Successes and Challenges in Applications of a Laboratory-Based Scanning XPS/HAXPES Instrument

PHYSICAL ELECTRONICS
A DIVISION OF ULVAC-PHI

leti ceatech TECHNOLOGY RESEARCH INSTITUTE

imec

K. Artyushkova*[1], A.Vanleenhove[2], T.Conard[2], P. -M. Deleuze[3] and O. Renault[3] ,

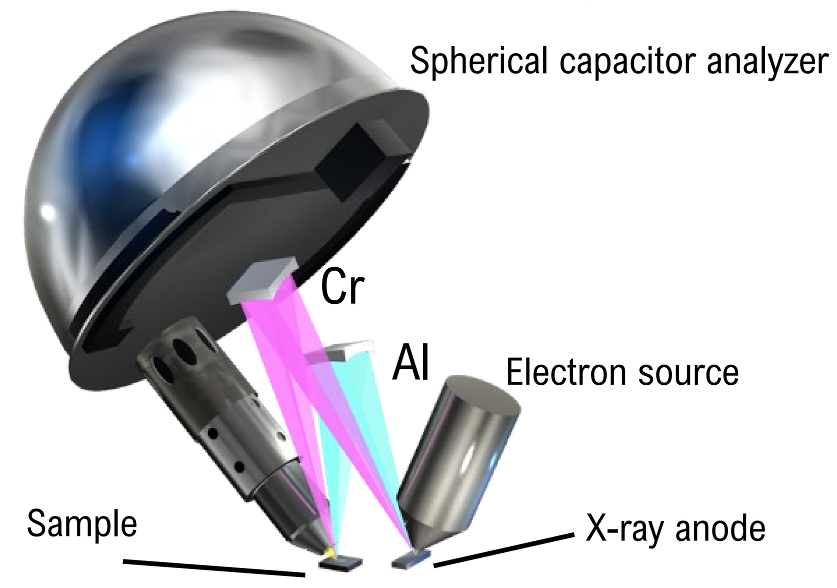
[1]*Physical Electronics Inc., 18725 Lake Drive E, Chanhassen, MN 55317, USA*

[2]*IMEC, 3001 Leuven, Belgium*

[3]*Univ. Grenoble-Alpes, CEA, Leti, 38000 Grenoble, France*

Introduction

With the recent development of lab-based Hard X-ray Photoelectron Spectrometers, there are exciting new opportunities for looking beneath the surface layers accessible using conventional soft X-ray sources in XPS. We describe the development and applications of a laboratory-based instrument, the PHI *Quantes*, equipped with two scanning microprobe monochromated X-ray sources, Al Kα (1486.6 eV) and Cr Kα (5414.8 eV), thus enabling both traditional XPS and HAXPES experiments in the same instrument.



Left, schematic of X-ray source and analyzer on **PHI *Quantes***. Software-controlled anode and shutter can automatically switch between Al and Cr X-rays in < 1 minute. Right, an overview photo of **PHI *Quantes***.

Benefits of HAXPES

- **Deeper depth of analysis:**
  - Buried interfaces:
    - many interfaces such as thin films on a substrate
    - active electronic layers below a surface capping layer
    - depth-profiling through heterostructures and e.g. layered low-dimension materials
    - probing of dopants and contaminants in the bulk of a material
  - Reduced effects of surface contamination
  - Reduced effects of ion beam damage at the interface in depth profiles
- **Access to higher energy core photoelectron peaks:**
  - Additional transitions of varied kinetic energy and hence sampling depth
- **Shifted Auger Transition:**
  - Avoid overlap between core electron lines and Auger peaks
  - Use of Auger Parameter

Analysis of Al_2O_3/GaN thick gate oxides

Challenge: *Analyzing thick oxide layers*

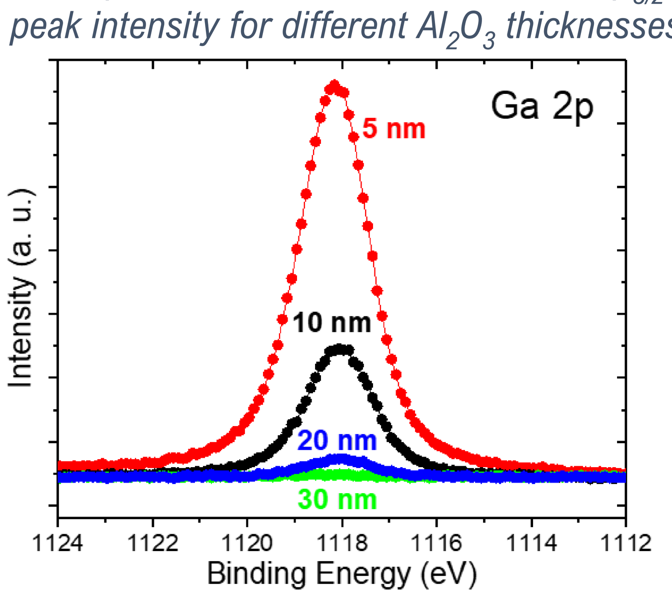
Benefits of using HAXPES:

- Probing beneath the thick oxide layer without sputtering
- Avoiding critical overlap between N 1s and Ga LMM Auger line when using Al Kα source.

Goal of analysis:

- Probe GaN layer beneath a 30 nm oxide layer which is identical to that used in MOSc-HEMTs devices
- Analyze samples with increasing thickness from 5 till 30 nm

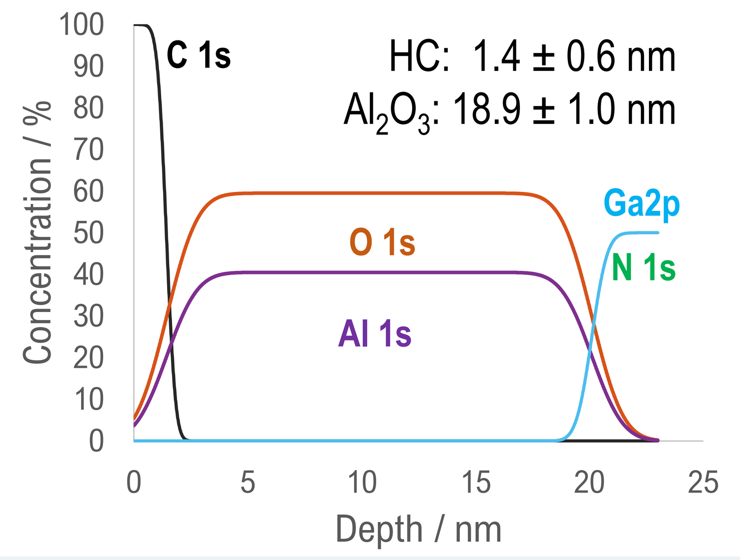
Comparison of the Cr Ka HAXPES Ga2p$_{3/2}$ peak intensity for different Al_2O_3 thicknesses.



Thickness, nm

nominal	HAXPES
5 nm	4.5
10 nm	8.2
20 nm	18.9
30 nm	27.8

Structure of 20 nm Al_2O_3 film modeled using StrataPHI



Success:

- Ga was detected even for 30 nm oxide layer sample
- The thickness of alumina layers estimated using *Strata*PHI software for thin-film structure optimization is within 10% of the nominal value.

Damage-free depth profiling

- **Challenge:** *Probing beneath ion beam damage*
- For efficient and accurate chemical analysis of buried layers and interfaces, the photoelectrons analyzed must originate from below the ion beam damage depth, from depths of ~15 nm or more.

Sampling depth using different X-ray sources, nm (highlighted depth > 15 nm)

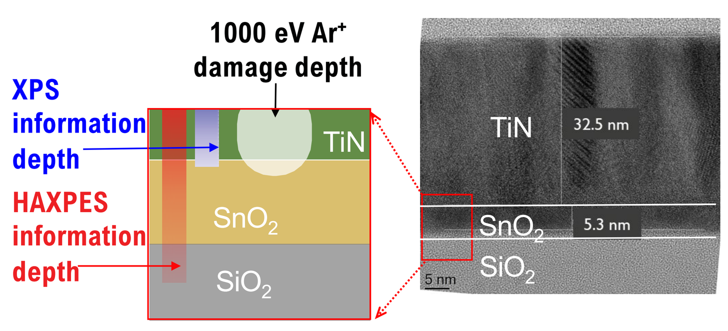
	BE, eV	Al	Ag	Cr
Ga 2p	1120	3.4	11.1	22.1
Zn 2p	1022	3.0	8.7	16.7
Ni 2p	850	3.3	8.3	15.2
Sn 3d	486	7.6	15.5	26.9
Ti 2p	458	6.6	13.3	20.4
C 1s	285	9.2	17.6	29.8
Si 2p	100	9.2	16.6	27.9
Al 2p	74	9.3	16.7	27.8
Hf 4f	17	8.4	14.4	23.7

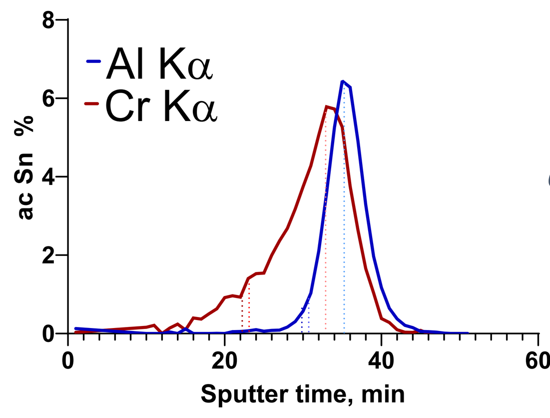
Benefits of using HAXPES:

- Probing beneath the ion beam damage depth

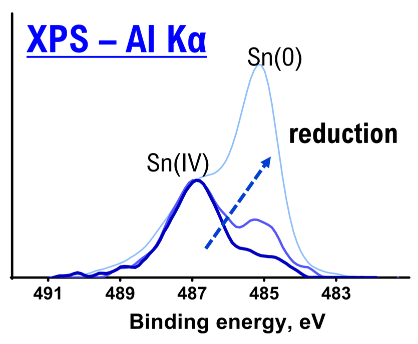
Goal of analysis:

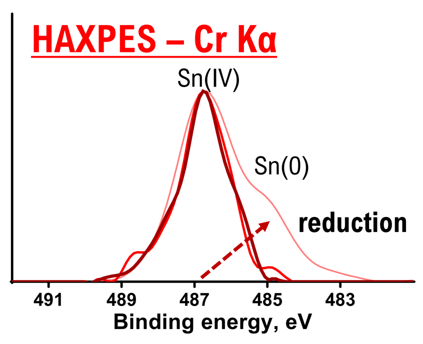
- For a direct comparison of the decreased sensitivity to ion beam damage using a Cr source versus an Al source, acquire depth profile from a stack of 30 nm TiN/ ~5 nm SnO_2 films on a SiO_2/Si substrate using both X-ray sources.





The atomic concentration of Sn as a function of sputter time obtained using Al Kα and Cr Kα sources. Sn is detected much earlier in the Cr profile than in the Al profile





The spectra shown are at 30, 31, and 37 minutes for the Al profile and at 21, 22, and 33 minutes for the Cr profile

Success:

- The degree of reduction observed in HAXPES data at the maximum concentration of Sn is much smaller than in XPS data obtained using the Al X-ray source.

Experimental elemental RSF database

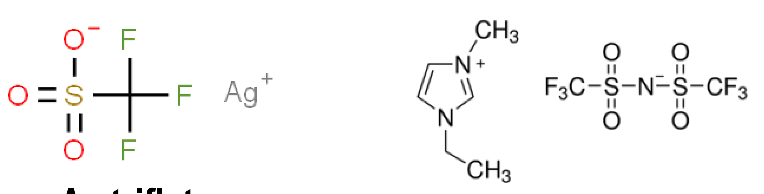
Challenge: *Accurate quantification of HAXPES data*

Protocol:

- RSF of transitions was derived based on the ratio of intensities with respect to pure silver

$$\frac{RSF_{transition}}{RSF_{Ag3d}} = \frac{\frac{Intensity_{transition}}{TFC_{transition} \cdot Asymmetry_{transition}}}{\frac{Intensity_{Ag3d}}{TFC_{Ag3d} * AsymmetryAg_{3d}}}$$

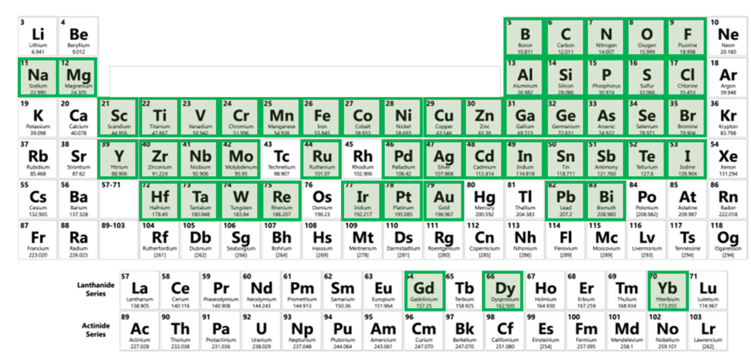
- RSF_{Ag3d} wrt to RSF_{F1s}=1 was derived by analyzing Ag triflate and ionic liquid on three different instruments



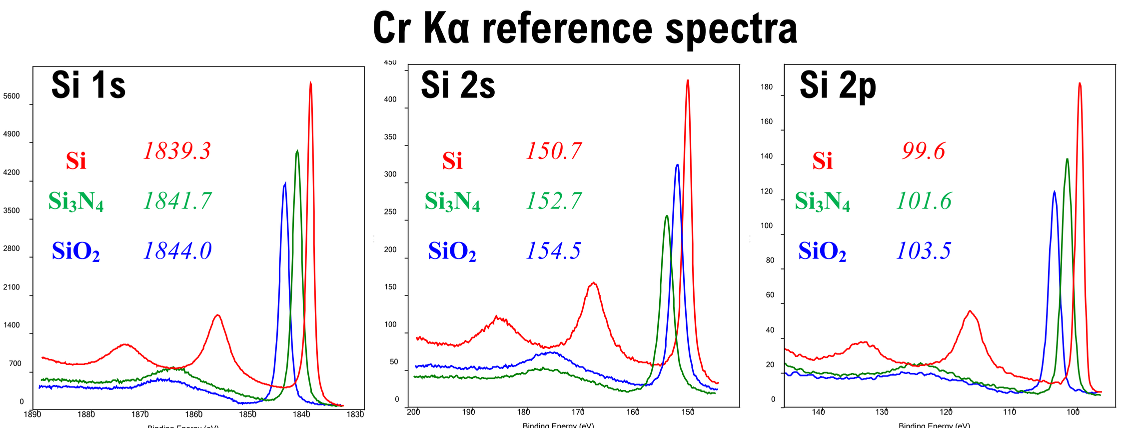
Ag triflate **Ionic liquid EMIMIm $C_8H_{11}F_6N_3O_4S_2$**

Beta database v2 released:

- Transitions for 52 elements
- Reference ionic liquid for F, C, O, N and S
- Pure bulk metals for all others



Cr Kα reference spectra



- Reference compounds providing necessary chemical shift information for newly observed transitions

Success:

- Accurate quantification using all transitions

	Nominal	Si1s	Si2s	Si2p
SiO_2	33.3%	33.1%	31.8%	32.9%
SiC	50.0%	49.4%	47.9%	50.9%
Si_3N_4	42.9%	42.8%	39.6%	42.5%
		Al1s	**Al2s**	**Al2p**
Al_2O_3	40.0%	38.5%	36.2%	37.1%
AlN	50.0%	51.4%	50.0%	51.2%
Mo/Se		**2s/2s**	**2p/2p**	**3p/3p**
$MoSe_2$	33.3%	35.7%	33.8%	31.6%

Analysis of 2D materials

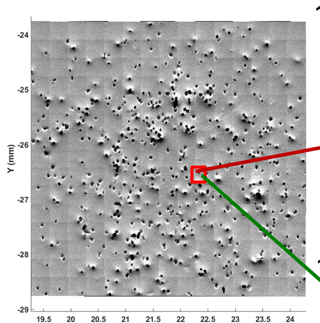
Challenge: *Effect of surface contamination on quantification*

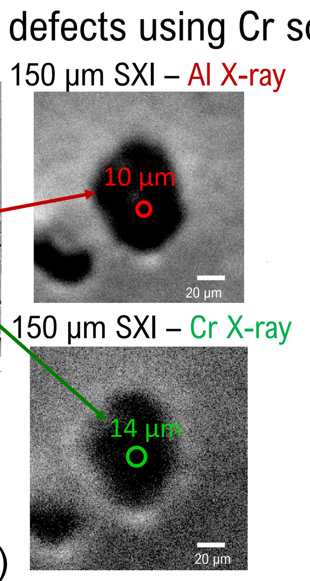
Benefits of using HAXPES:

- Probing beneath the adventitious carbon and oxygen without using ion beam sputtering

Goal of analysis:

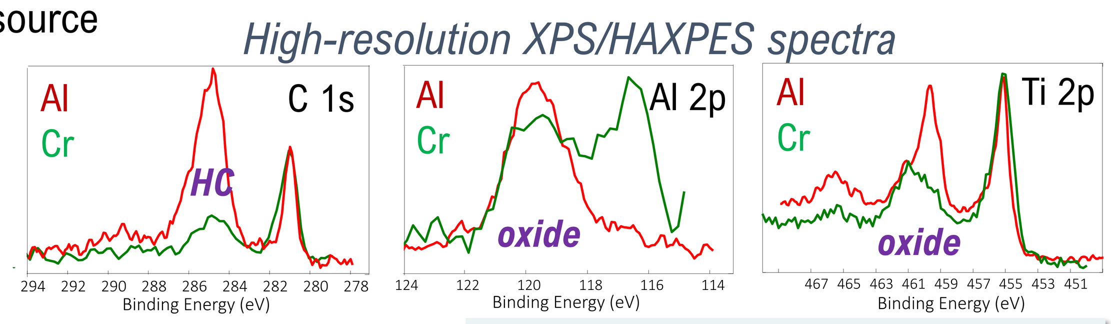
- $M_{n+1}AX_n$ (MAX) are precursors for MXenes – 2D transition metal carbides and nitrides
- Use Cr X-ray microprobe to analyze individual MAX particles of proper orientation
- Quantify oxygen defects using Cr source





5x5 mm^2 mosaic of stitched X-ray induced secondary electron images (SXI)

High-resolution XPS/HAXPES spectra



Quantification results

theory	*Ti/Al=3*	*Ti/C=1.5*	*O1s*
Al (4-6 nm)	0.70	0.27	51.6
Cr (16-20 nm)	3.28	1.70	29.6

Success:

- Can easily find the crystal with the correct orientation

Success:

- As-expected stoichiometry is seen from HAXPES data
- A significant amount of oxygen is present at deeper sampling depths, suggesting oxygen defects within the MAX structure