Phys. 111, 054110 (2012)

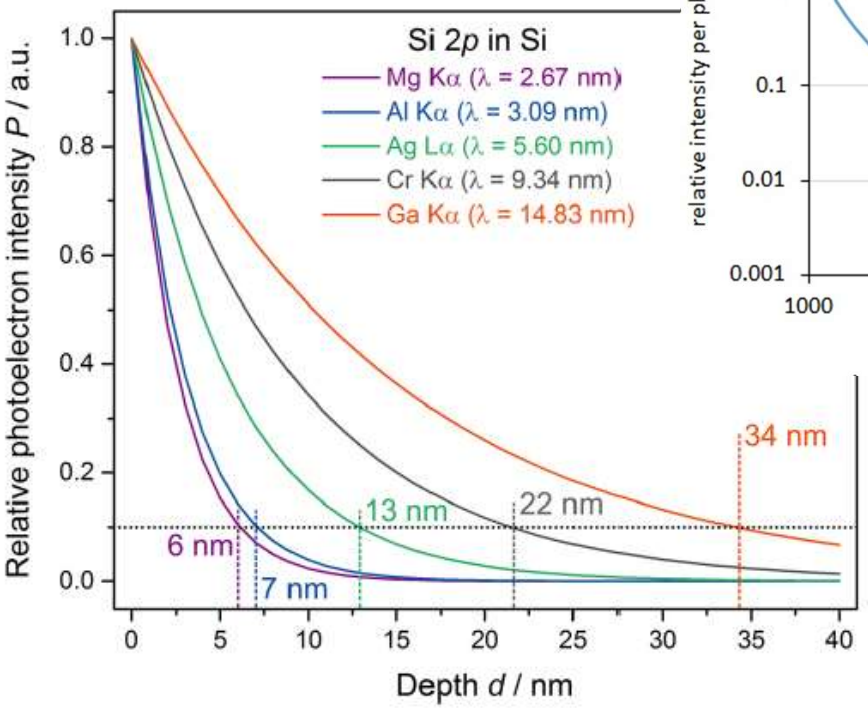


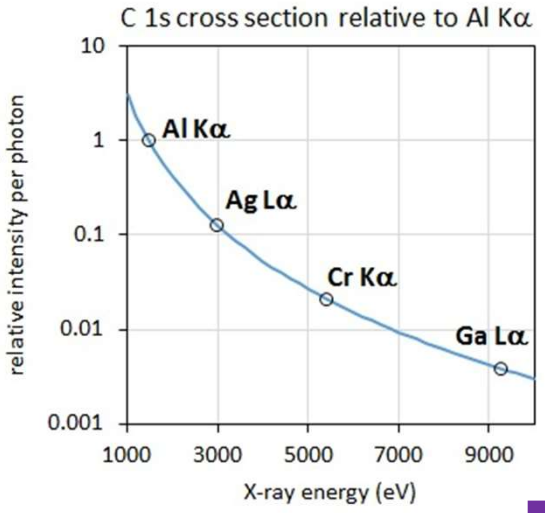




Martinez, Renault, Zegenhagen *et al.*, JVST B. 25, 86 (2006)
Rubio-Zuazo, Martinez et al., AIP Conf. Proc. 931 (1), 329 (2007)

# Lab-scale HAXPES

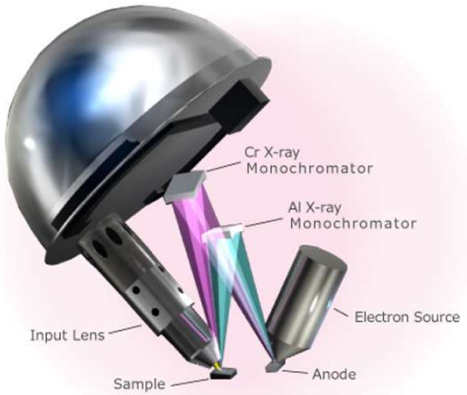



Regoutz *et al.*, *Rev. Sci. Instrum* **89**, 073105 (2018).

- **Pro's**
  - ✓ Routine characterization
  - ✓ Combined XPS-HAXPES
  - ✓ Quantification
- **Con's**
  - ☹ Fixed photon energy
    - Photon flux
    - Energy resolution > 0.5 eV

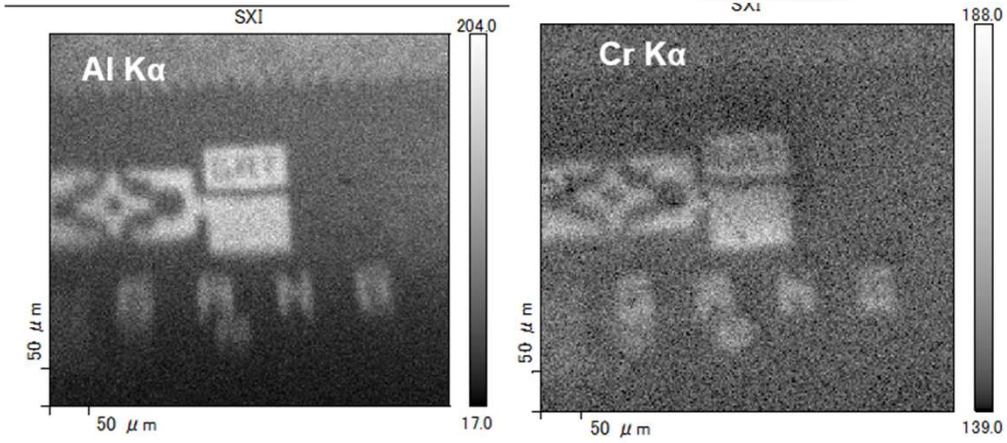
➡ ***Suitable for process developments***



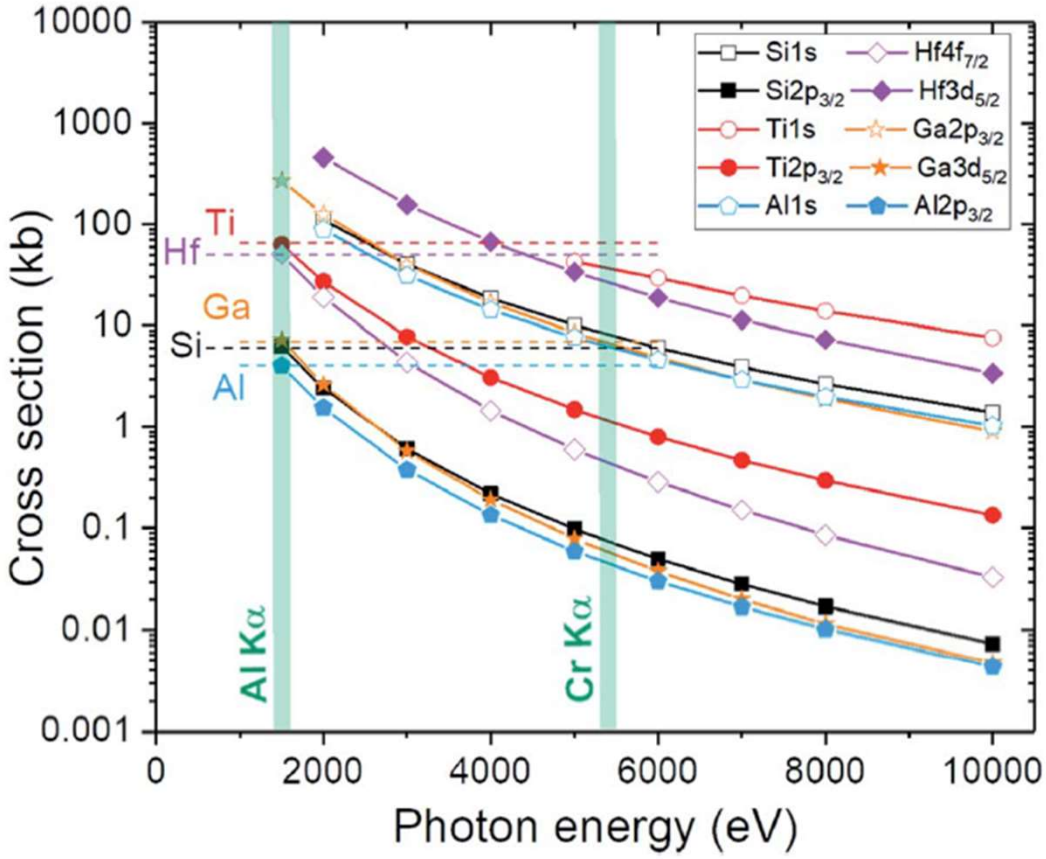

***Poster 009 K. Artyushkova***

# Lab-scale Cr Kα HAXPES

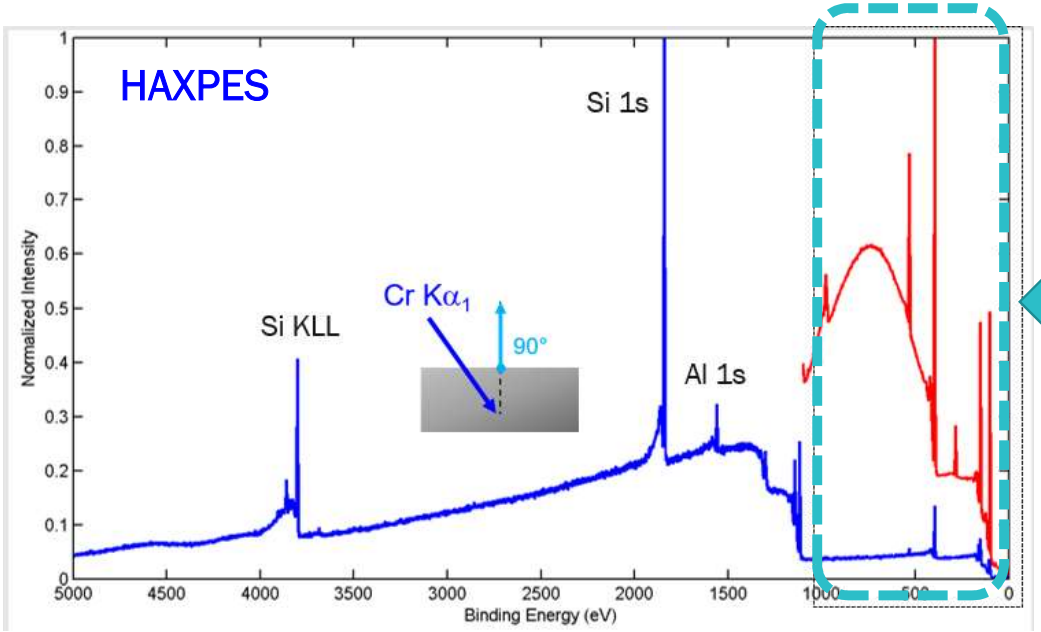
- Extended core-line w/o sensitivity loss
- ×3 depth sensitivity
- Confocal µm-size X-ray sources

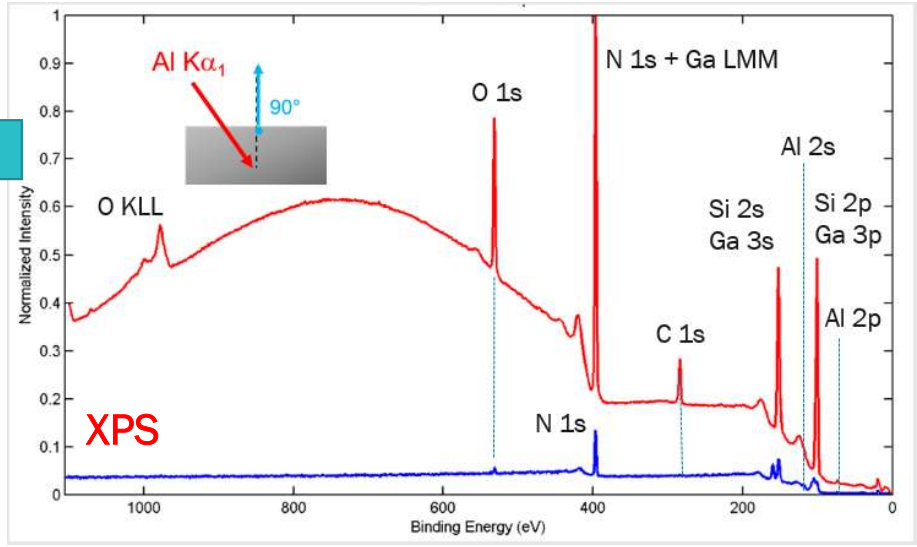




Renault *et al.*, *Faraday Disc.*(2022)



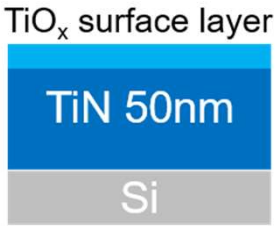
# Extending core-lines availability

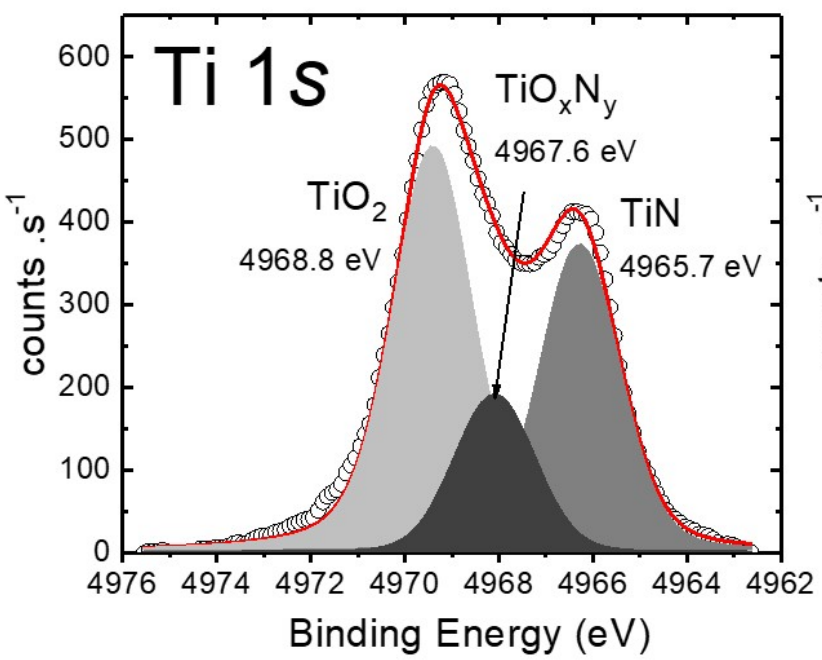


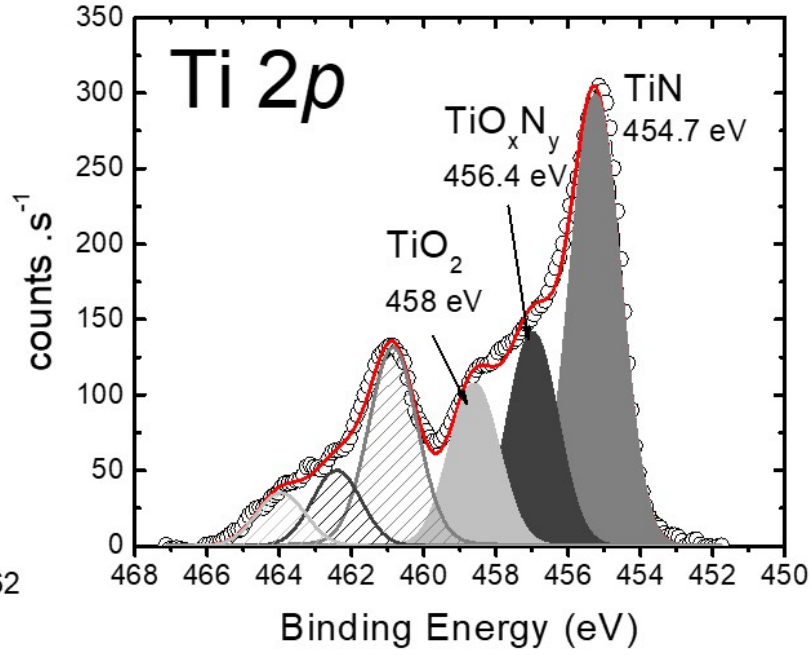




# Extending core-lines availability

| Photoelectron | Ti 1s | Ti 2p |
|---|---|---|
| Kinetic Energy (KE), eV | 449 | 4962 |
| Material | Pt (TiN) | Pt (TiN) |
| Inelastic mean-free path, nm | 0.77 (1.08) | 4.50 (6.93) |

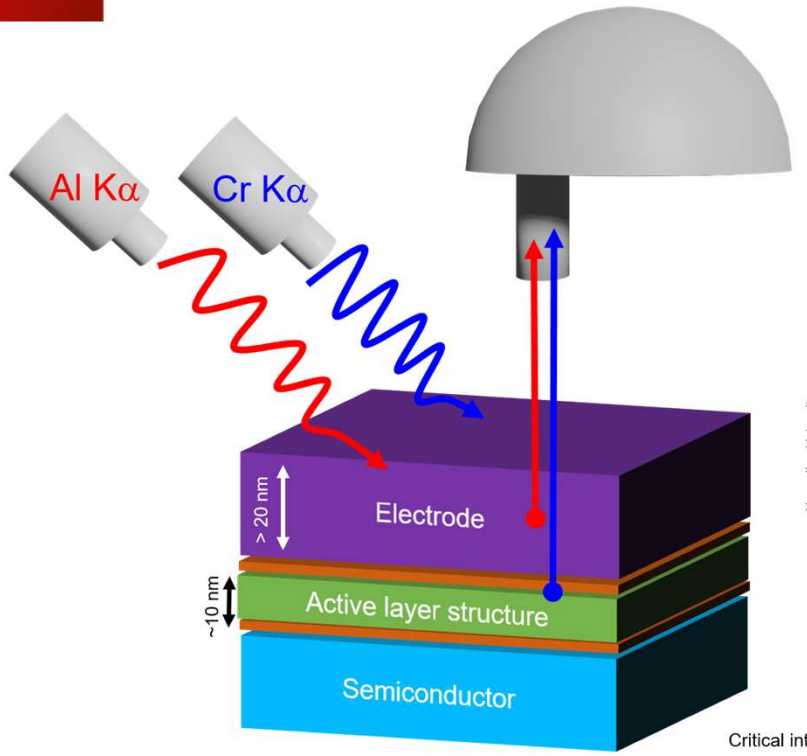


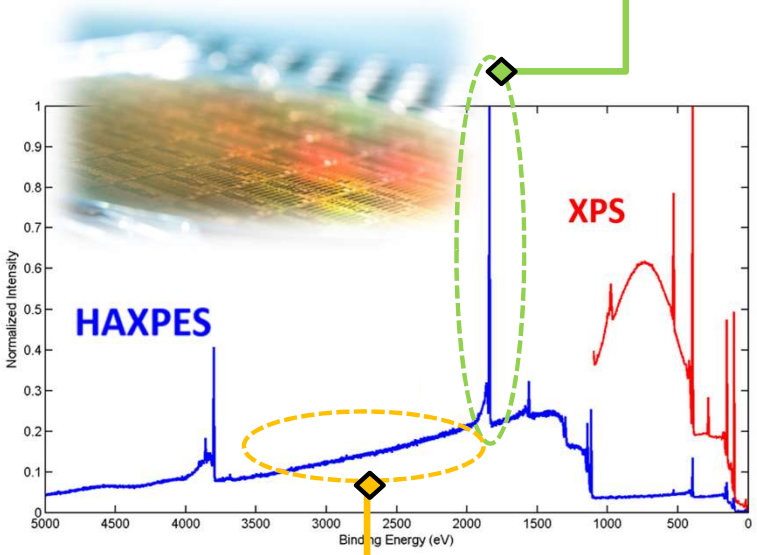




O. Renault, E. Martinez *et al.*, *Surf. Interface Anal.* **50**, 1158 (2018).

# Agenda



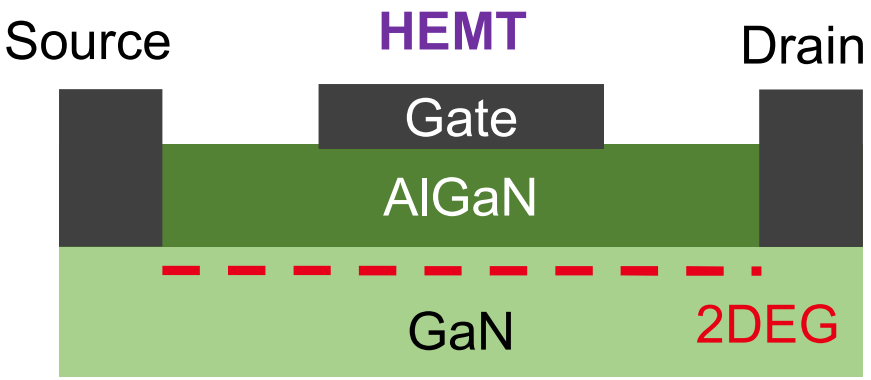

Critical interfaces

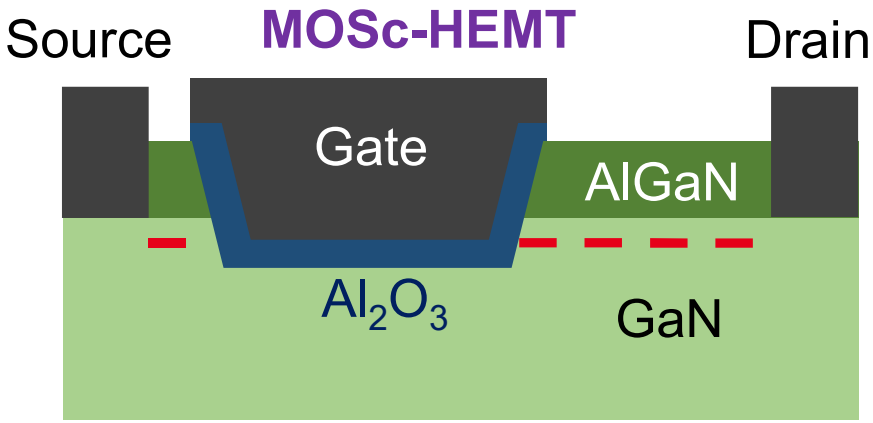
1. **Corel-level analysis**
Chemistry
at. %
z ~ 3×IMFP

2. **Inelastic background analysis**
Depth distribution
z ~ 8×IMFP

Outlook: operando analysis
In situ bias

# Critical $Al_2O_3$ GaN buried interface in HEMTS




- Maximum voltage (~ 650V)
- Low energy loss at ON-state = **Low $R_{ON}$**
- OFF-state = negative $V_{Gate}$ ➔ **Normally-On**

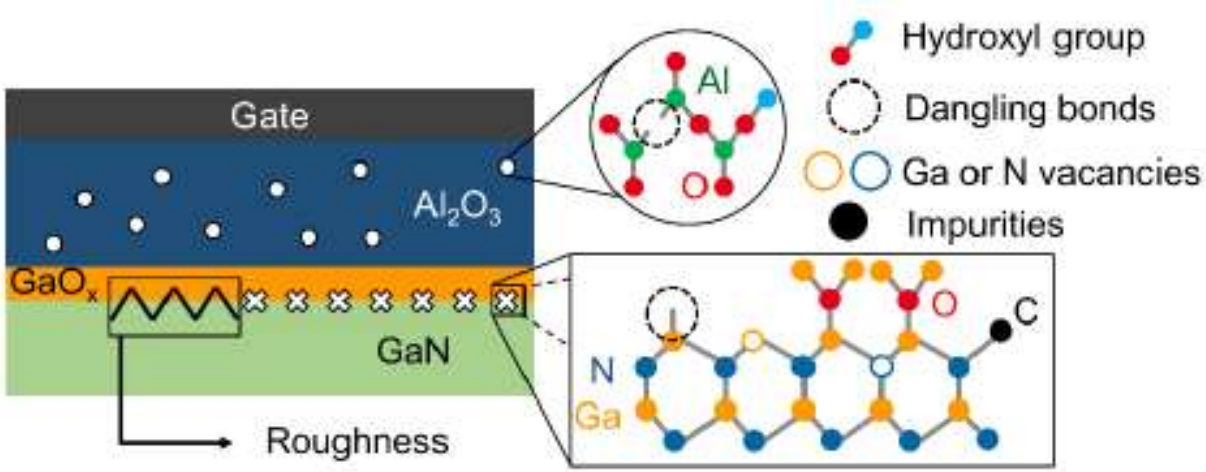
**Normally-Off** by depleting the 2DEG

➔ ***MOSc-HEMT***

- AlGaN etch = 2DEG depletion
- Dielectric deposition (e.g. $Al_2O_3$)
- Metal deposition

✓ **Positive Threshold voltage ($V_{TH}$)**

# Critical $Al_2O_3$ GaN buried interface in HEMTS

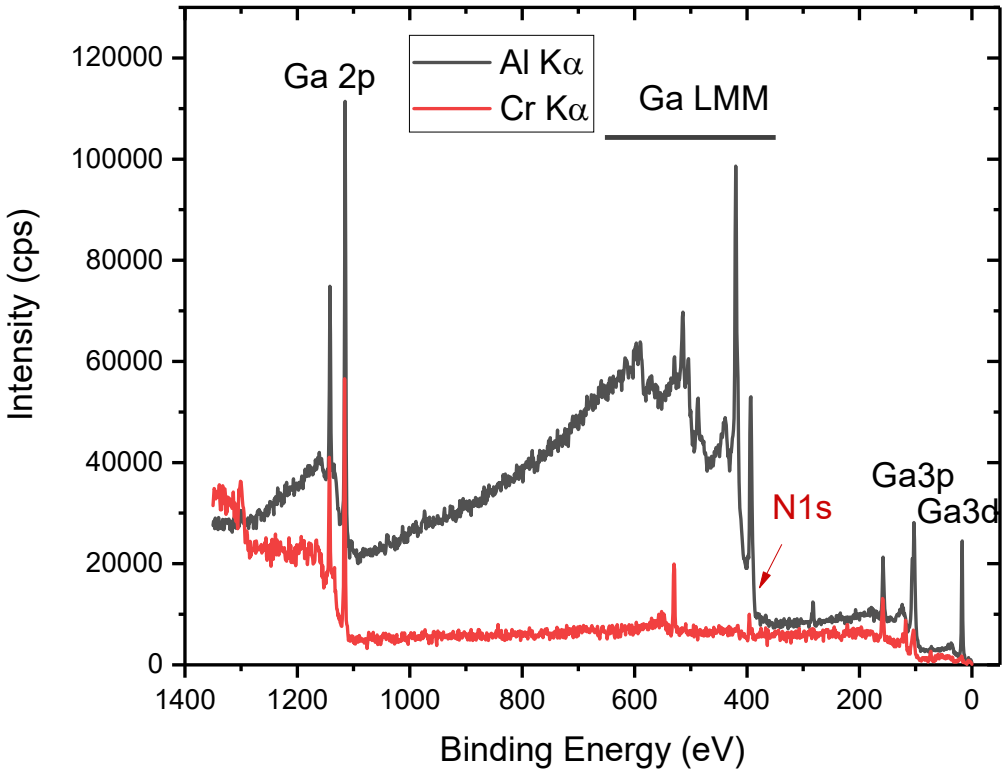


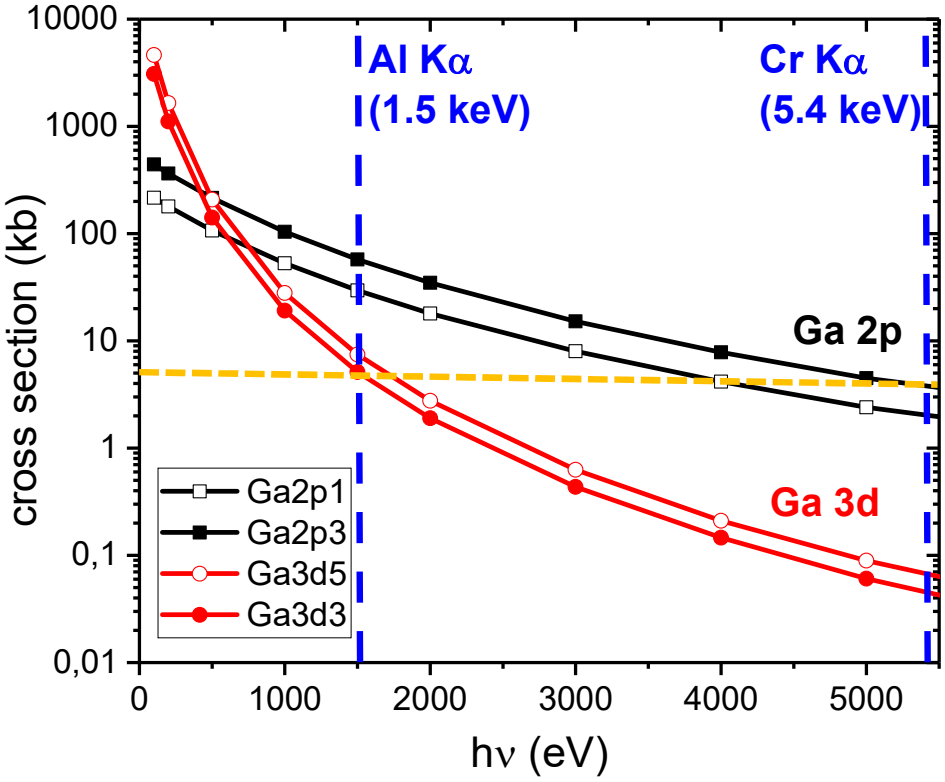

- Ga oxydation $\Rightarrow$ $GaO_x$
- Defects $\Rightarrow$ dangling bonds, vacancies (Ga, N), impurities
- Roughness

✓ Impact on electrical properties ($V_{TH}$, $\Delta V_{TH}$, $R_{ON}$)

- **$Al_2O_3$/GaN interface quality** required for good transistor performances

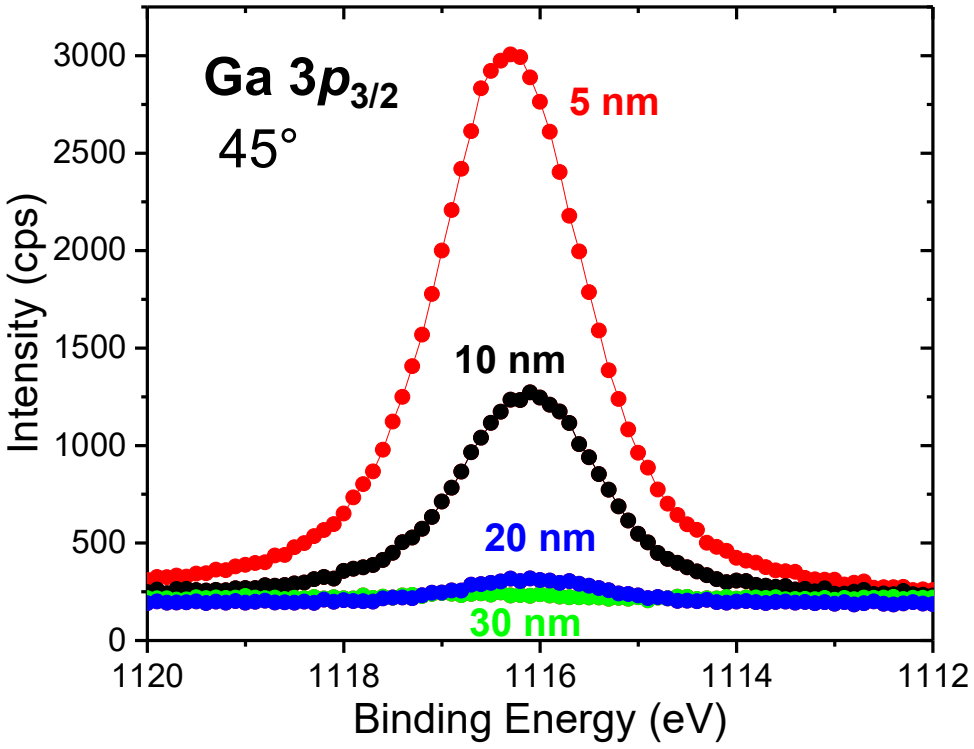
# HAXPES of GaN-based materials

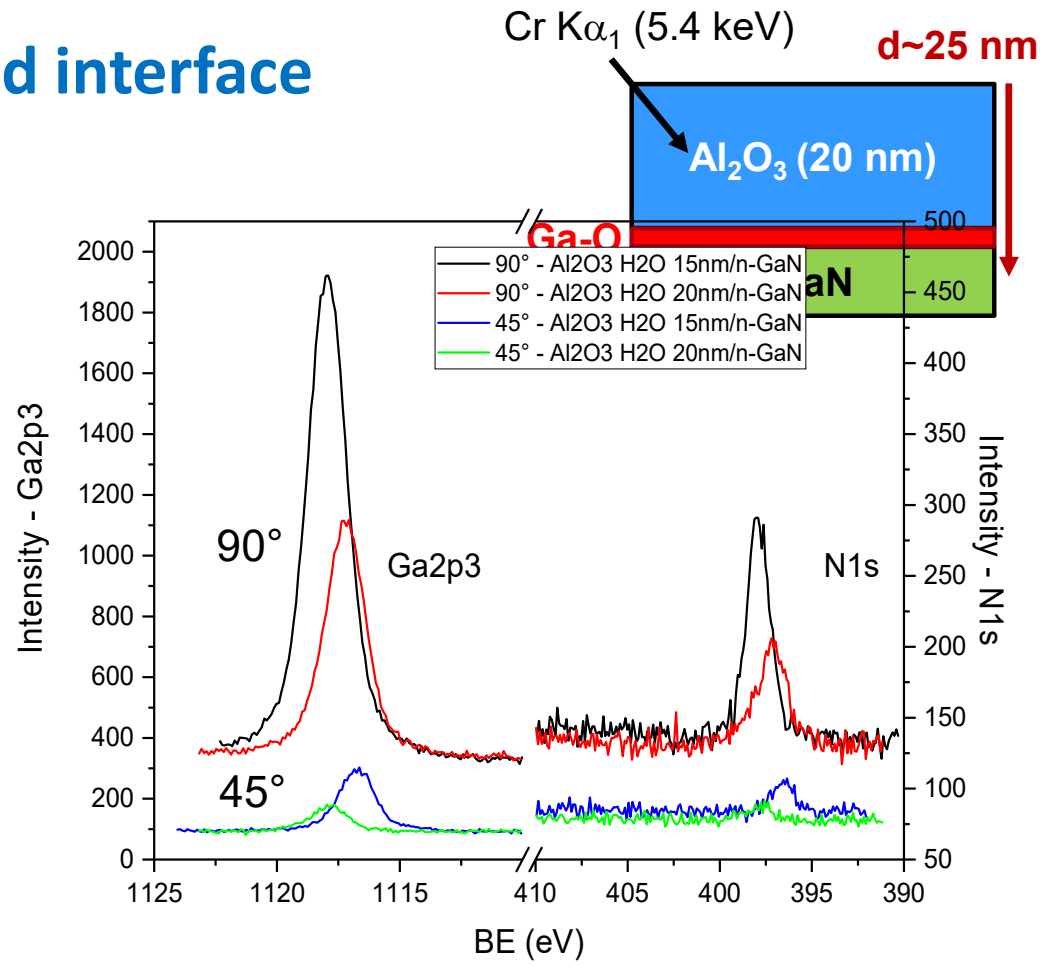



- HAXPES avoids the **overlap between N 1s & Ga LMM**
- **Trade-off** between sensitivity & probing depth with Ga 2p/Ga 3d

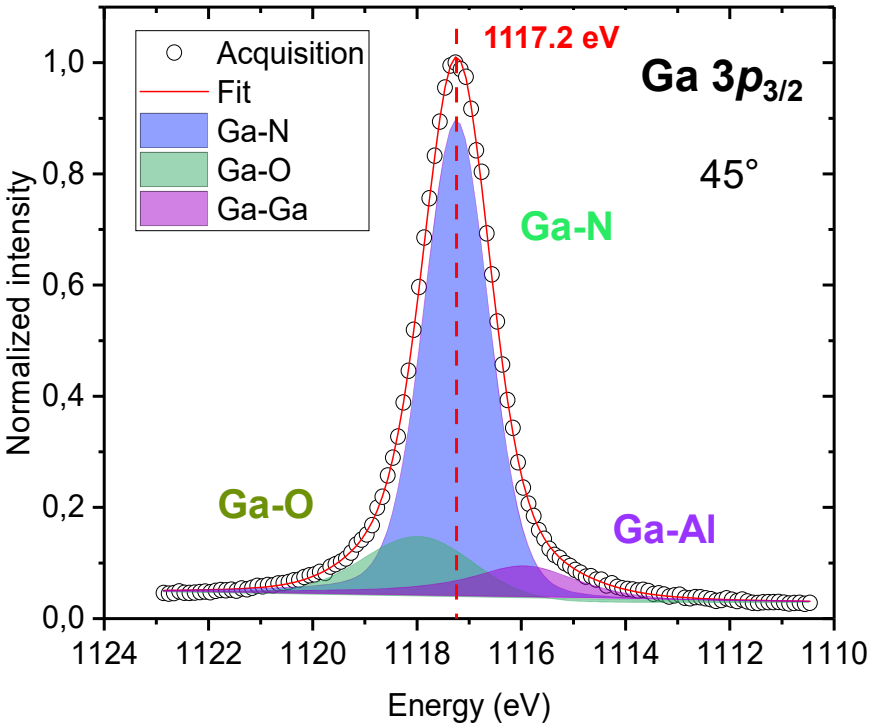
# HAXPES of $Al_2O_3$-GaN buried interface

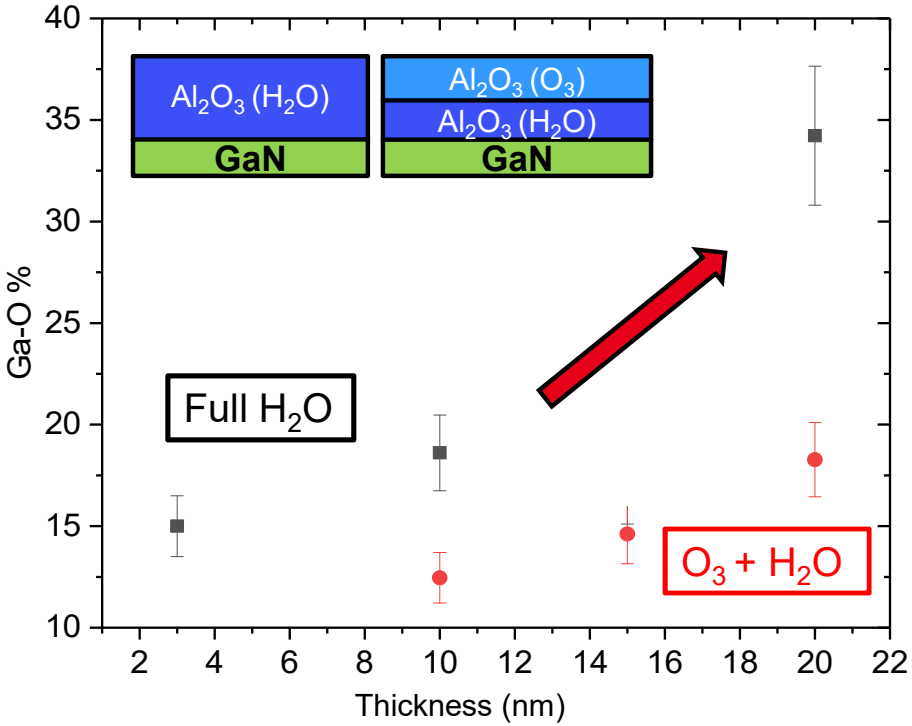



- Investigate the GaN interface with a **20 nm-thick $Al_2O_3$ upper layer**

# HAXPES of $Al_2O_3$-GaN buried interface



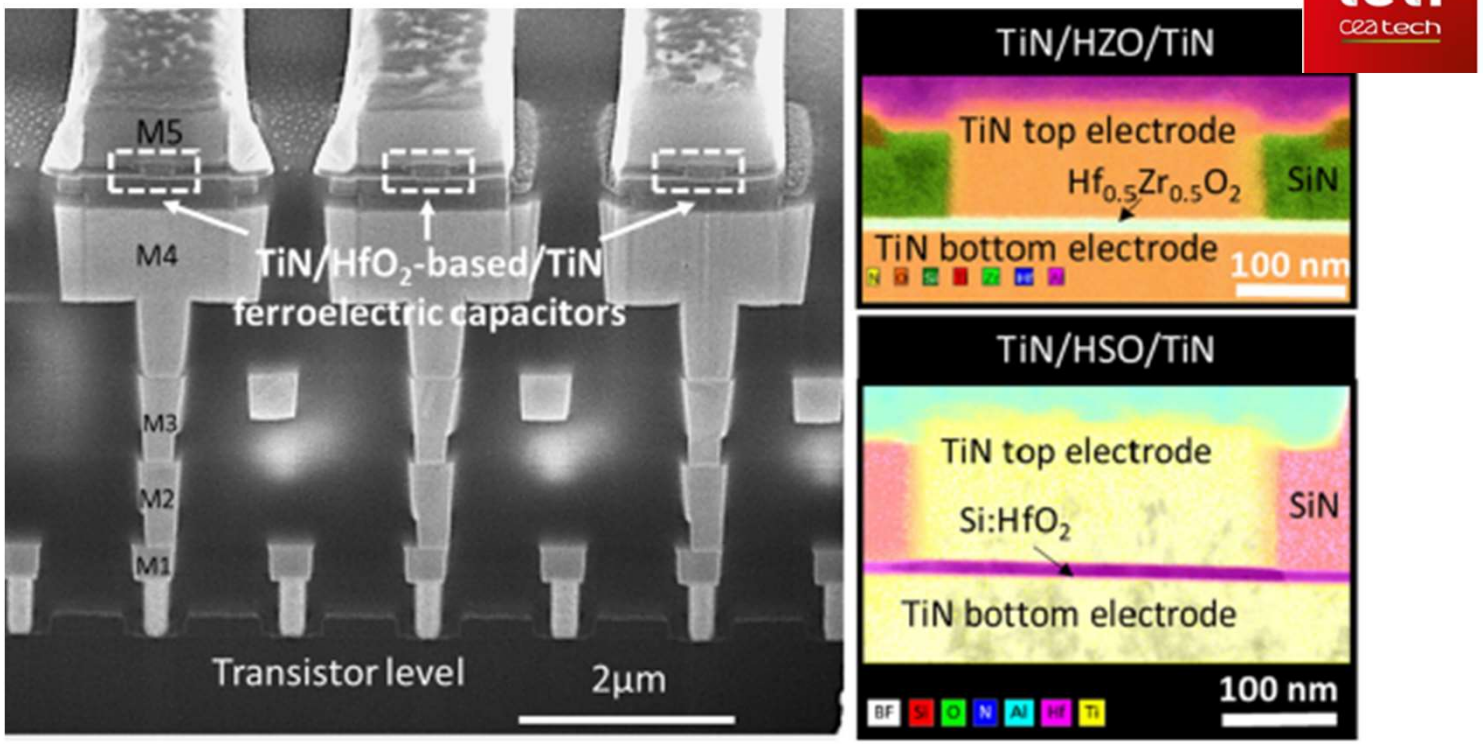




- **Impact of alumina thickness & processing on GaN oxidation**
- Increase of Ga-O bonds at the GaN surface with increasing $Al_2O_3$ thickness

Renault et al., Faraday Discuss. (2022)

# $HfO_2$ stacks for FERAMs

- **Ferroelectric** $HfO_2$ phase
- Oxygen vacancies or Si/La doping stabilize the ferro phase



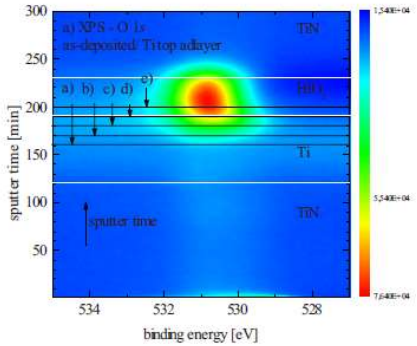

François *et al.*, Appl. Phys. Lett. **118**, 062904 (2021)

# $HfO_2$ stacks for FERAMs

- Ferroelectric $HfO_2$ phase
- Oxygen vacancies or Si/La doping stabilize the ferro phase

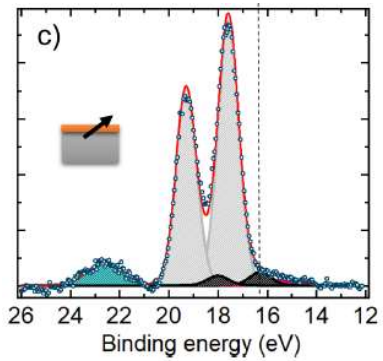
- **Analysis of $HfO_2$ /top electrode interface:** different approaches

XPS sputter profiling



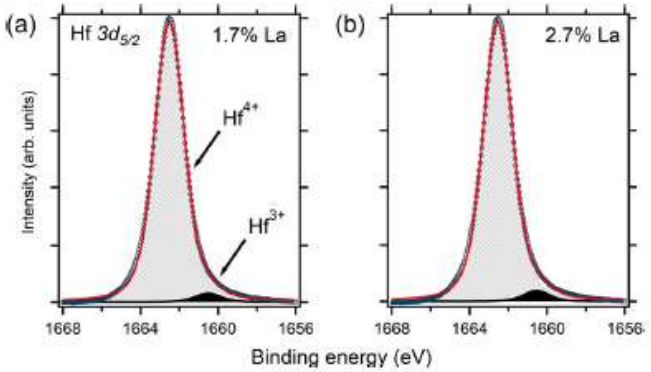

Walczyk *et al.*, J. Vac. Sci. Technol. B **29** (2011)

XPS with ultra-thin electrode




Hamouda *et al.*, J. Appl. Phys. **127,**064105 (2020)

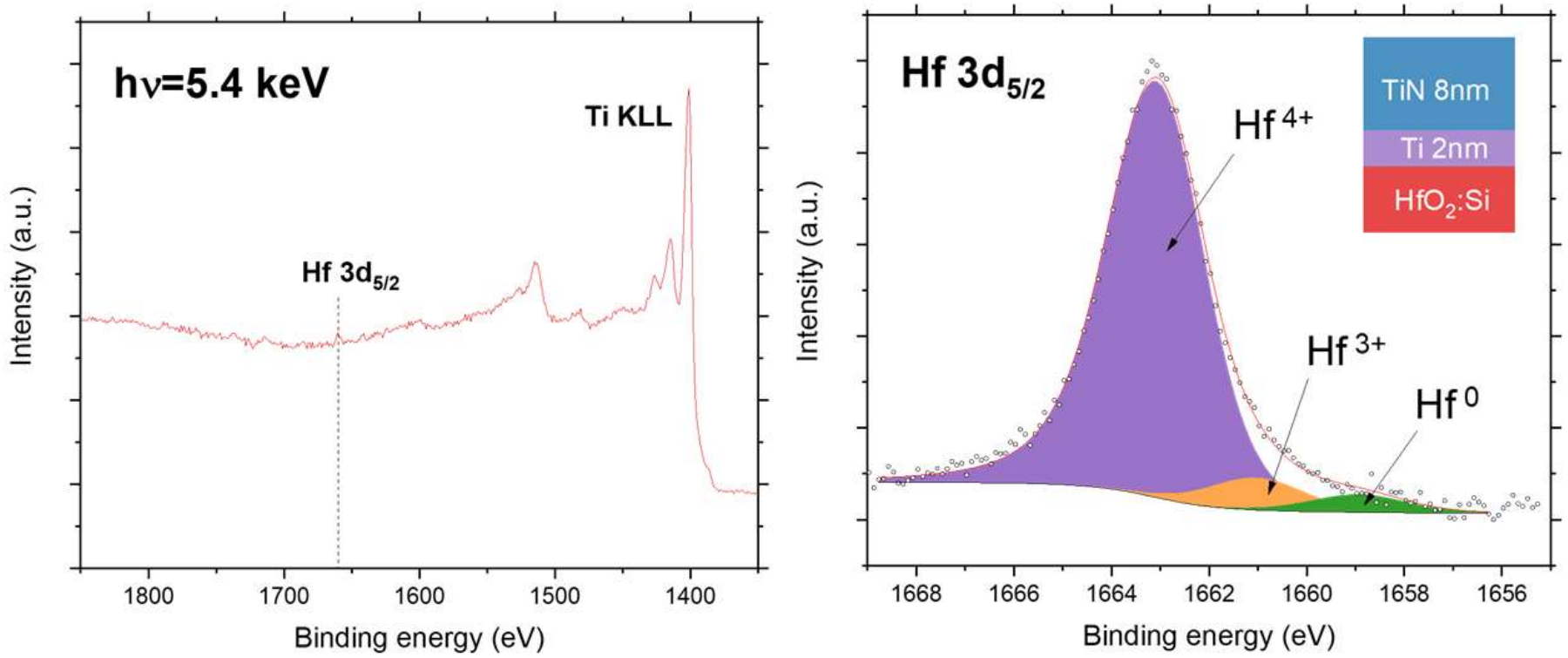
HAXPES with synchrotron radiation



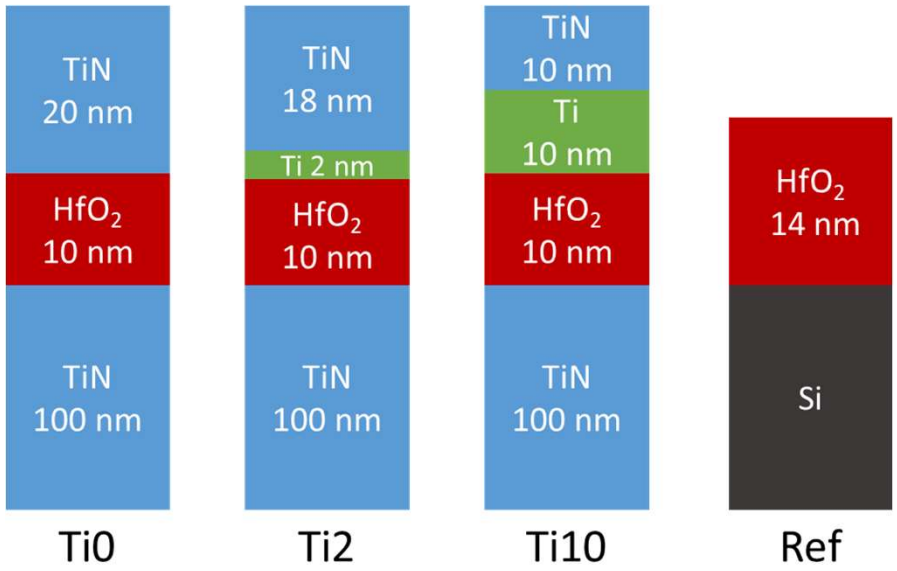

Hamouda *et al.*, Appl. Phys. Lett. **116**, 252903 (2020)

# $HfO_2$ stacks for FERAMs

- **Analysis of $HfO_2$ /top electrode interface:** lab-scale Cr Kα HAXPES

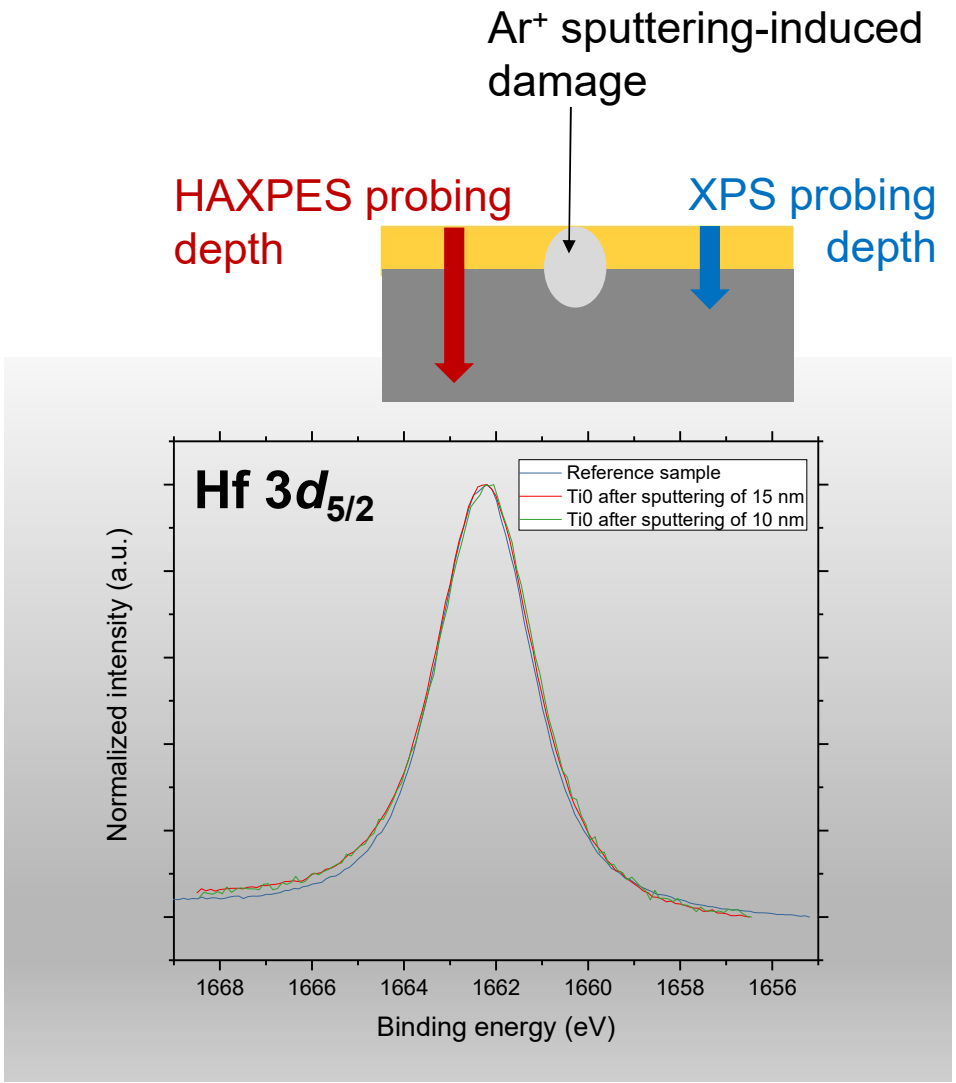


# HAXPES of $HfO_2$-TE interface




$\lambda_{Hf3d}$(TiN)=5.5 nm → Probing depth <16 nm

***Partial sputter of the top electrode***

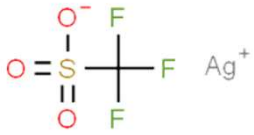


# HAXPES quantification: elemental RSFs

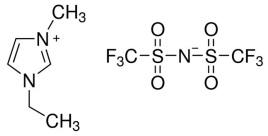
- **Pure element RSFs (PERSF)** derived based on the intensity ratios with respect to pure silver:

$$\frac{RSF_{transition}}{RSF_{Ag3d}} = \frac{\frac{Intensity_{transition}}{TFC_{transition} \times Asymetry_{transition}}}{\frac{Intensity_{Ag3d}}{TFC_{Ag3d} \times Asymetry_{Ag3d}}}$$

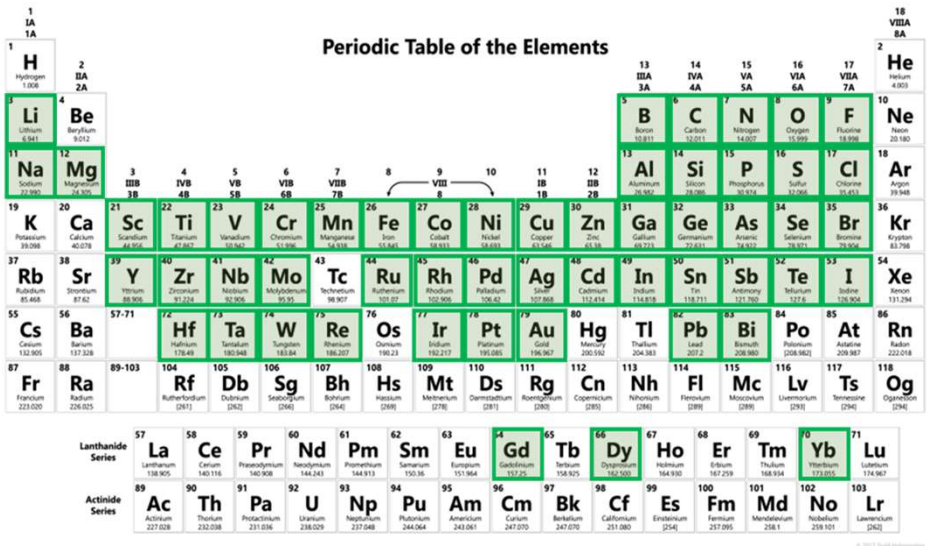
- $RSF_{F1s}$= 1
- PERSF for 54 elements



Silver (trifluoromethyl)sulfonate
$AgCF_3SO_3$



EMIM TFSI
$C_8H_{11}F_6N_3O_4S_2$




PHYSICAL ELECTRONICS
A DIVISION OF ULVAC-PHI

imec

# HAXPES quantification: elemental RSFs for compounds

| SiC | Si at.% | % error |
|---|---|---|
| Si1s | 51.0 | 2% |
| Si2s | 48.2 | -3% |
| Si2p | 51.4 | 3% |

| $Si_3N_4$ | Si at.% | % error |
|---|---|---|
| Si1s | 43.4 | 1% |
| Si2s | 40.4 | -6% |
| Si2p | 43.2 | 0% |

| $MoSe_2$ | Mo at.% | % error |
|---|---|---|
| 2s-2s | 31.7 | -5% |
| 2p-2p | 30.0 | -10% |
| 3p-3p | 31.1 | 7% |

| $Al_2O_3$ | Al at.% | % error |
|---|---|---|
| Al1s | 38.1 | 5% |
| Al2s | 35.8 | 10% |
| Al2p | 37.8 | -6% |

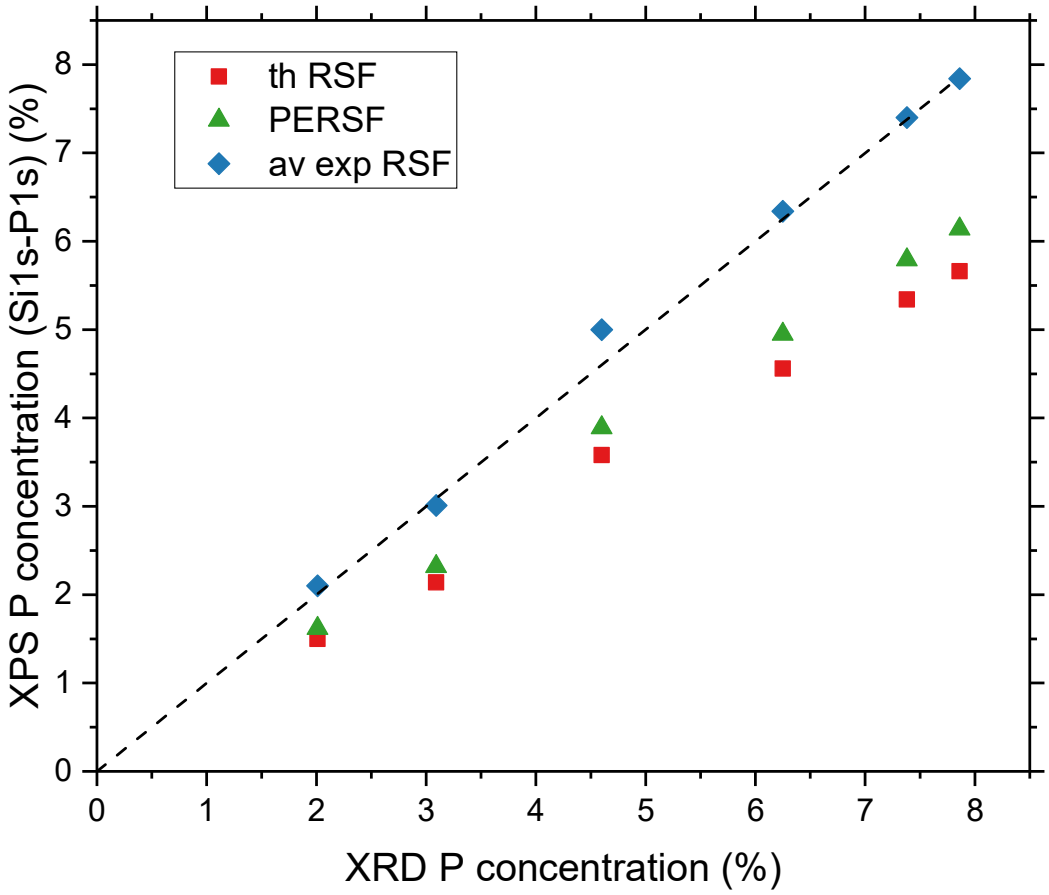
| AlN | Al at.% | % error |
|---|---|---|
| Al1s | 50.2 | 0% |
| Al2s | 48.1 | -4% |
| Al2p | 49.4 | 1% |

➡ **Average error is less than 5%**

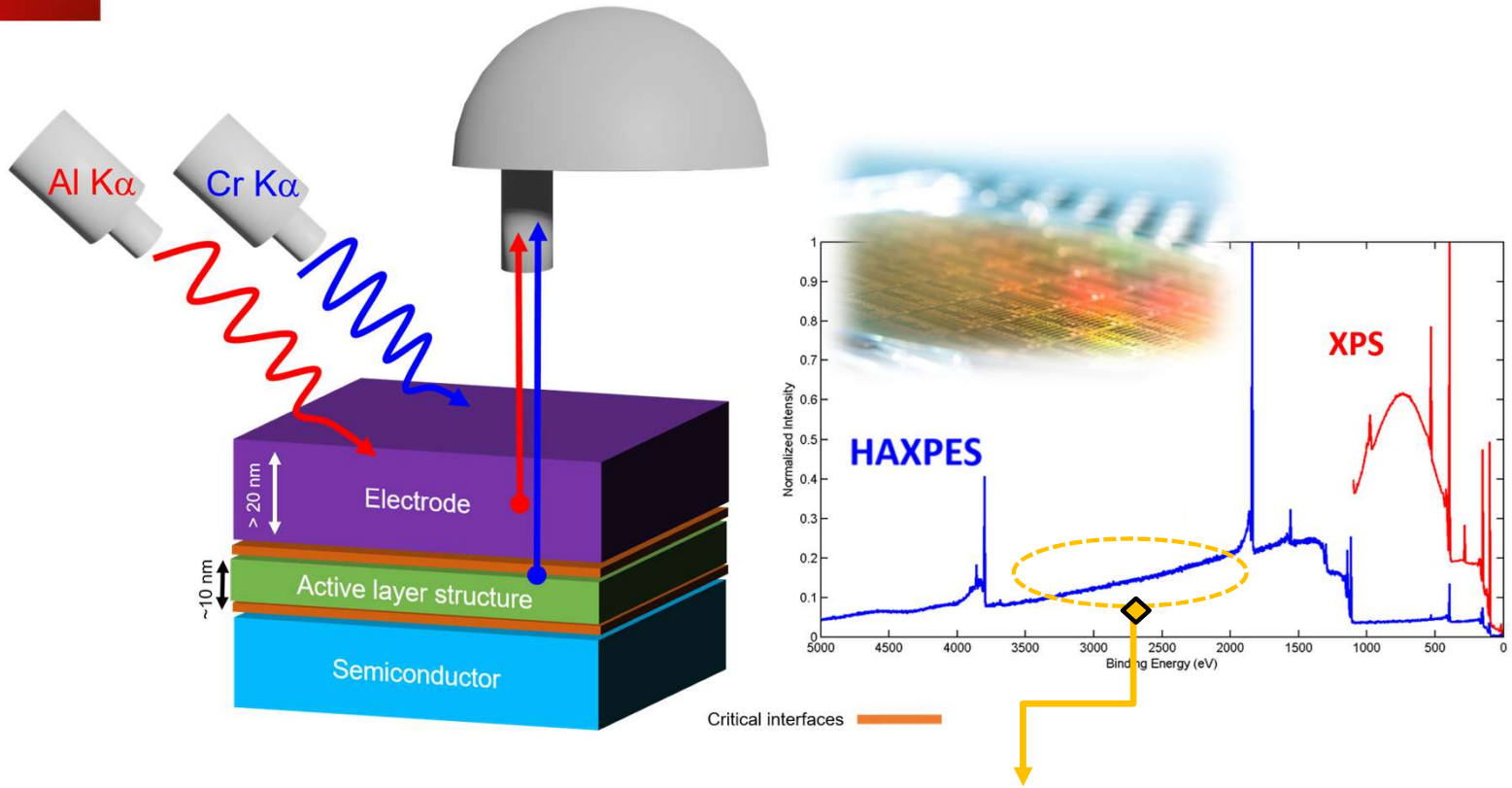
Deleuze, Renault *et al., Surf. Sci. Spectra* **29**, 014003, 04, 06, 07 (2022)

# **HAXPES quantification:** average experimental RSFs

- **Si:P layers** quantified by XRD
- Use of average experimental RSF's (compounds derived)



# Agenda

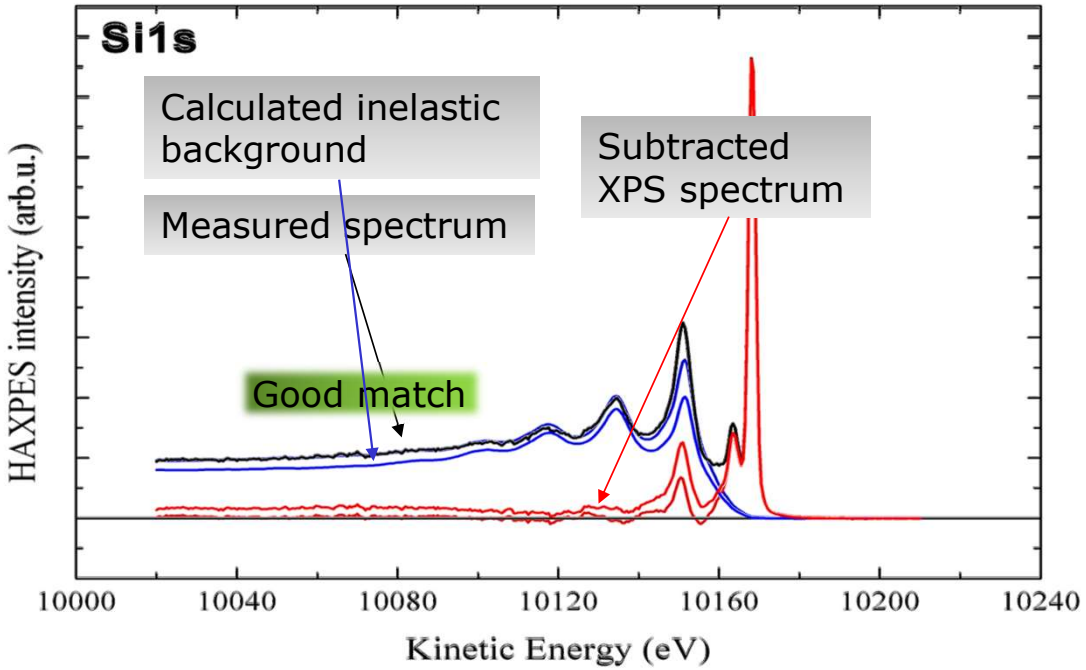


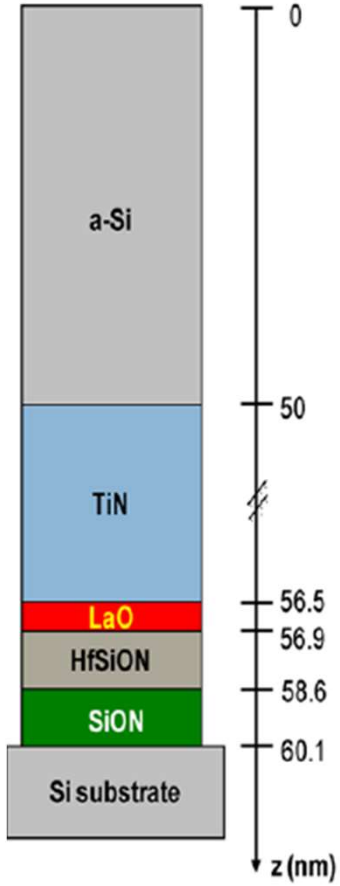

2. **Inelastic background analysis**
Depth distribution
z ~ 8×IMFP

# Inelastic background analysis in HAXPES

**XPS**

S. Tougaard, J. Vac. Sci. Technol. A, 5, 1275 (1997)
S. Tougaard, Surf. Interface Anal. 2018; **50**: 857 (2019)
S. Tougaard, J. Vac. Sci. Technol. A, 39, 011201 (2021)

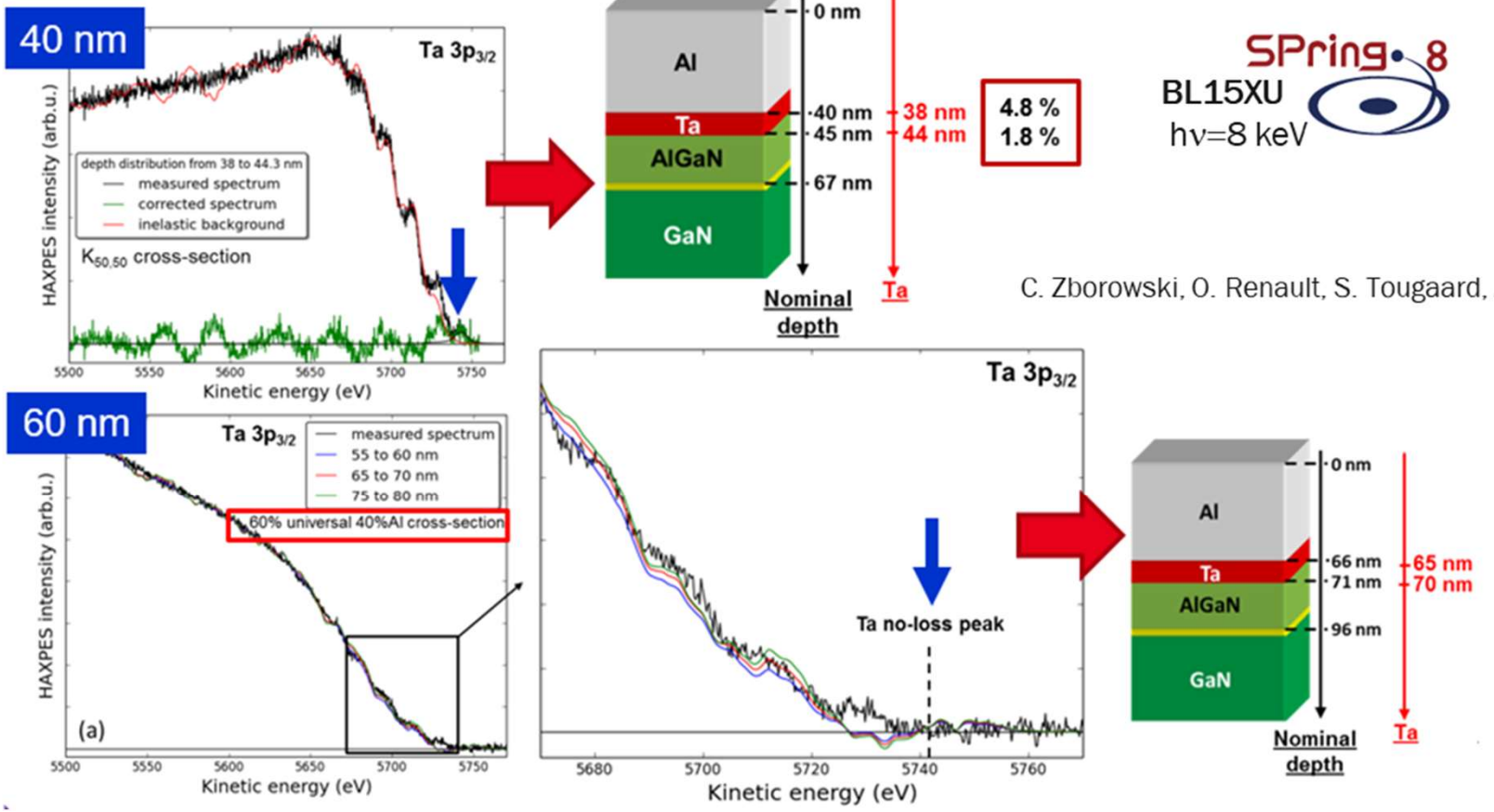


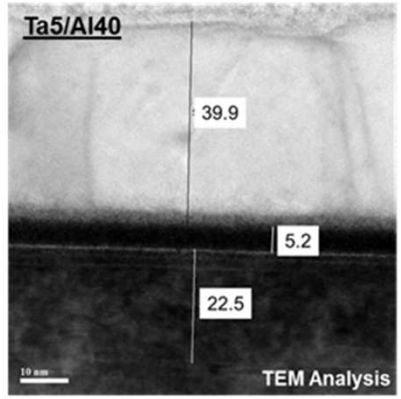




**HAXPES**

Risterucci, Martinez, Tougaard, *Appl. Phys. Lett.* **104** (5) (2014)
Risterucci, Renault, Tougaard, *Appl. Surf. Sci.* **402** 78 (2017)
Zborovski, Renault, Tougaard, *Appl. Surf. Sci.* **432** 60 (2018)
Zborowski, Renault, Tougaard, *J. Appl. Phys.* **124** 085115 (2018)
Zborowski, Tougaard, *Surf. Interface Anal.* 2019; **51**: 857 (2019)
Spencer, Shard, Tougaard, *Appl. Surf. Sci.* **541** 148635 (2021)

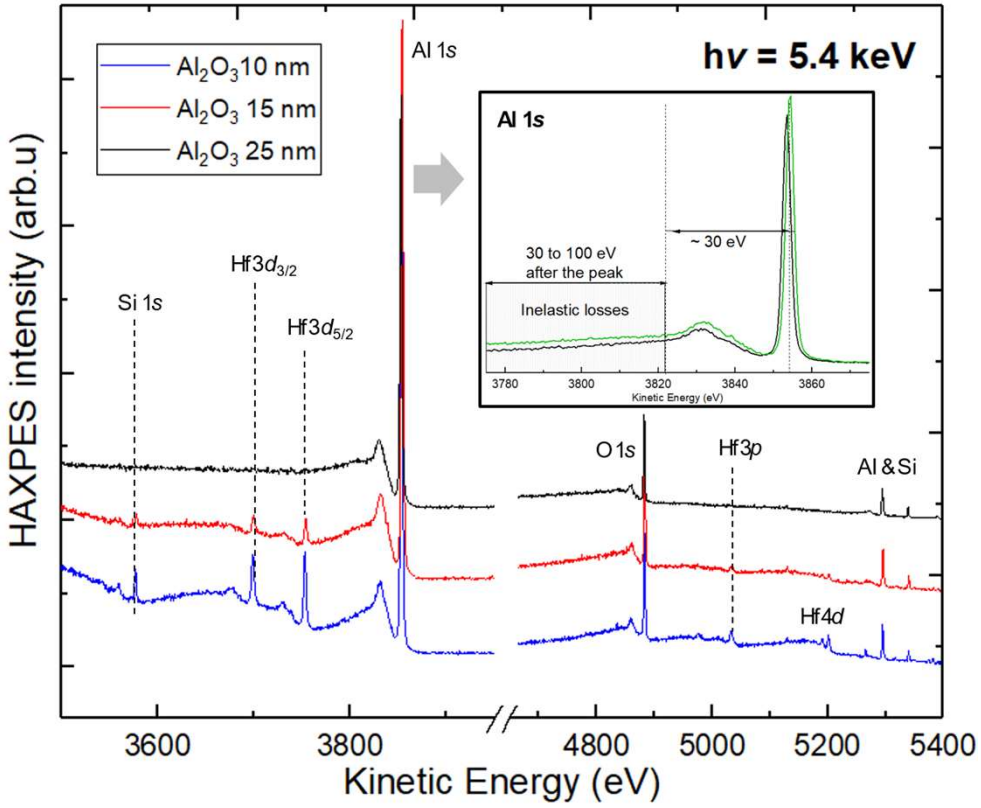
# Inelastic background analysis in HAXPES

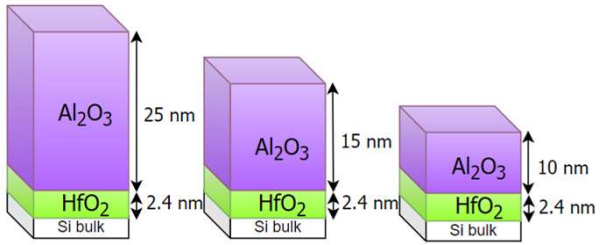


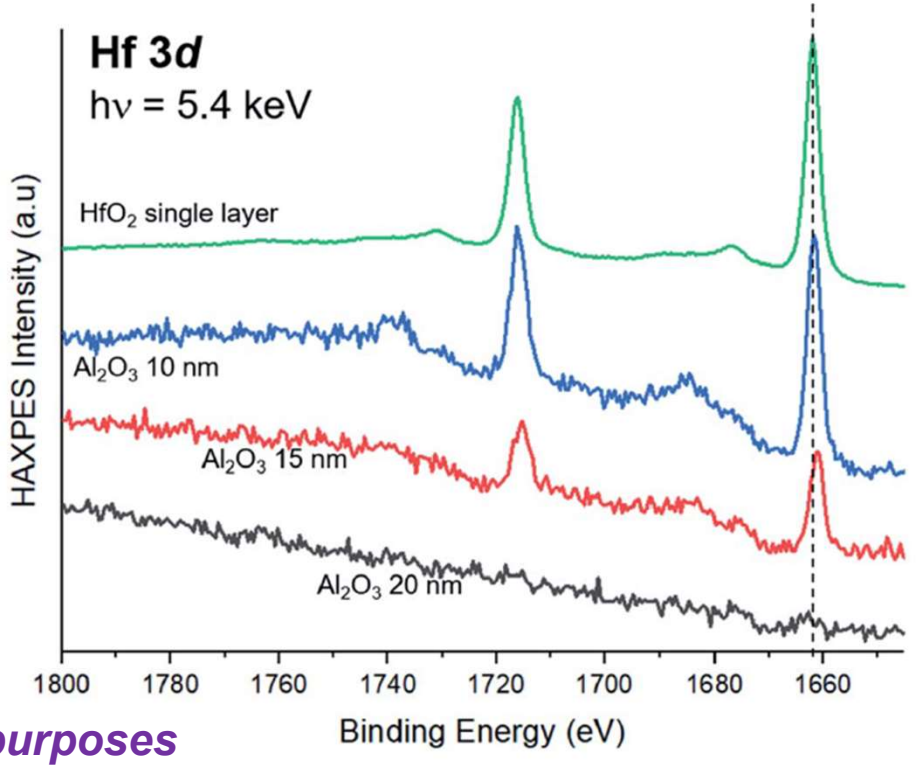




C. Zborowski, O. Renault, S. Tougaard, *Appl. Surf. Sci.* **432** 60 (2018)

# Background analysis in Cr Kα HAXPES



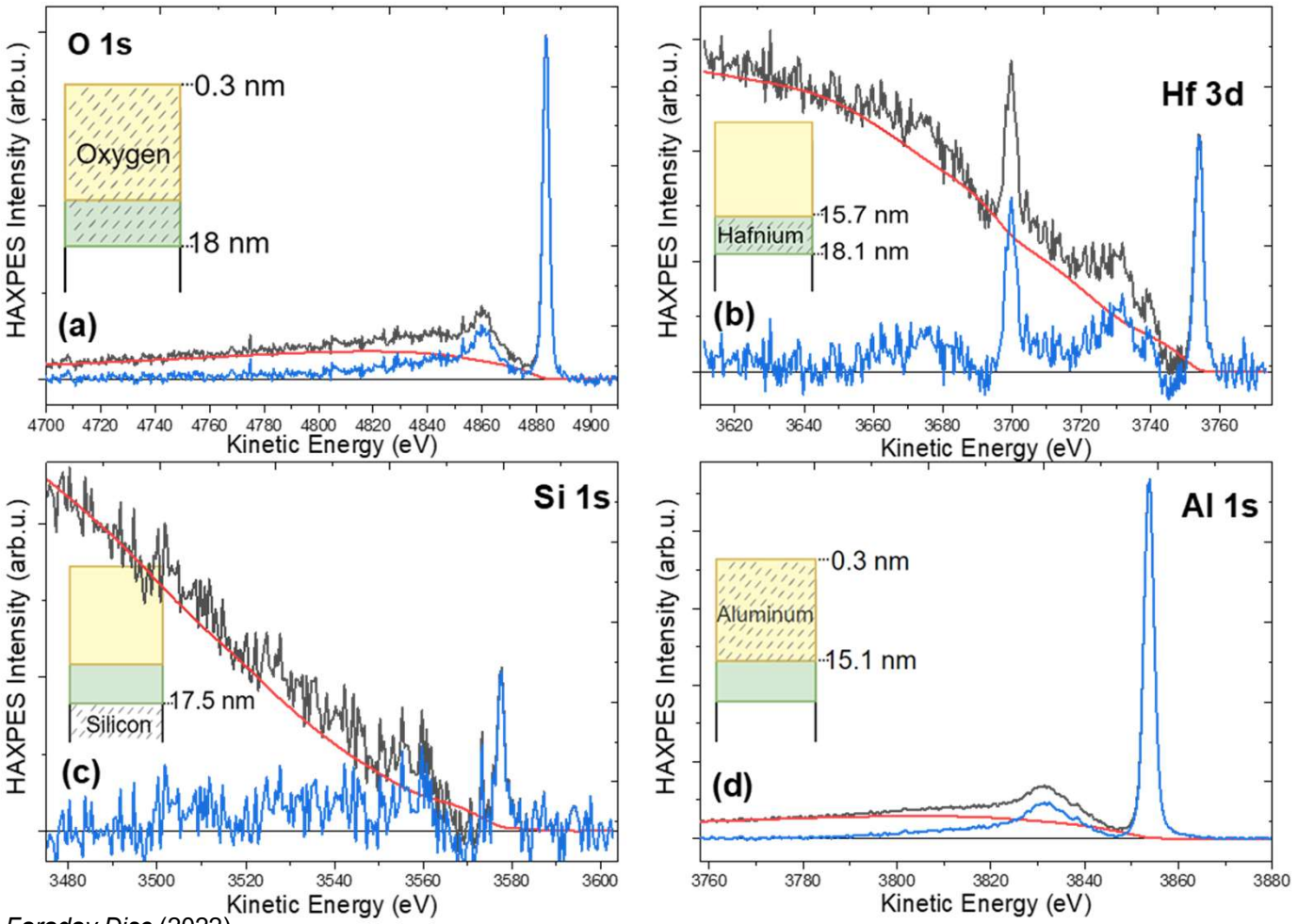



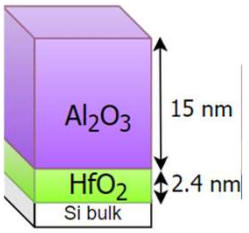




➡ ***Testing accuracy of IBA towards metrology purposes***

Renault, Bure *et al.*, *Faraday Disc.*(2022)

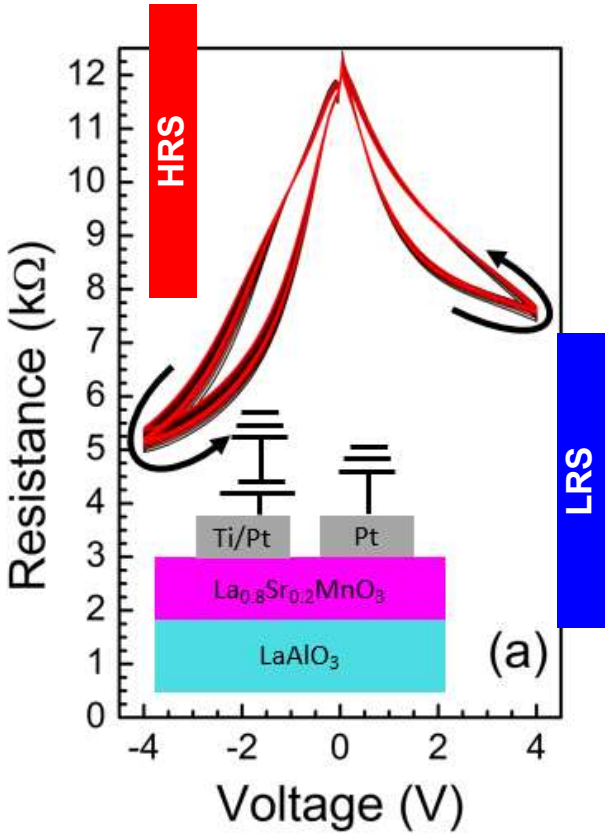
# Background analysis in Cr Kα HAXPES

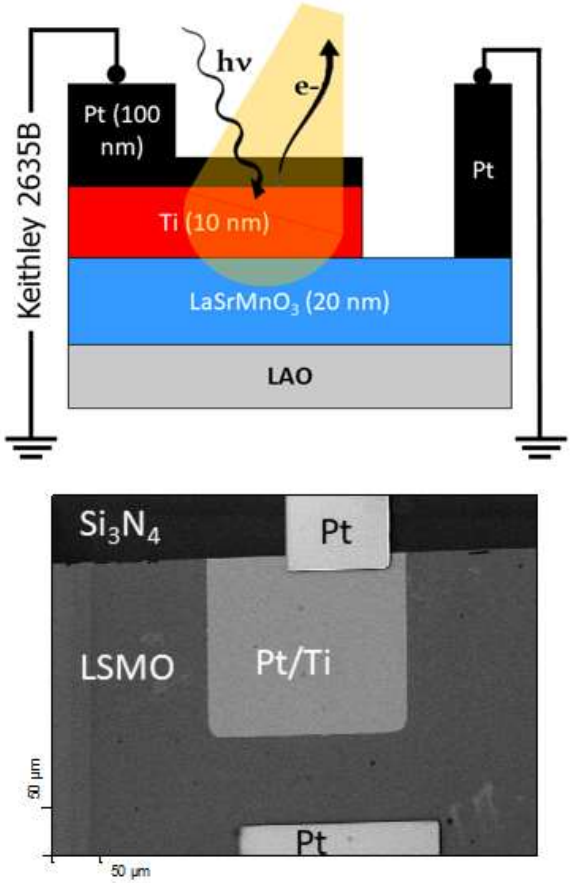


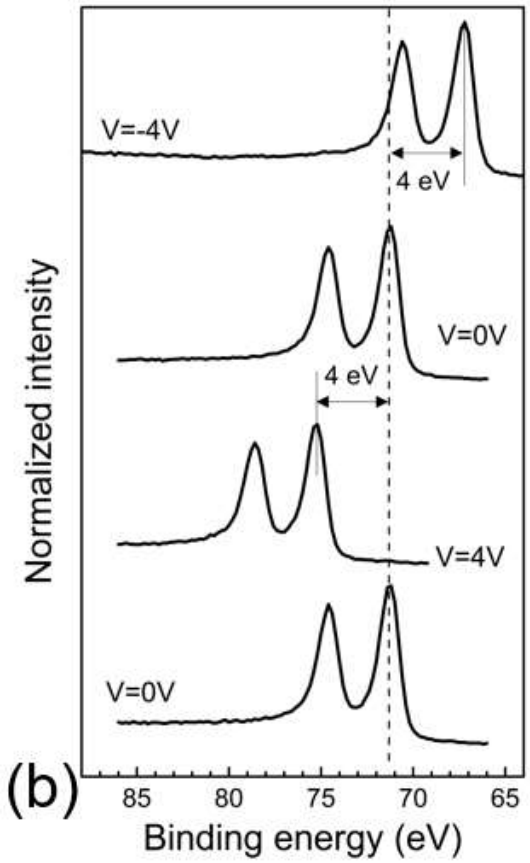




Renault, Bure *et al.*, *Faraday Disc.*(2022)

# Operando Kα HAXPES of prototypical devices

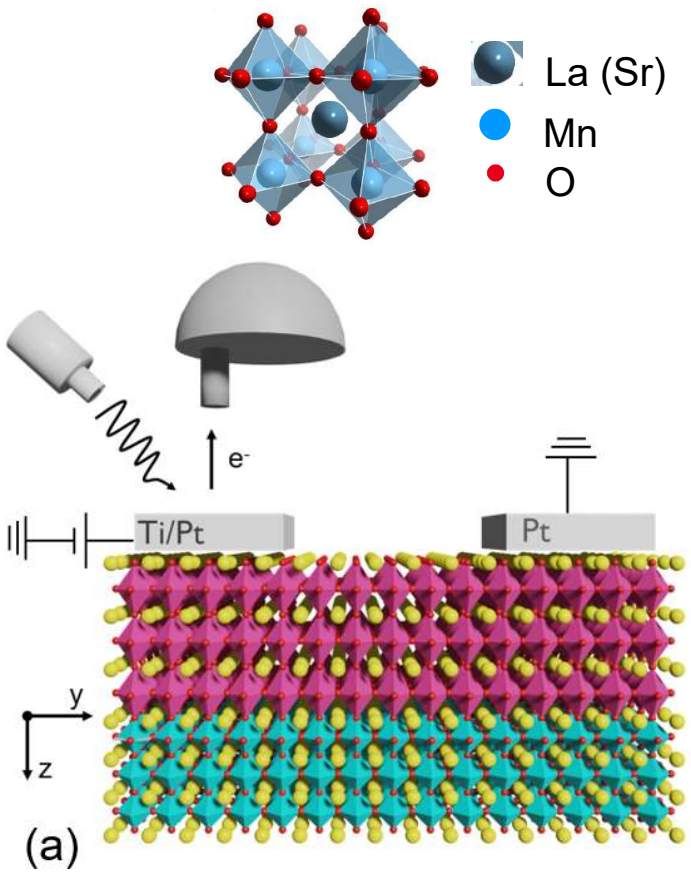


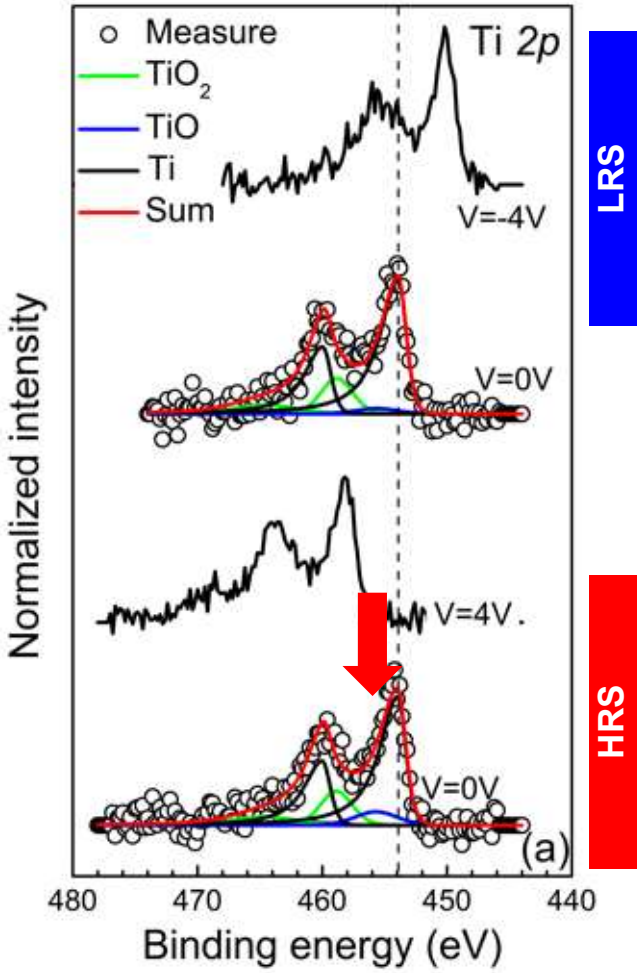



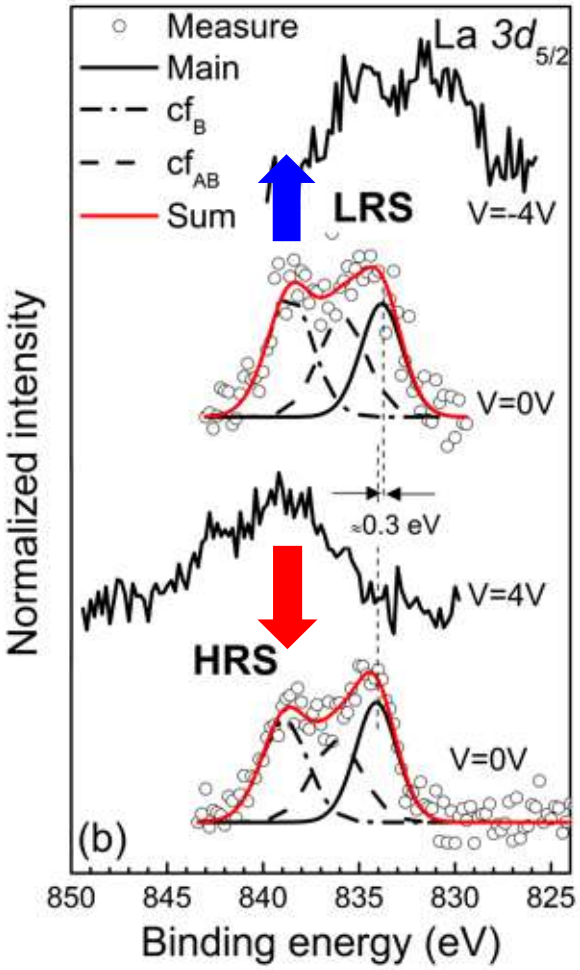




Renault, Courtin *et al*., *Faraday Disc*.(2022)

# Operando Kα HAXPES of prototypical devices



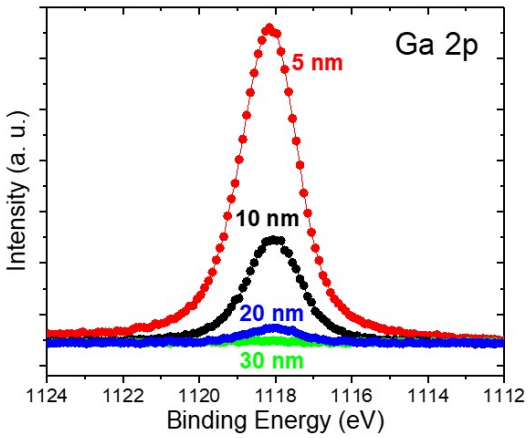



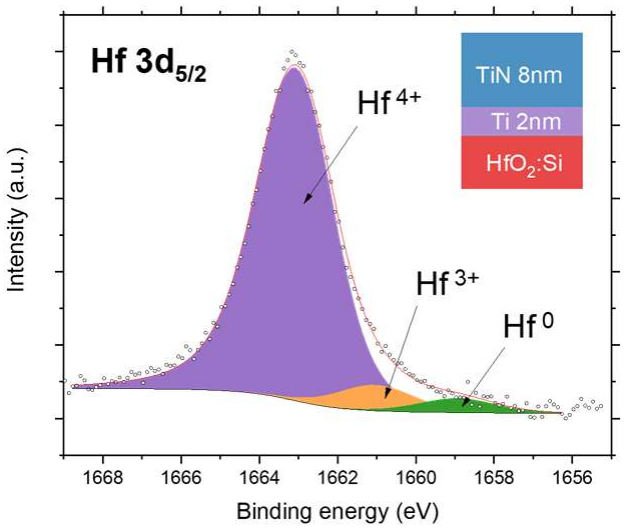



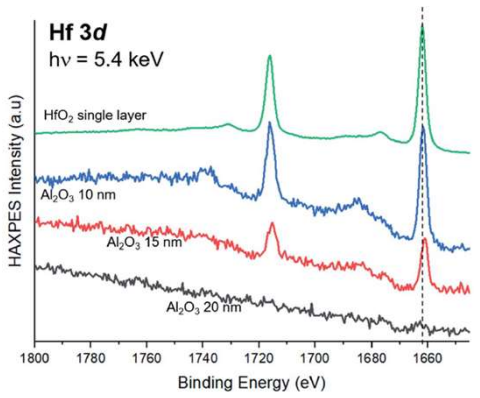

Renault, Courtin *et al*., *Faraday Disc*.(2022)

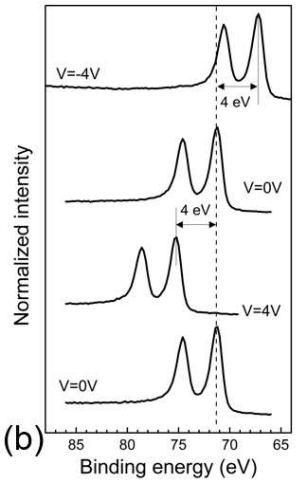
# Conclusion

- **Lab-scale HAXPES with Cr excitation** is promising for device technology
- **Progress in quantification:** updated t-RSFs & extended PERSF databases.
- Extended use of **inelastic background analysis** in lab-HAXPES.
- Novel characterization ***operando*** **approach**.



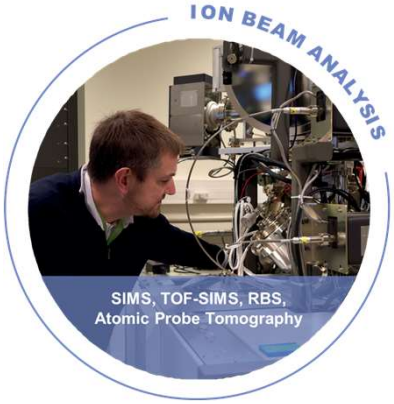



# PlatForm for NanoCharacterisation

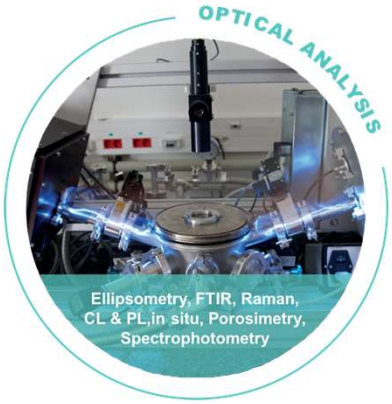
*Characterisation of advanced materials and components supporting disruptive innovation*

This unique tool in the world, supported by three **CEA** Grenoble institutes (**CEA-Leti**, **CEA-Irig** and **CEA-Liten**), aims to develop new characterisation techniques for micro and nanotechnologies, nanomaterials, materials for energy, etc. ; and to carry out the characterizations needed for the advancement of the programs of the CEA and its academic or industrial partners. The expertise of the PFNC covers eight competence centres, including one dedicated to sample preparation, a key step for observations at the nanoscale.













**Steering Committee :** vincent.delaye@cea.fr (CEA-Leti), thierry.deutsch@cea.fr (CEA-Irig), samir.derrough@cea.fr (CEA-Liten)