HAXPES-Lab:

How does it work and what it can do for the electronics industry?

Presented by Dr. Matt Wahila

Moderated by Dr. Jenny Amey

BINGHAMTON UNIVERSITY
STATE UNIVERSITY OF NEW YORK

Electronics Research at Binghamton University

SUNY RF — The Research Foundation for The State University of New York

Binghamton University — State University of New York

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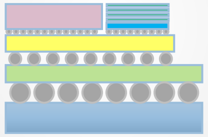
Electronics Packaging

New York State of Opportunity. Division of Science, Technology & Innovation

NYS CAT

CHIRP
Prof. Bahgat Sammakia; Prof. Kanad Ghose; Prof. Ganesh Subbarayan (Purdue), Co-directors

Heterogeneous Integration



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Energy-Smart Electronic Systems

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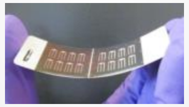
Advanced Solar Energy



NSF

NSF Partnership for Industry

NECCES
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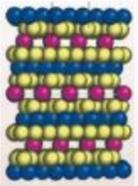
2019 Chemistry

Advanced Batteries



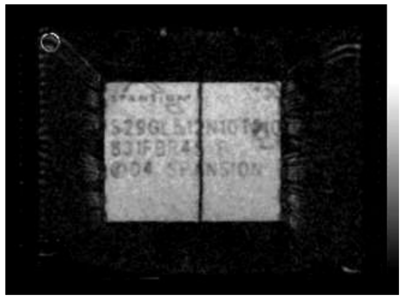
U.S. Department of Energy

DoE EFRC

ADL
Dr. In-Tae Bae, Chief Technology Officer
Dr. Jennifer Amey, Chief Business Development Officer

HSCF
Dr. Yan Sun, Manager

ADL Capabilities



C-SAM image of a package (showing cracked die) damaged in an accident .

Advanced, multi-disciplinary lab with 24/7 equipment access.

PhD educated staff perform analyses and instrument training.

Can characterize materials, surfaces, interfaces, and fully manufactured electronic devices.

Thermal Analysis Suite

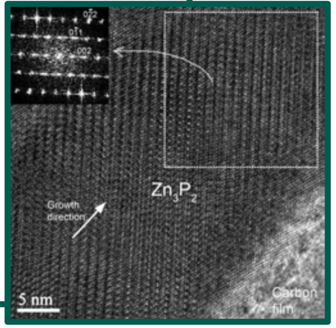
- DSC
- TGA & TGA-MS
- TMA
- DMA
- Flash diffusivity
- Rheometer
- Infra-red microscopy

Surface & Interface Suite

- XPS
- AFM
- FTIR
- LEED
- Stylus and optical profilers
- Spectroscopic ellipsometry
- ***And now HAXPES!***

Electron Microscopy Suite

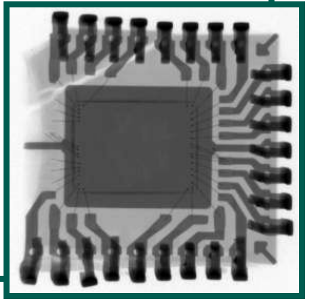
- TEM
- High-resolution SEMs
- FIB/SEM
- Carbon/metal coaters



TEM image with diffractogram from a Zn_3P_2 nanowire.

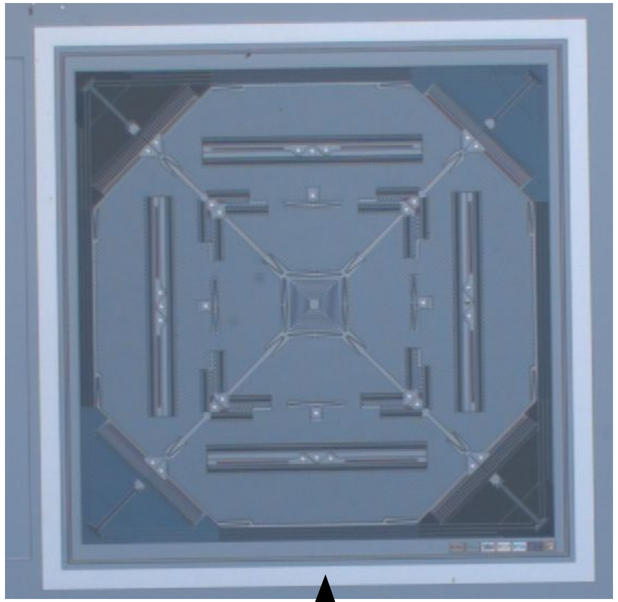
Non-destructive Testing

- XRD
- C-SAM
- X-ray radiography with 3D CAT scans



X-ray image of package showing undamaged die but broken wire bonds.

ADL Example – *XPS Analysis of MEMS Device Contamination*



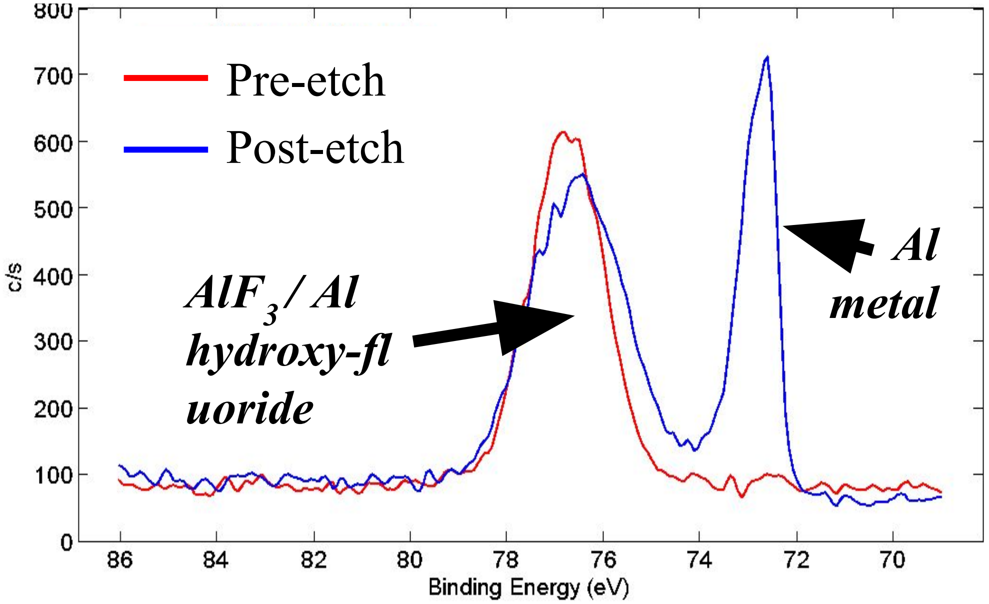
Al seal ring

A company had issues with Al seal bonding.

XPS was used to investigate the Al seal both before and after an etching process.

Significant Fl contamination was found on Al seal surface.

Al 2p



Sample	F (at%)	Al (at%)	O (at%)	C (at%)	Si (at%)	N (at%)
Pre-etch	**52.6**	16.9	18.6	1.9	5	4.9
Post-etch	**54.3**	26.7	11.8	4	2.3	0.9

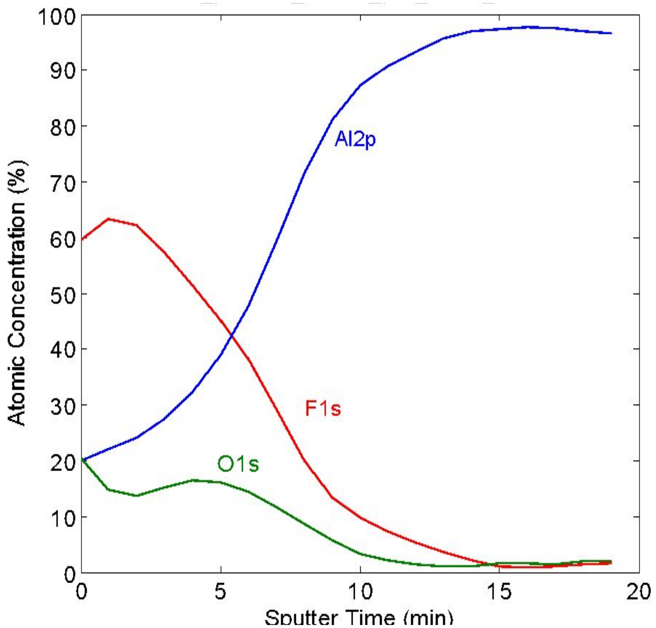
ADL Example – *XPS Analysis of MEMS Device Contamination*

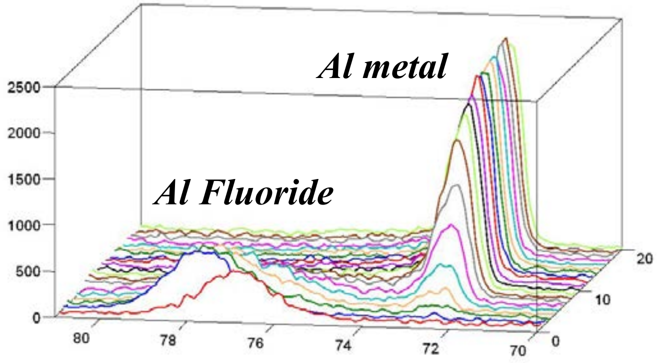
Destructive sputter depth profiling showed layer of AlF_3 / Al hydroxy-fluoride.

Etch removes most of this surface AlF_3 layer, but a significant amount remains.

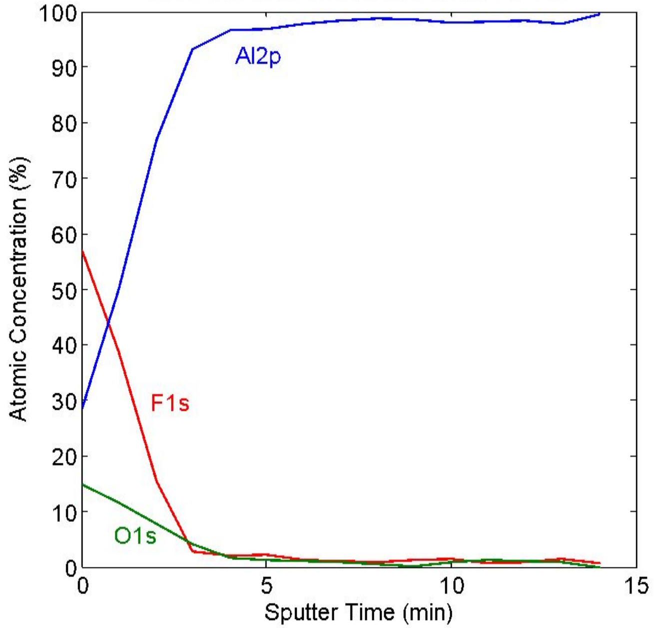
Presence of aluminum fluoride compounds is detrimental to bonding!

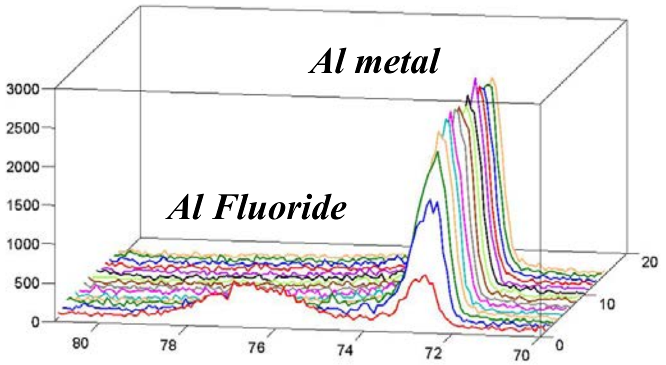
Pre-etch

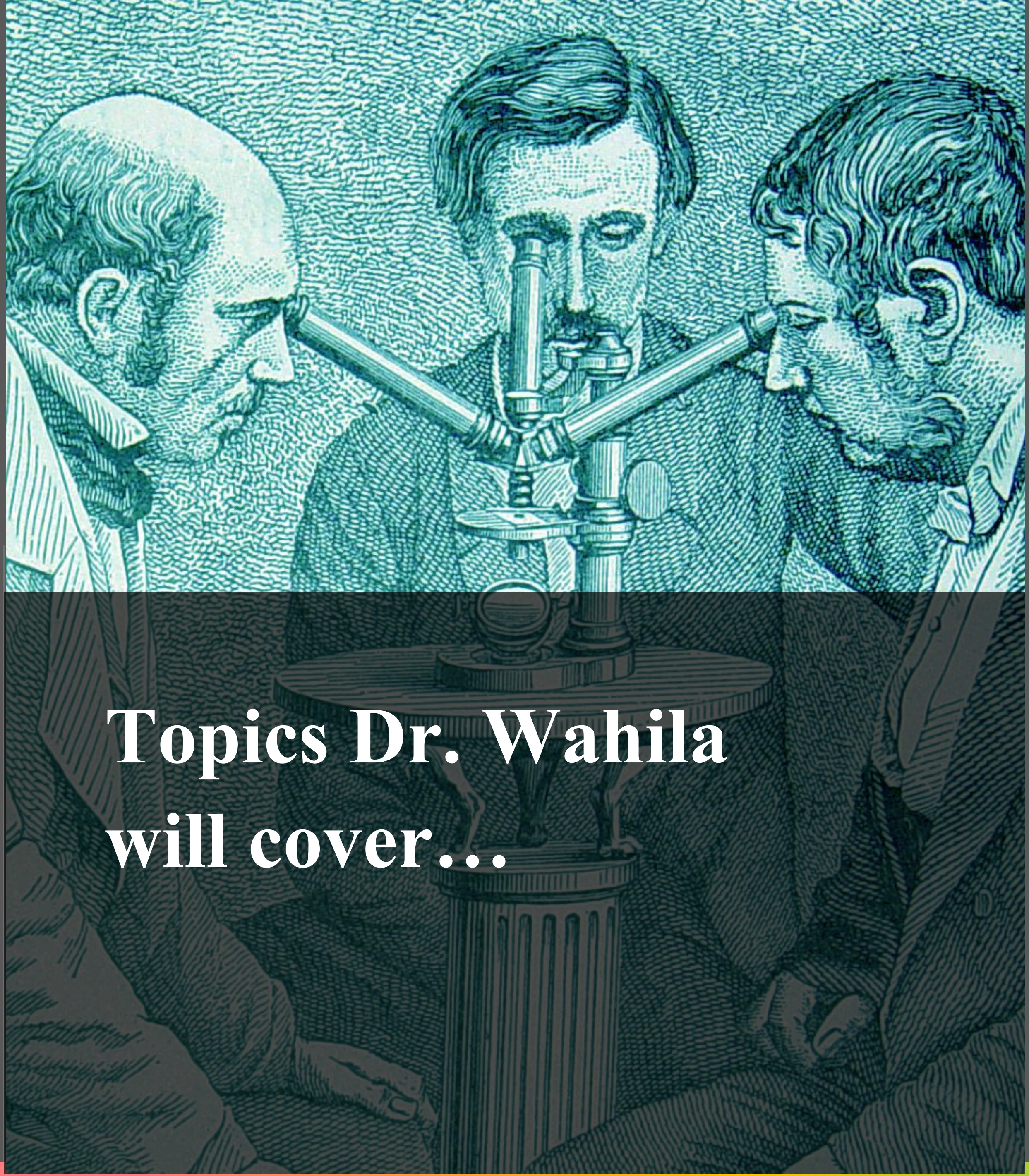




Post-etch







Topics Dr. Wahila will cover…

What is HAXPES?

What is the HAXPES-Lab?

What can you do with the HAXPES-Lab?

Using the HAXPES-Lab at Binghamton University.

What is HAXPES?

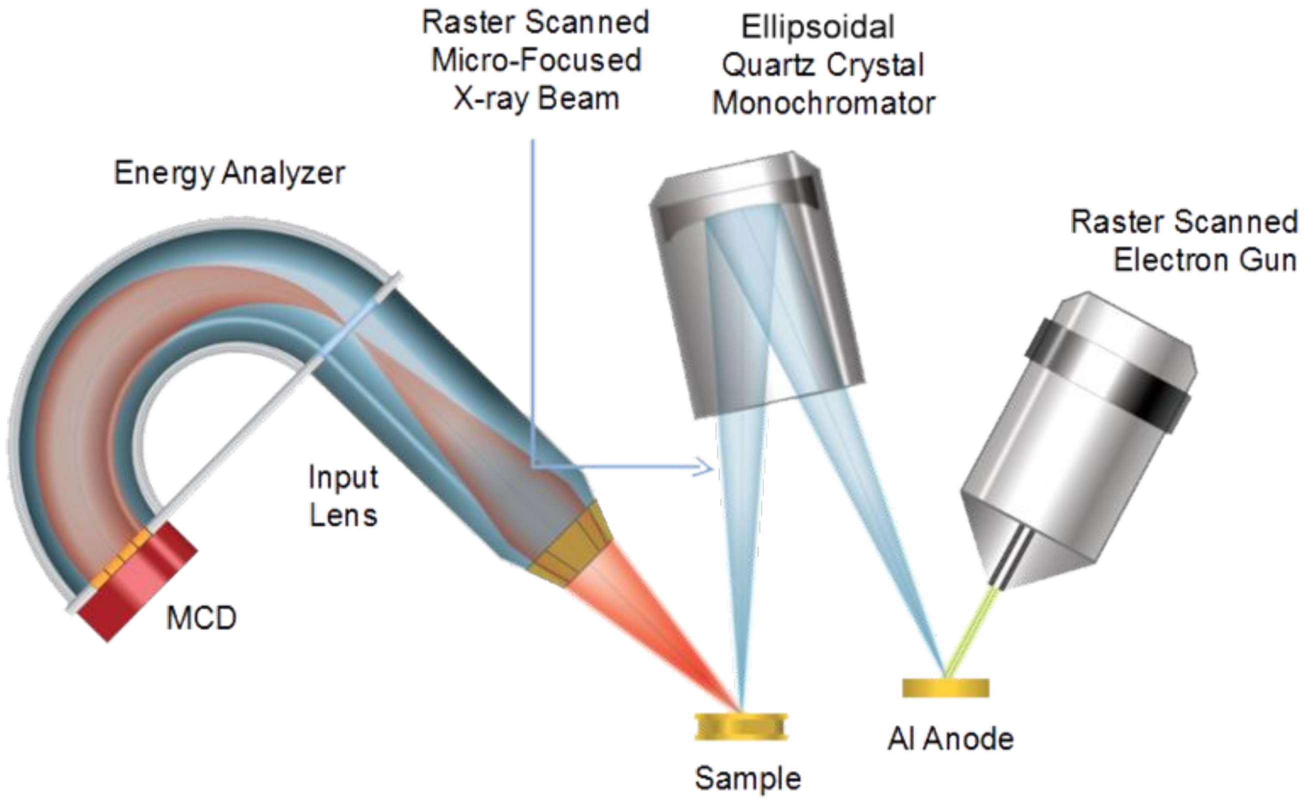
Hard X-ray Photoelectron Spectroscopy

First, What is X-ray Photoelectron Spectroscopy (XPS) ?

XPS is a ***highly surface sensitive*** technique that utilizes the photoelectric effect to probe electronic states of a material.

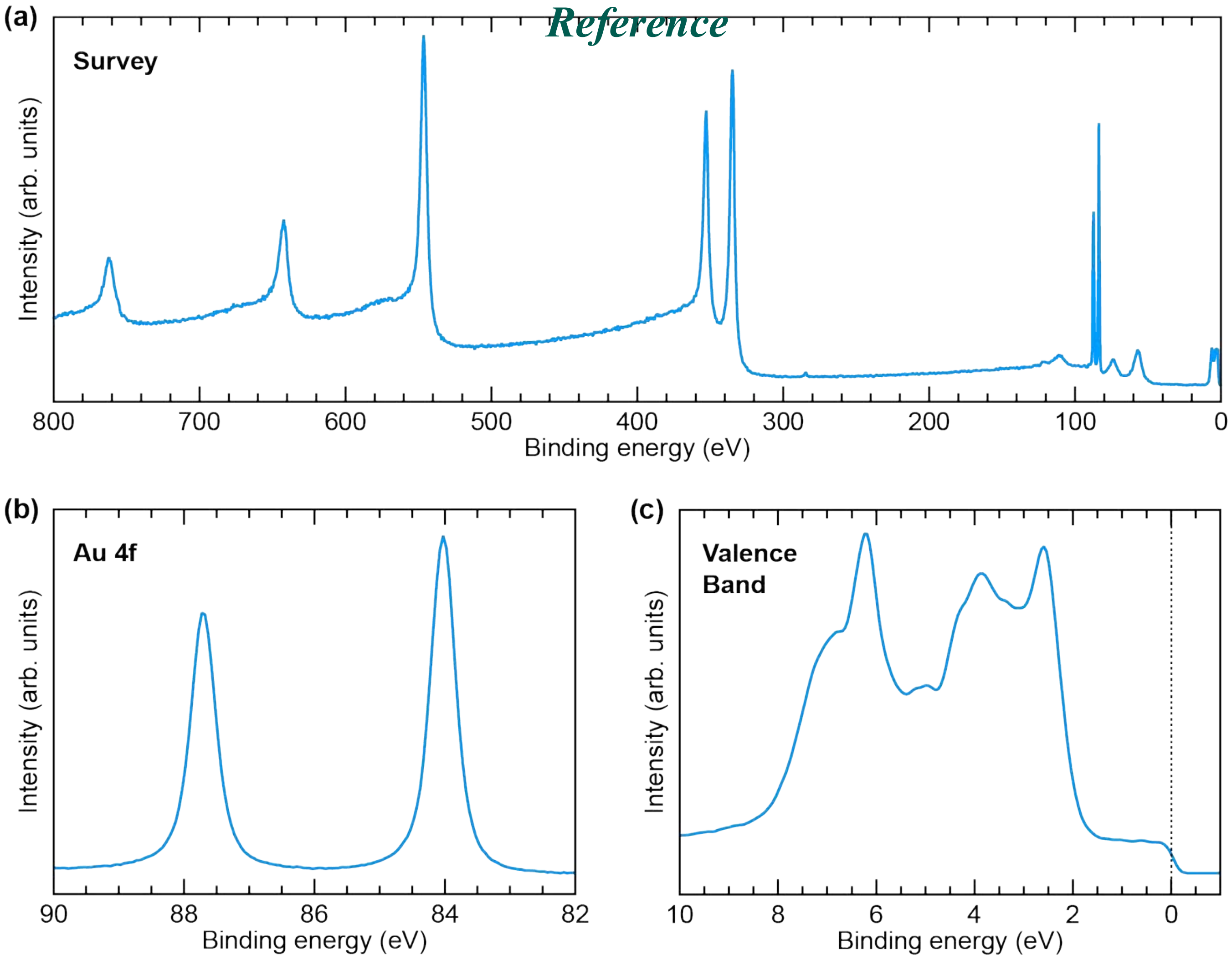
A **monochromatic photon beam** is used to excite electrons within a material, allowing some to escape and become ***"photoelectrons."***

Their **final kinetic energy** then provides info on ***elemental composition, atomic charge state, and other material properties.***



Example Spectra

Gold Foil Reference



XPS measures a material's **occupied electronic states**.

Core levels mainly provide info on ***atomic composition*** and ***elemental charge states***.

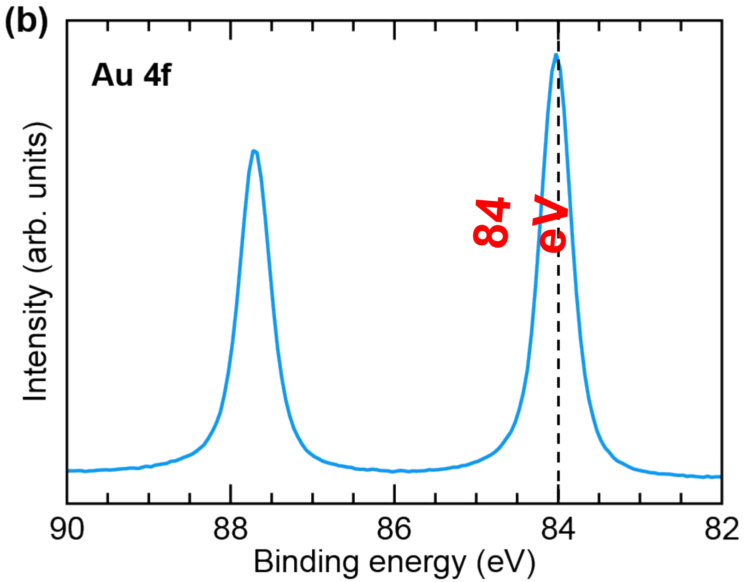
Valence band provides info on ***interatomic bonding*** and ***optoelectronic properties***.

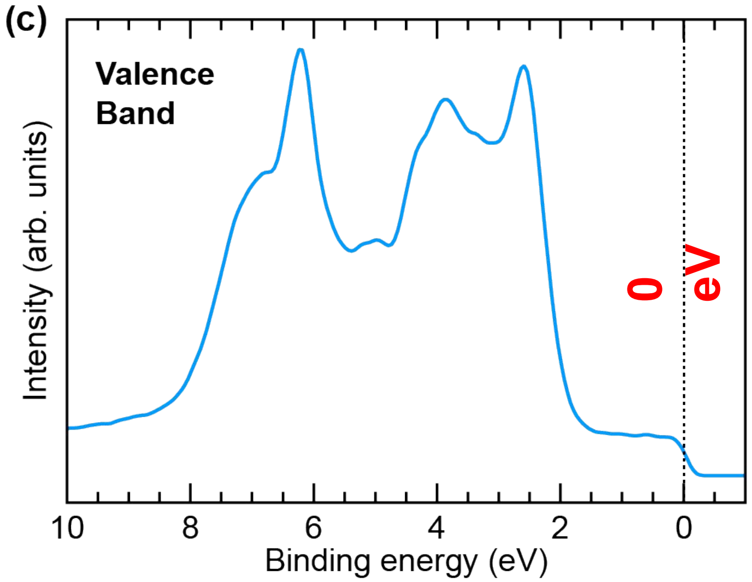
Core Levels *vs* Valence Band

Core levels are ***only weakly affected by bonding*.**

Core level "**Binding Energy**" is characteristic of the element, but chemically shifted by interactions with valence electrons and surrounding atoms.

Valence bands can have ***complicated structure*** due to the bonding, hybridization, and other interactions with neighboring atoms.



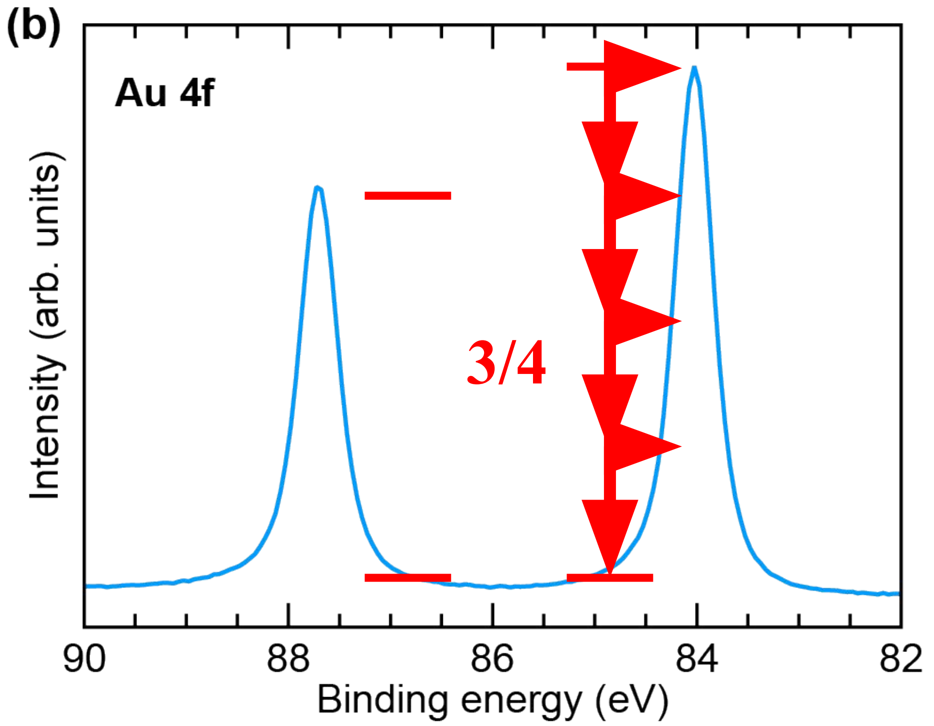


Core Levels

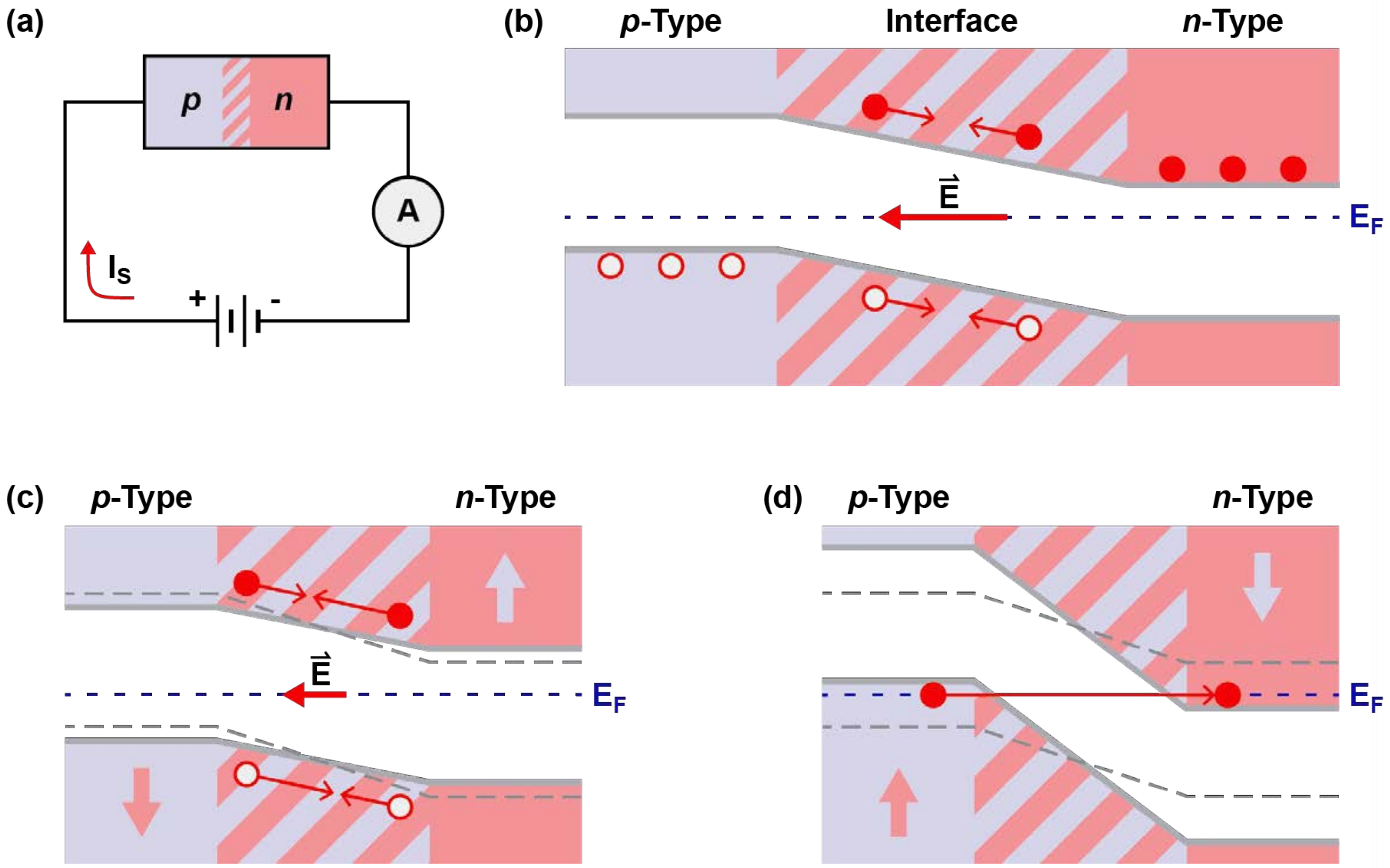
Core level peaks **are symmetric for insulators,** but **asymmetric for metals** due to the excitation of conduction band electrons.

($p_{3/2}$, $p_{1/2}$), ($d_{5/2}$, $d_{3/2}$), and ($f_{7/2}$, $f_{5/2}$) levels will show **two peaks** due to spin-orbit coupling with ratios of 2/1, 3/2, and 4/3, respectively.

Area under a core level peak is proportional to the **atomic concentration** of that element.



Valence Band – *Band alignment*



Band alignment between materials is often what determines the operating behavior of devices!!

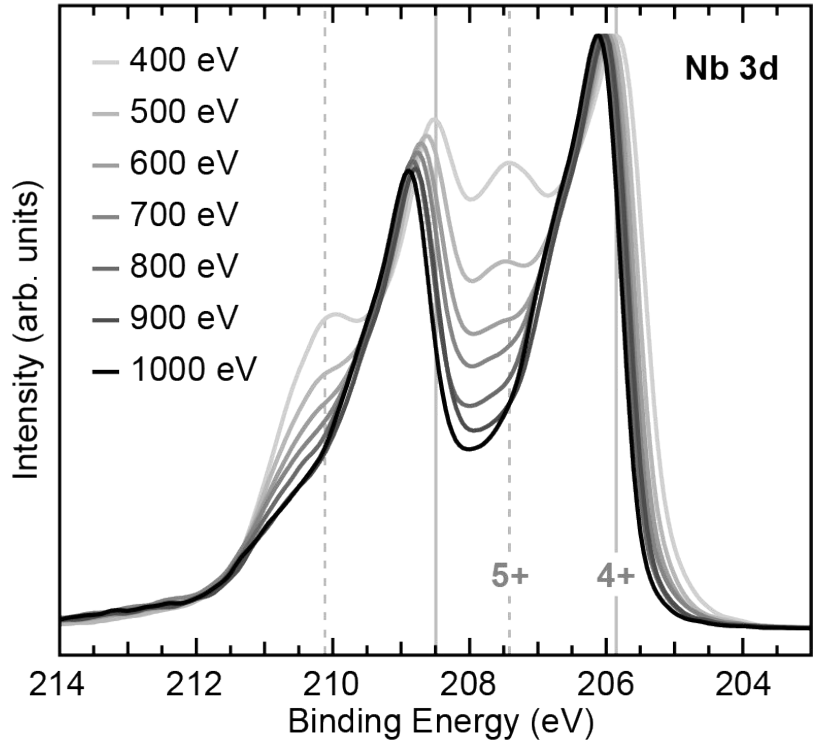
Valence band spectra (together with X-ray/Optical Absorption, Kelvin Probe, or other measurements) can be used to determine band alignment of materials.

Effects of Photon Energy

Different photon energies result in <u>different photoelectron escape depths</u>!

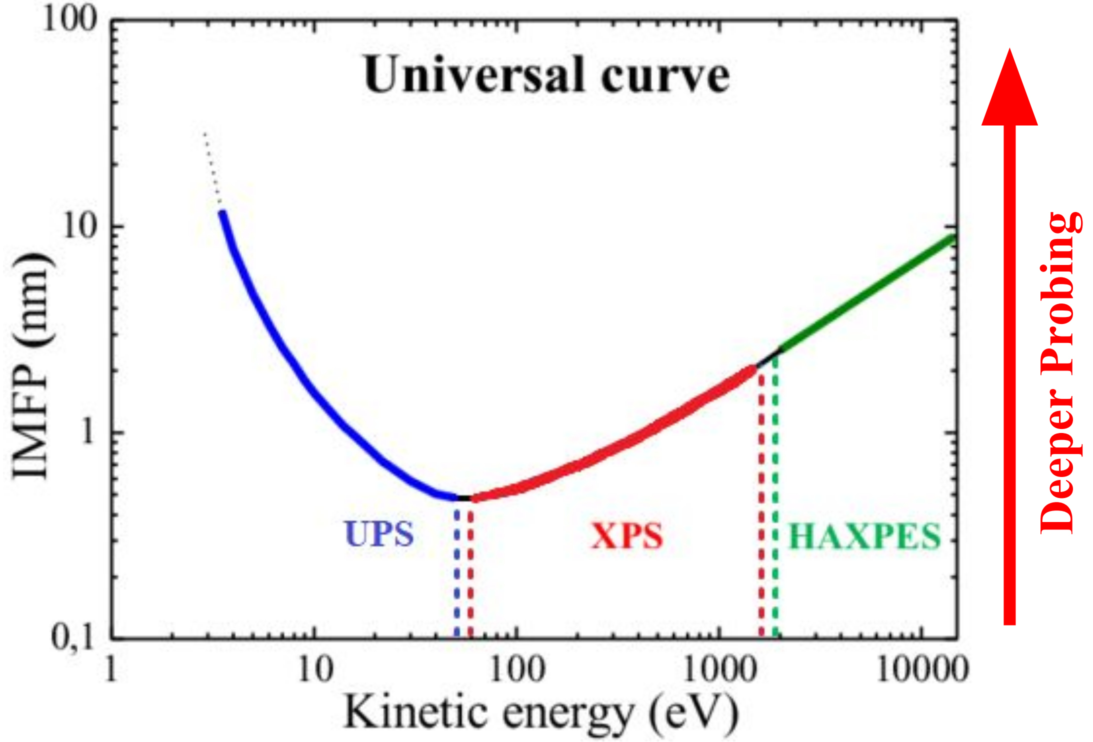
<u>**Lab-based XPS systems**</u> have ***limited photon energies***. Some systems can be equipped with multiple photon sources (*Al/Mg Kα, UV, etc*), but typically only range from ***UV to "soft" X-rays***.

<u>**Synchrotrons**</u> generate ***continuously variable photon energies*** from ***UV to "hard" X-rays***.



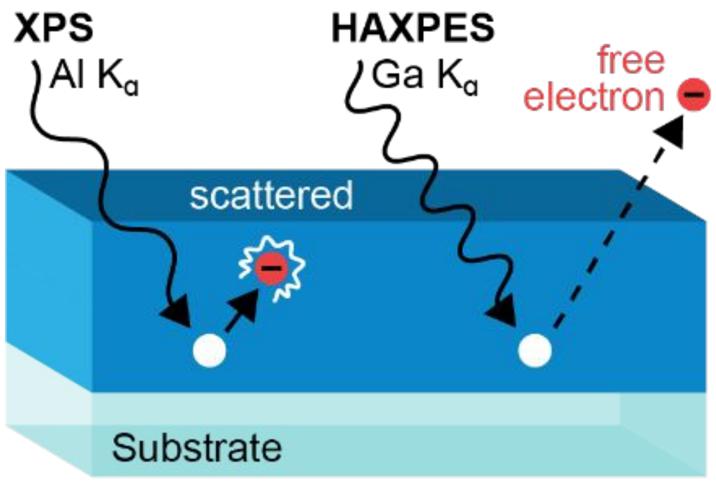
In this case, a thin over-oxidized (Nb 5+) surface layer was found to exist purely on the surface due to atmospheric exposure.

HAXPES *vs* XPS *vs* UPS?



Low energy X-rays provide mainly surface information (topmost ~3 - 4 nm).

High energy X-rays can access tightly electrons much deeper inside a sample.



Hard X-ray Photoelectron Spectroscopy (HAXPES) typically uses high energy, synchrotron X-ray radiation (> 4,000 eV) giving probing depths in the ***tens of nms***.

Benefit of HAXPES

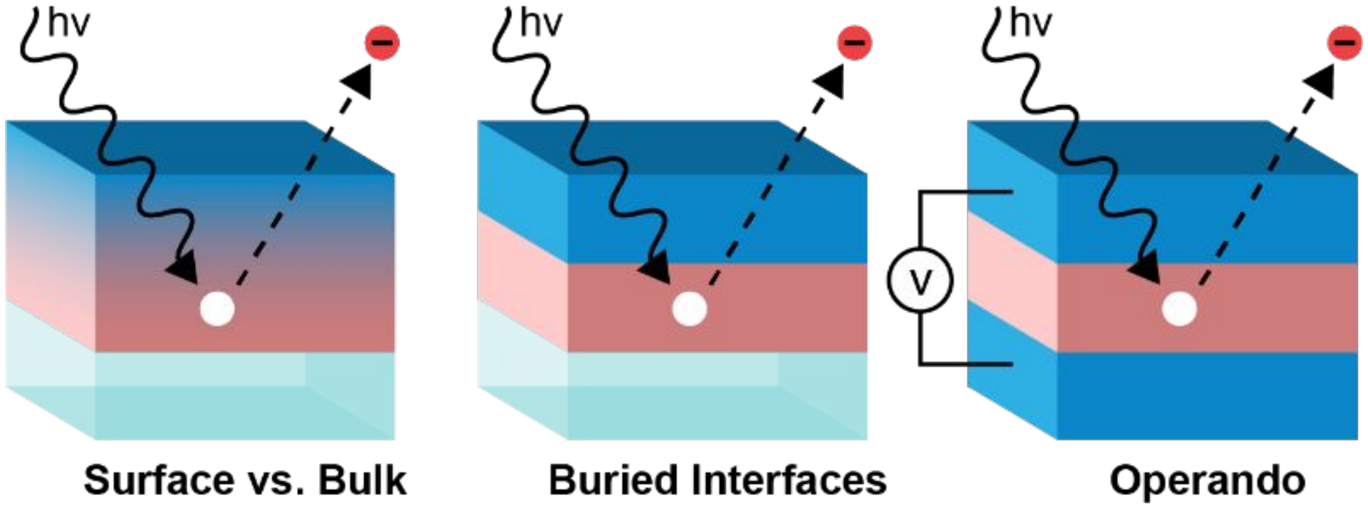
Real devices are usually composed of <u>multiple buried material interfaces</u>.

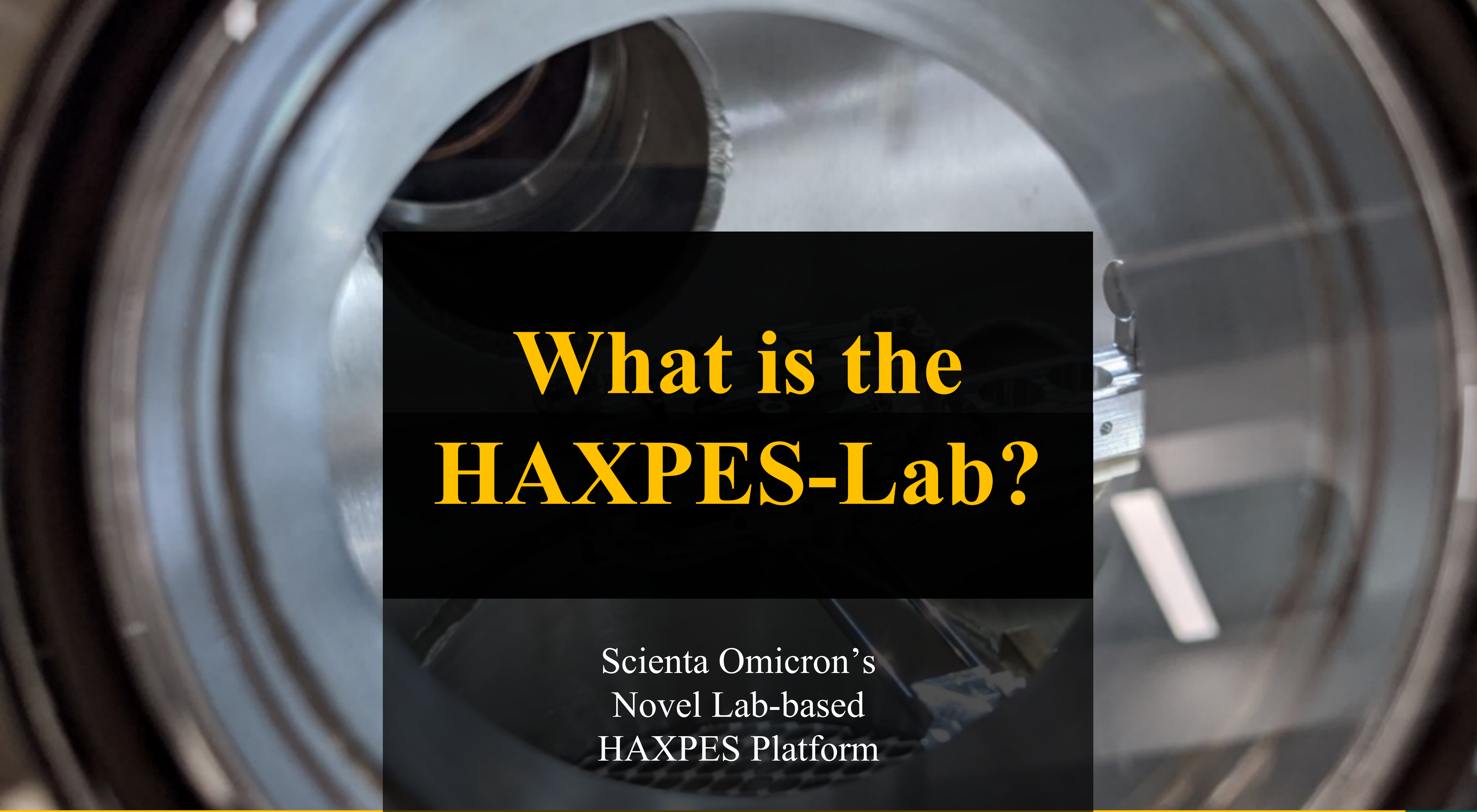
“The interface is the device” - Herbert Kroemer

But XPS is a surface science technique…

“God made solids, but surfaces were the work of the devil!” - *Wolfgang Pauli*

Probing beyond the surface with HAXPES allows us to study subsurface regions, including buried device interfaces!





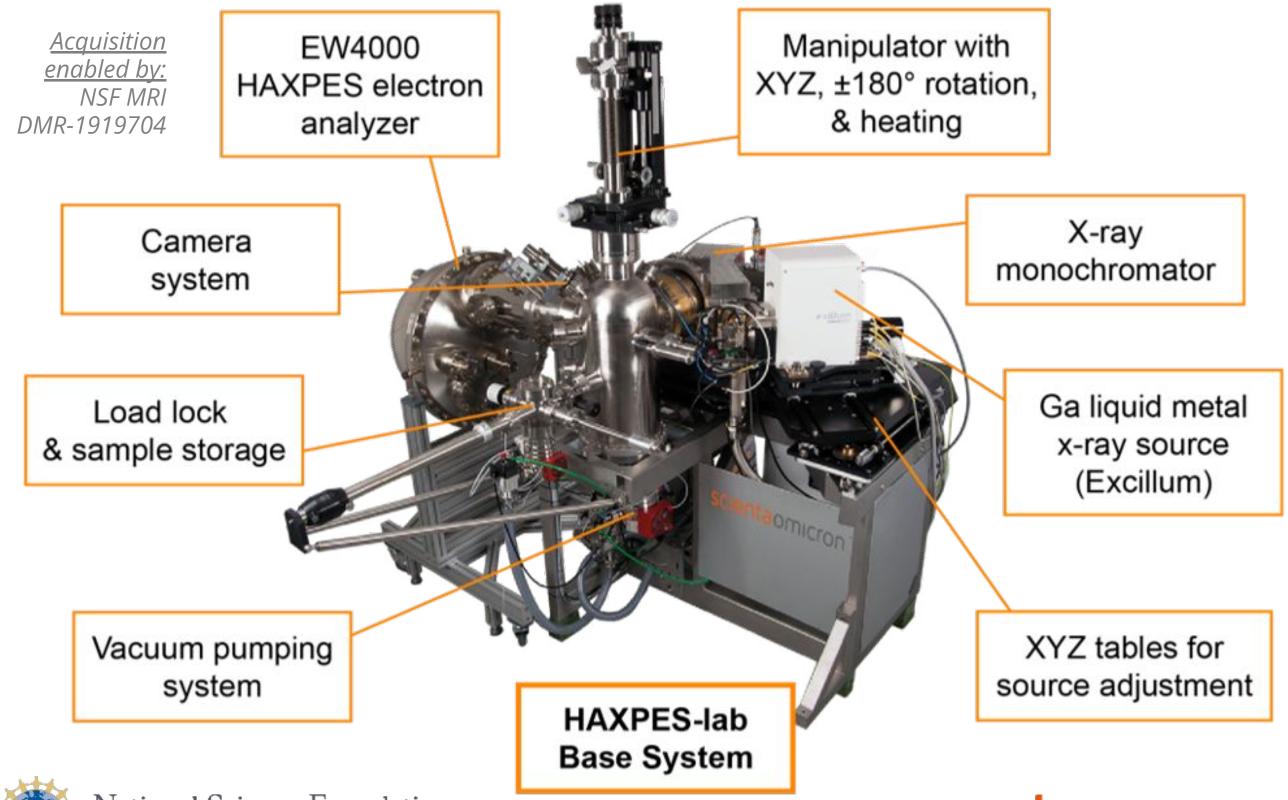
What is the HAXPES-Lab?

Scienta Omicron's
Novel Lab-based
HAXPES Platform

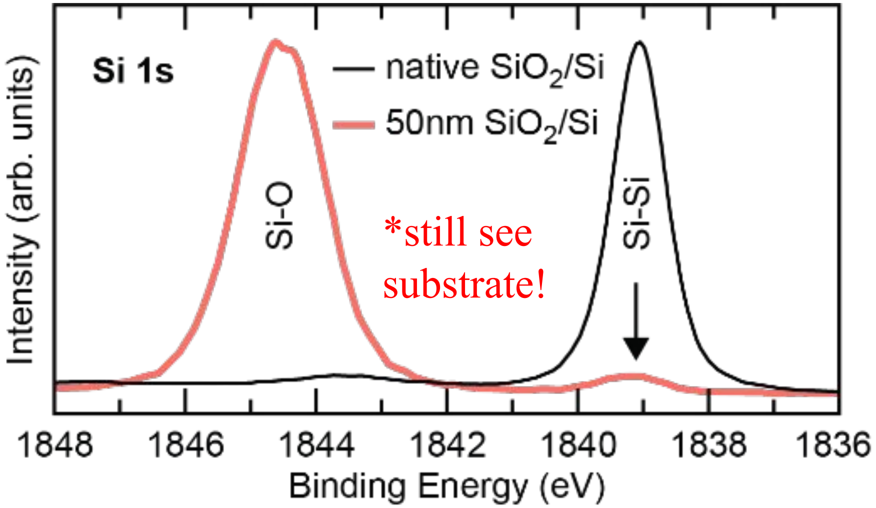
What is the HAXPES-Lab?

The Scienta Omicron HAXPES-Lab is a small, laboratory-based system that provides synchrotron-comparable HAXPES spectra.

Acquisition enabled by: NSF MRI DMR-1919704



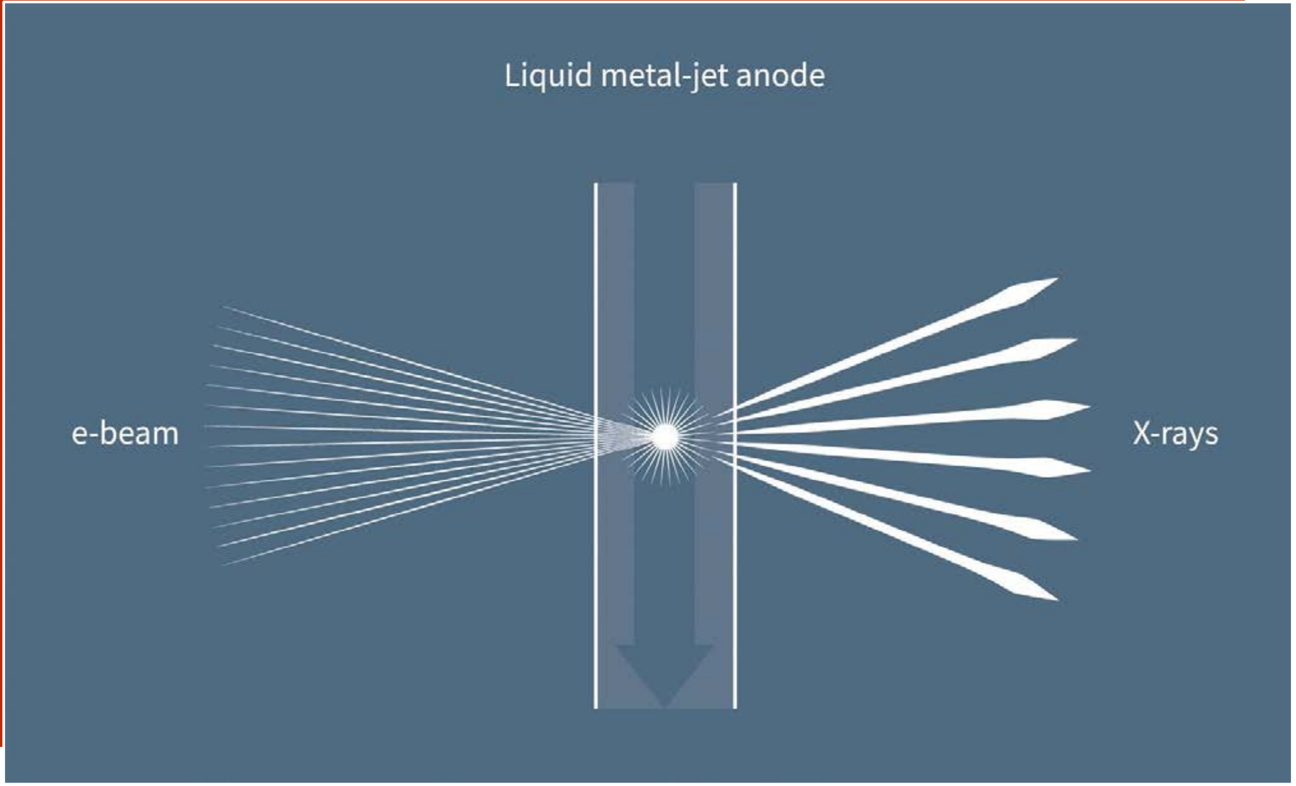
The system at Binghamton U. is the 1st lab-based Ga-Kα HAXPES in the U.S.



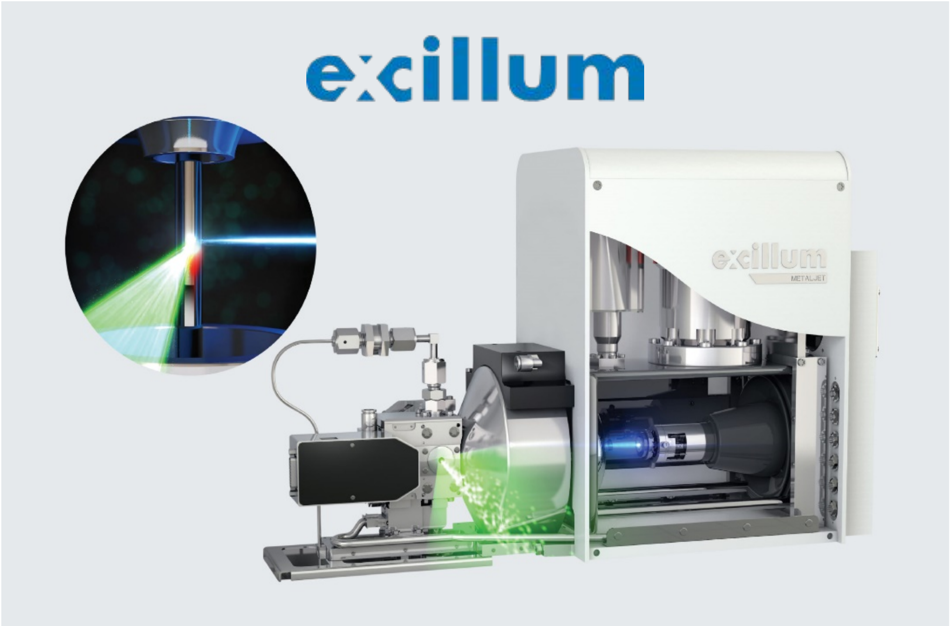
The 9.2 keV x-rays produced by the Ga jet source can probe up to 60 nm deep. This can circumvent surface contamination and overlayers.

What is a MetalJet X-ray Source?

<u>**Solid anodes have limited brightness**</u> **due to material limitations (melting/heat damage)…**



Why not use an anode that's <u>already melted</u>??



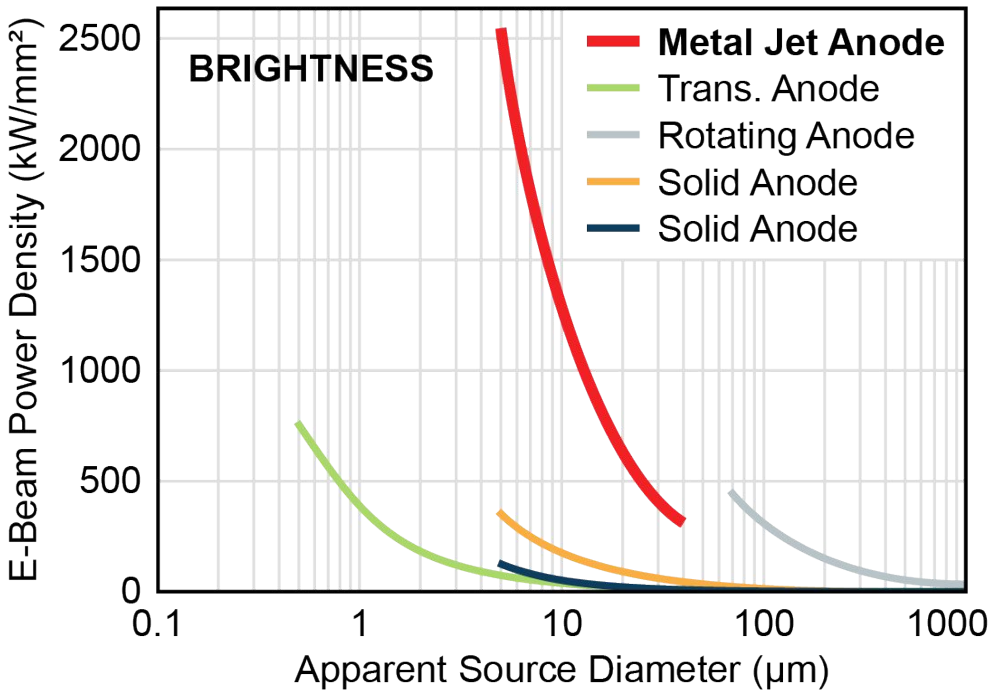
https://www.excillum.com/our-products/metaljet/

The Excillum MetalJet source uses a laminar flow of liquid Ga/In alloy as the X-ray generating anode.

This enables the rapid removal of excess heat from the anode, allowing for high brightness without melting.

What are the Capabilities? – *Brightness*

The *brightness*, small spot size, and high resolution of the lab-based HAXPES make it ideal for investigating complex systems such as real-world microelectronic devices.



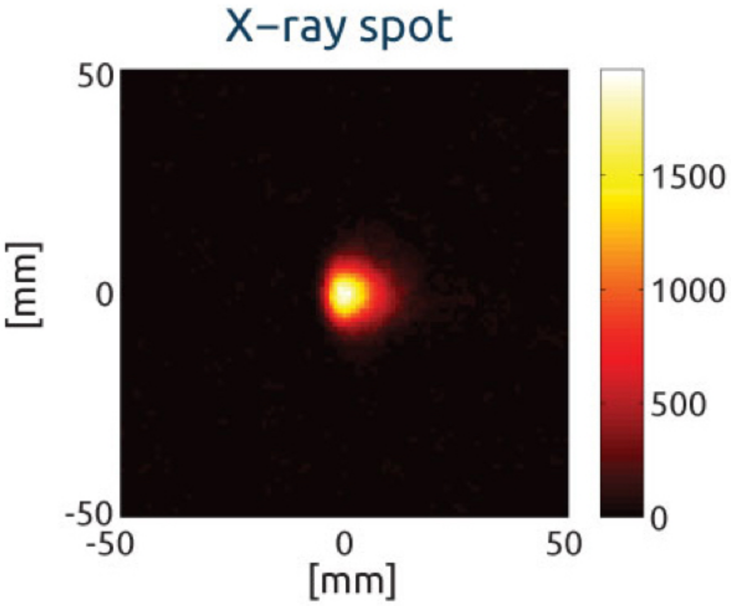
The Excillum MetalJet source provides a massive increase in brightness over traditional lab-based X-ray sources.

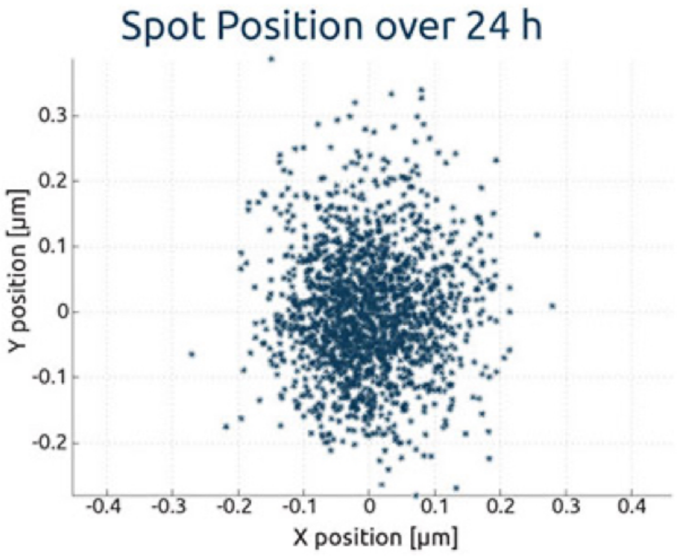
This drastically reduces the time it takes to acquire usable lab-based HAXPES spectra, making it more comparable lab-based XPS systems and even some HAXPES beamlines.

What are the Capabilities? – *Spot Size & Stability*

The brightness, *small spot size*, and high resolution of the lab-based HAXPES make it ideal for investigating complex systems such as real-world microelectronic devices.

The MetalJet X-ray source and monochromator optics provide a small minimum spot size (~35 µm) and stable spot position over time.

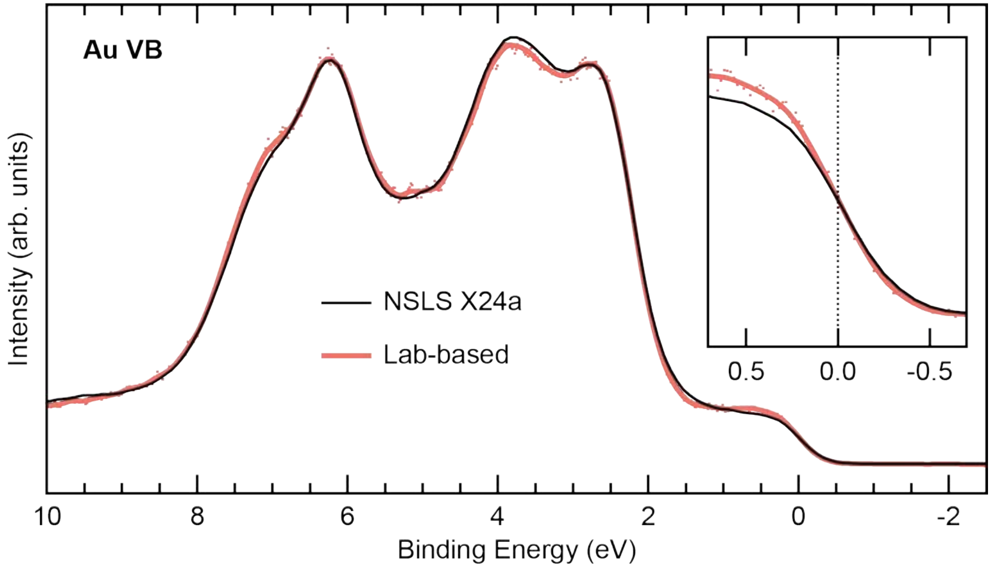




This enables investigation of much smaller sample features than is possible with most lab-based XPS systems.

What are the Capabilities? – *Energy Resolution*

The brightness, small spot size, and <u>*high resolution*</u> of the lab-based HAXPES make it ideal for investigating complex systems such as real-world microelectronic devices.



EW4000 Analyzer

https://scientaomicron.com/en/Instruments/Electron-Analysers/EW4000

The HAXPES-Lab utilizes the same hemispherical analyzer as some synchrotron HAXPES beamlines.

This analyzer provides excellent energy resolution.

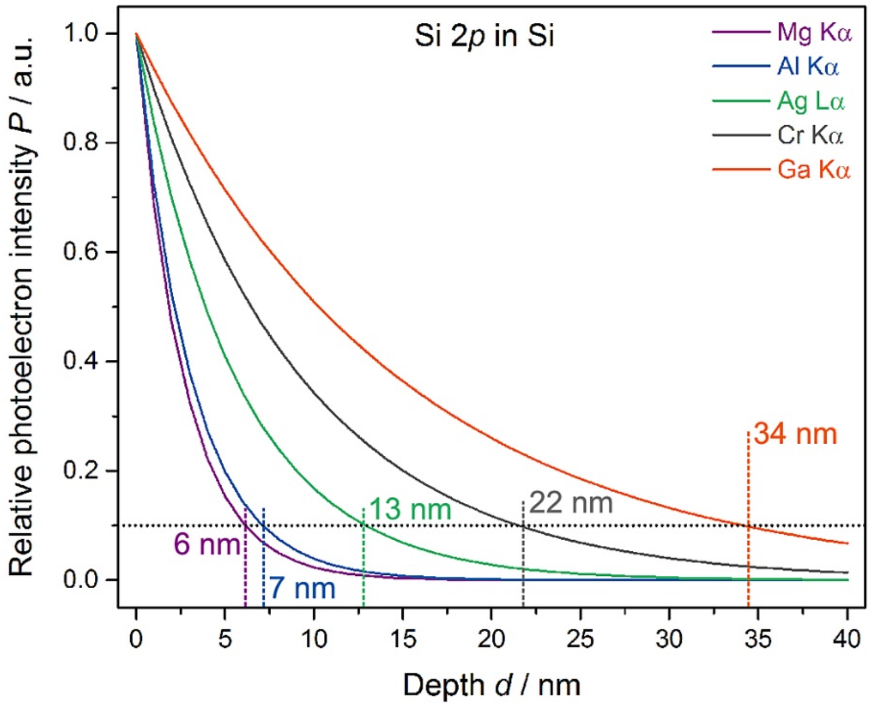
(Less than 100 meV FWHM at 10 kV)

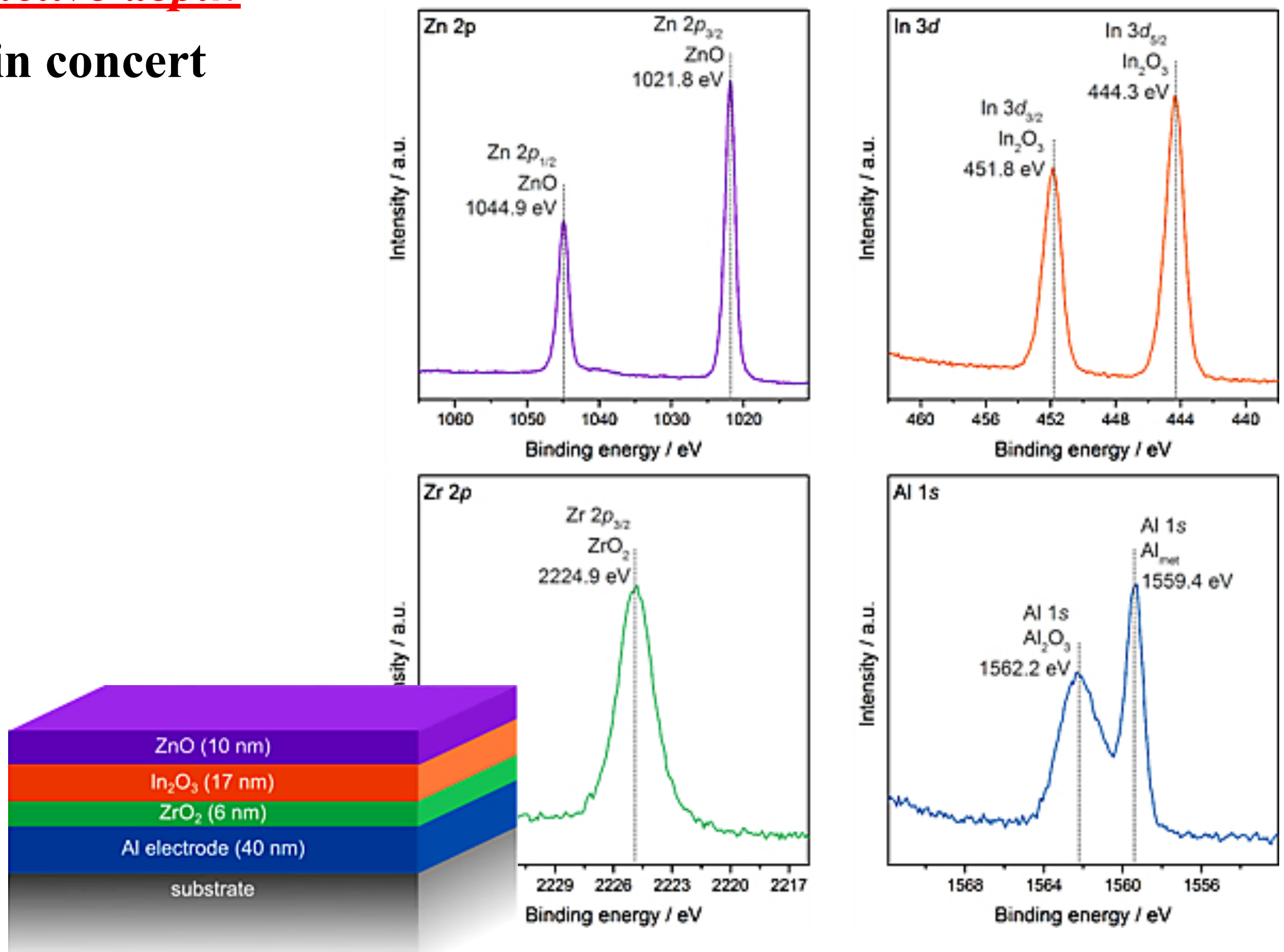
What can you do with the HAXPES-Lab?

Investigating the Electronic Structure and Properties of Materials

What can you do with the HAXPES-Lab?

The HAXPES-Lab can perform *non-destructive depth studies* using its traditional Al-Kα source in concert with the Ga-Kα source.

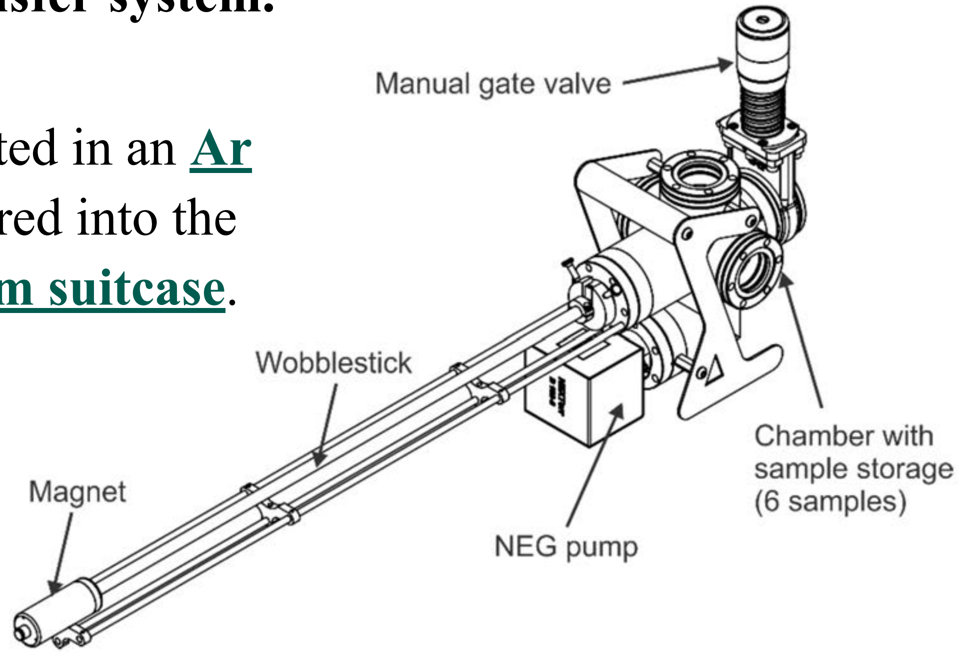


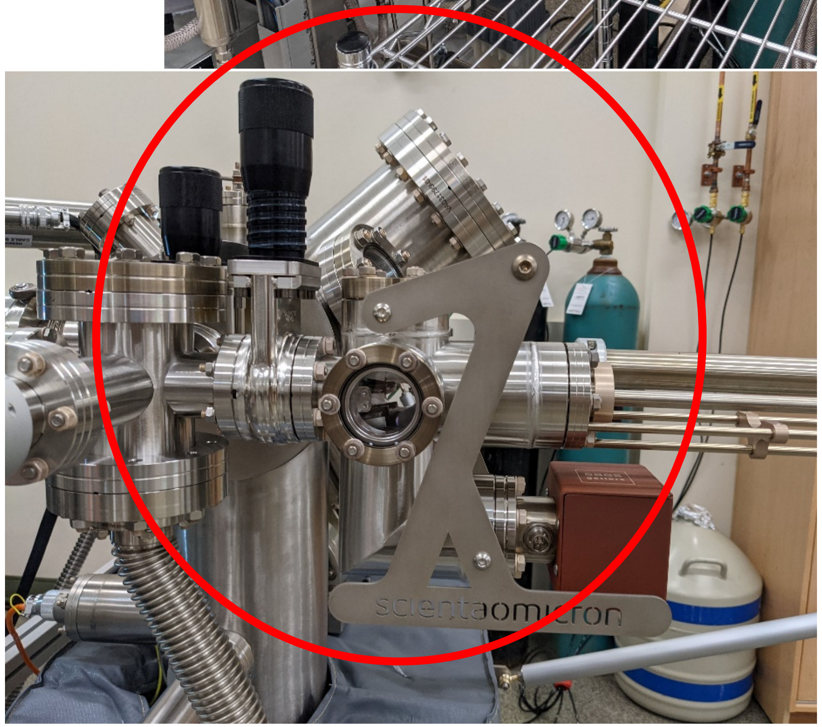


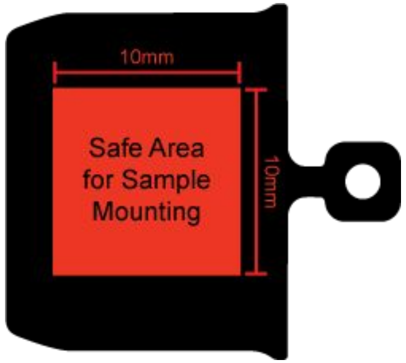
Sample Handling & Preparation

The HAXPES-Lab at Binghamton is equipped with a sample prep chamber & inert transfer system.

Samples can be mounted in an **Ar glovebox** and transferred into the system using a **vacuum suitcase**.





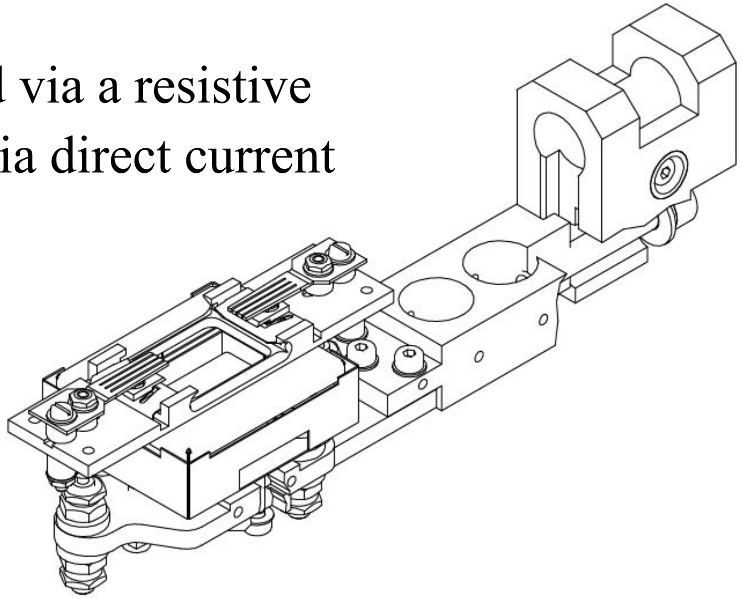


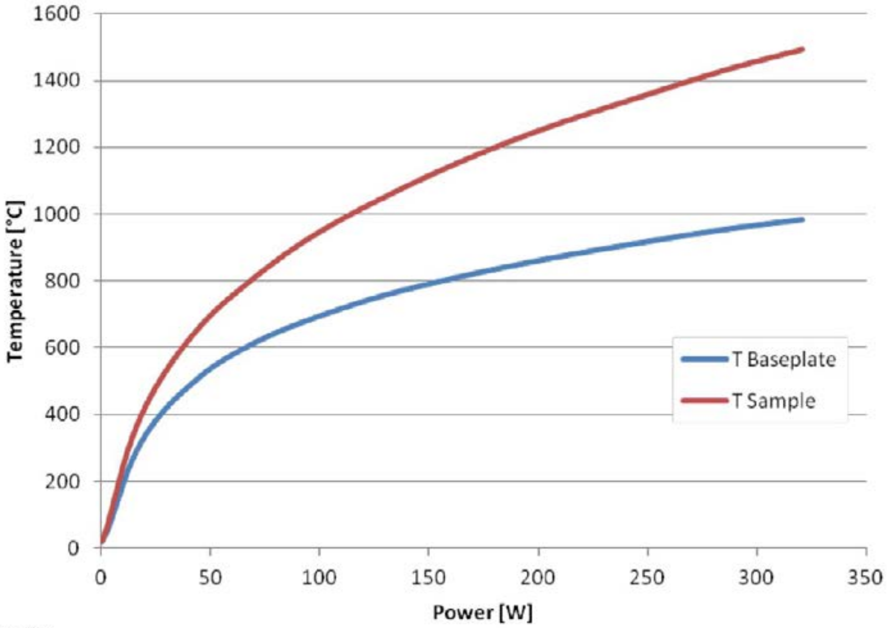
Standard **SHOM style plates** are used to mount samples up to **10 x 10 mm**.

Sample Heating in the Prep Chamber

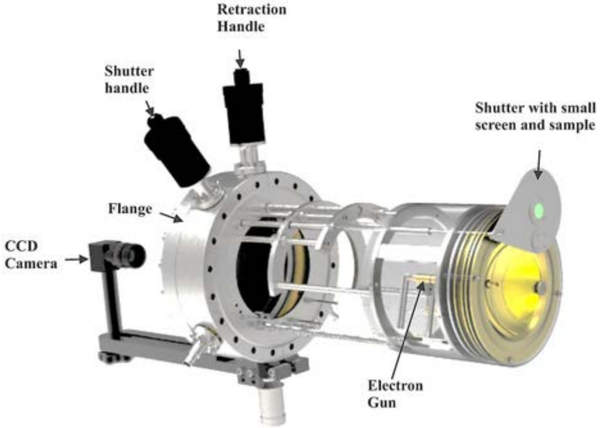
Samples can be *heated* (>1670 K) from behind under UHV conditions.

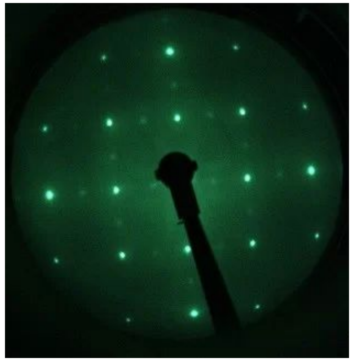
Heating from behind via a resistive heating element or via direct current heating of the sample using an applied bias.





Additional capabilities may be added to the prep chamber in the future, including a LEED system, Kelvin Probe, and/or RGA.



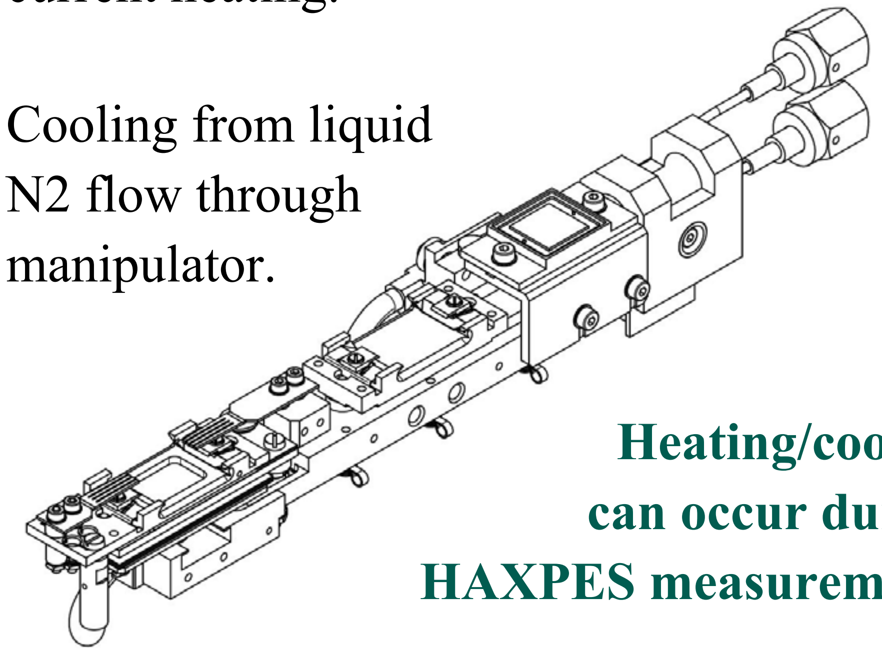


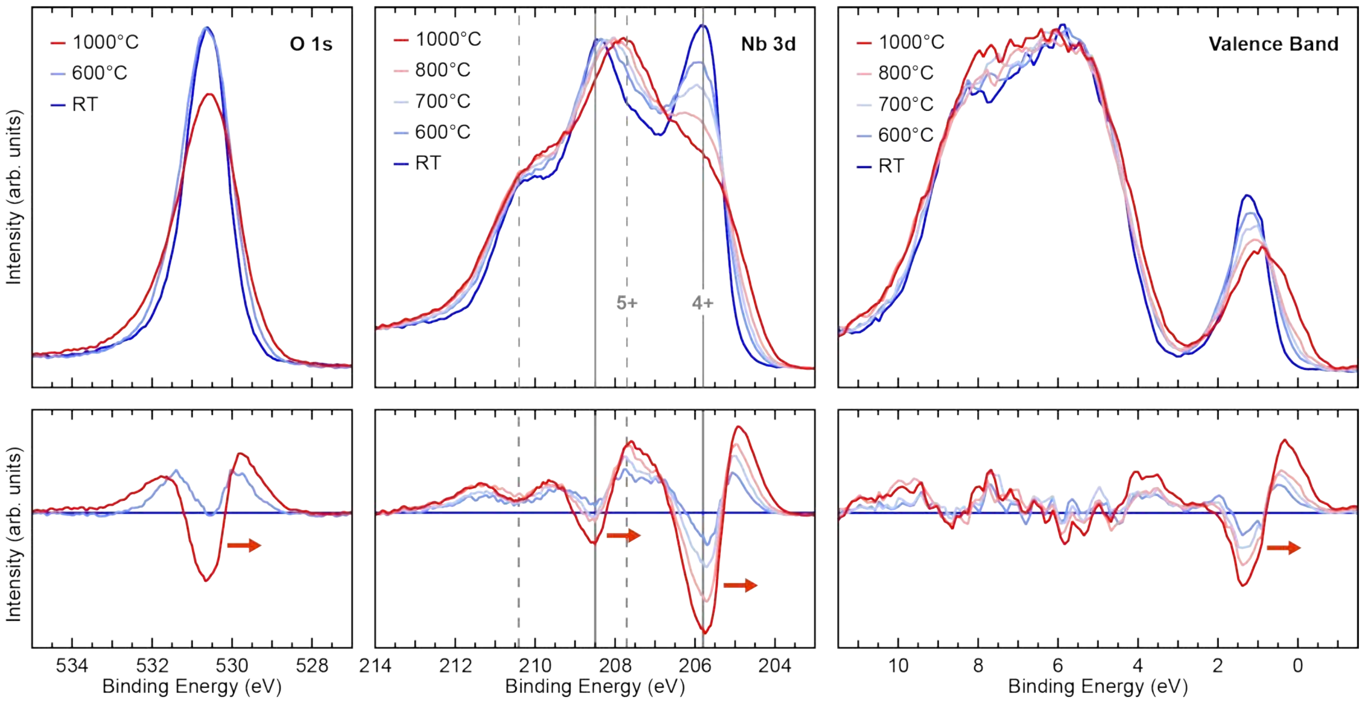
Sample Heating/Cooling in the Main Chamber

Samples can be *heated* (>1100 K) & *cooled* (~160 K) under UHV.

Again, heating from behind via a resistive heating element or via direct current heating.

Cooling from liquid N2 flow through manipulator.



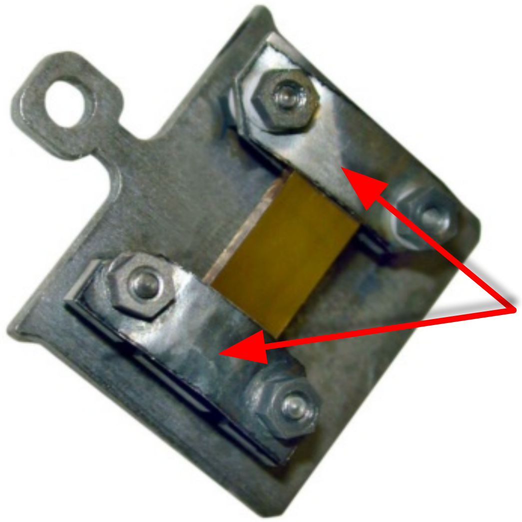


Heating/cooling can occur during HAXPES measurement!

Temp.-dependent XPS/HAXPES provides info on the evolution of electronic structure during SPTs, MITs, thermal decay, etc.

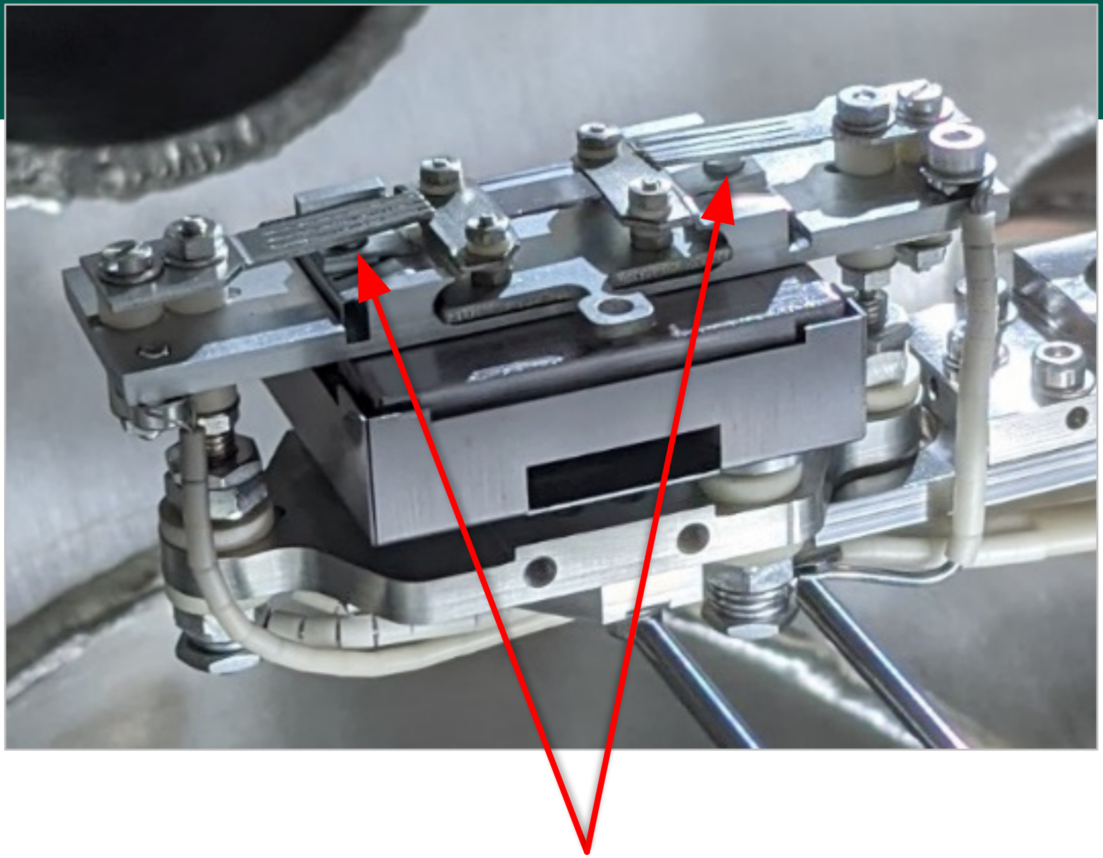
Operando Device Measurements

Operando measurements **can be performed on electronic devices using SHOMDC sample plates.**



Device terminals can be connected to the sample plate rails via wire bonding, spot welding, etc.

Both 2 or 3 terminal devices can potentially be investigated using the HAXPES-Lab.



Our HAXPES-Lab manipulators have "brush" contacts for biasing.

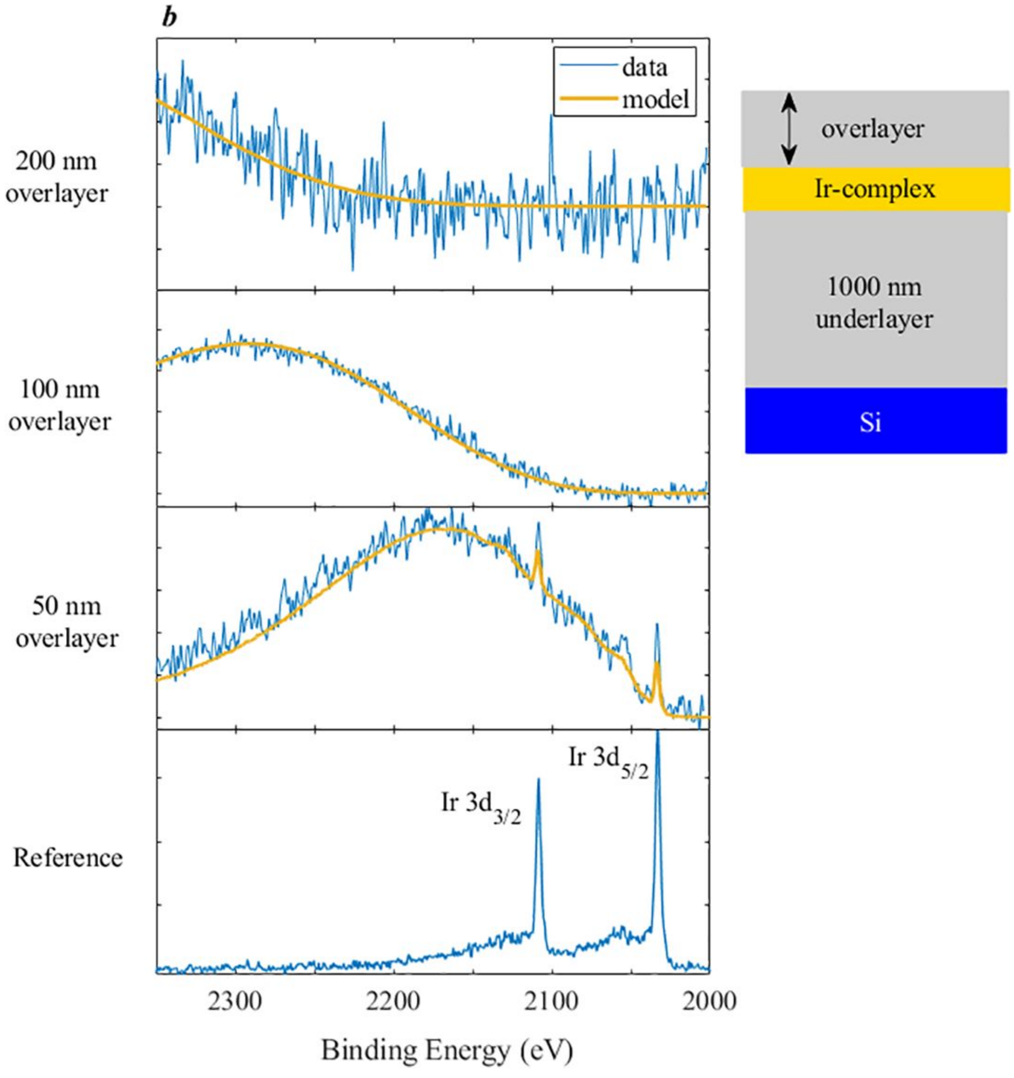
The sample plate itself can act as a 3rd electrical contact or ground.

Accurate Compositional Analysis

<u>Relative sensitivity factors</u> (RSFs) are necessary for quantitative XPS/HAXPES measurements.

RSFs cannot be reliably determined for variable energy <u>synchrotron-based</u> HAXPES!!!

Using the Ga-Kα source, a library of core levels for elements up to Z = 99 up to a binding energy of 9 keV has already been computed with ratification of the values ongoing.

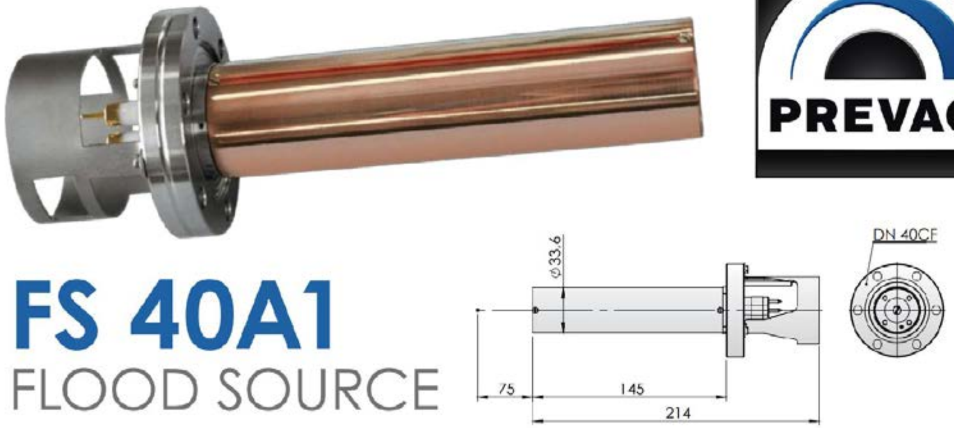


Spencer, B. et al. Appl. Surf. Sci. 541, 148635 (2021).

Some Additional Capabilities

Sputter Depth Profiling

FDG150 Ar-ion sputter gun can be used to **destructively etch** into a sample for surface cleaning or to measure spectra at different depths.



PREVAC

Charge Neutralization

Ar-ion sputter gun can be used in conjunction with a FS 40A1 e^- flood gun to neutralize any charging of **insulating samples**.

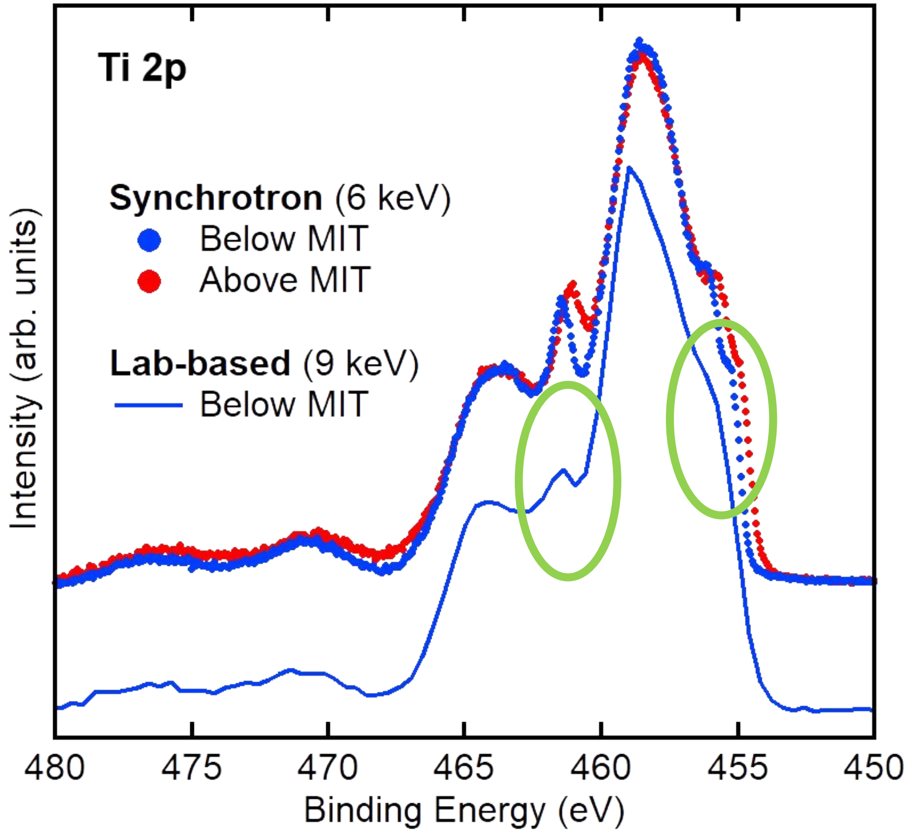
<u>Example</u> – *Investigating Temperature-dependent Phenomena*

High resolution synchrotron-comparable analyzer resolves very narrow features.

Previous work has shown a shift in 2 sharp features indicates the Metal-to-Insulator Transition (MIT) in Ti_2O_3, but these features are only evident in the bulk spectra!

Any surface oxidation/contamination *extinguishes* these features in XPS.

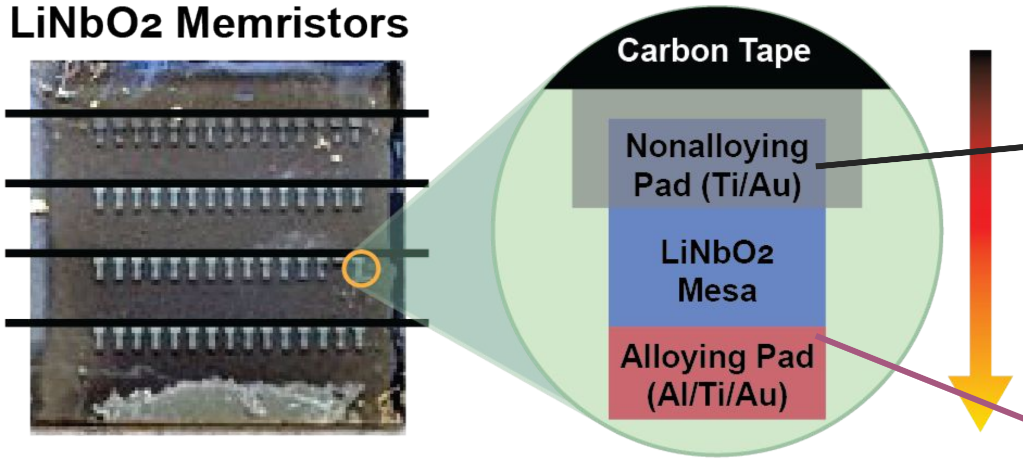
We see them using the HAXPES-Lab with no UHV anneals or other treatments!

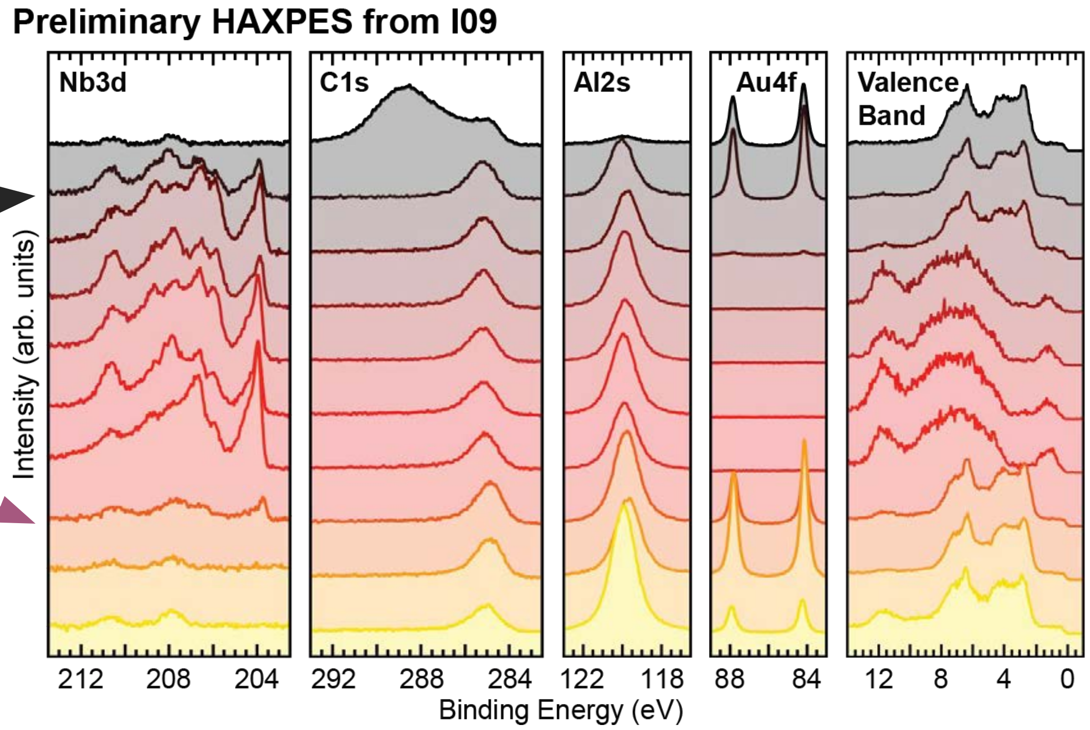


Example – *Probing Behavior of Thin Film Devices*

Small (~35 µm) HAXPES-Lab beam spot enables investigations of real devices, buried interfaces, charge state/composition changes, ion migration, etc.

To investigate Li^{+} or O^{2-} migration/gradient formation in real $LiNbO_2$ memristors, we measured HAXPES spectra at multiple spots along lateral test devices.





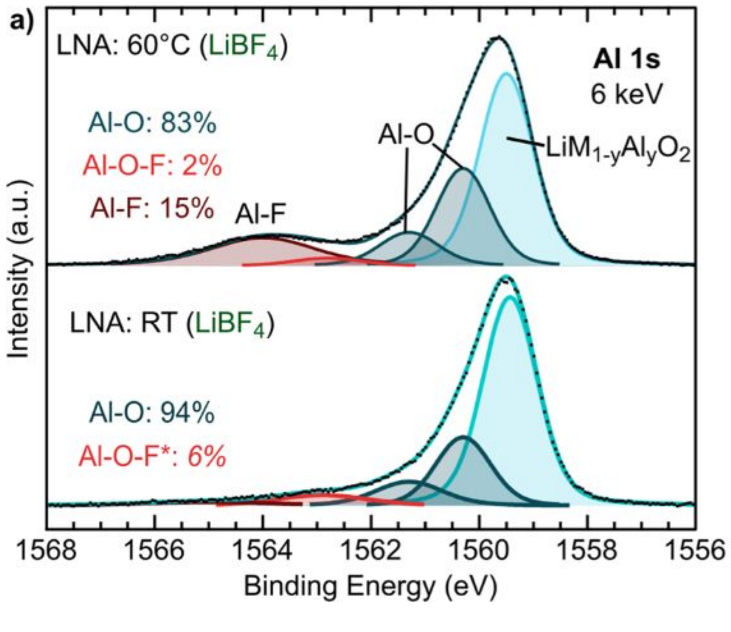
150 x 500 µm $LiNbO_2$ Mesa
250 x 250 µm Contact Pads

**6 keV HAXPES from synchrotron beamline (Diamond I09) with comparable capabilities.*

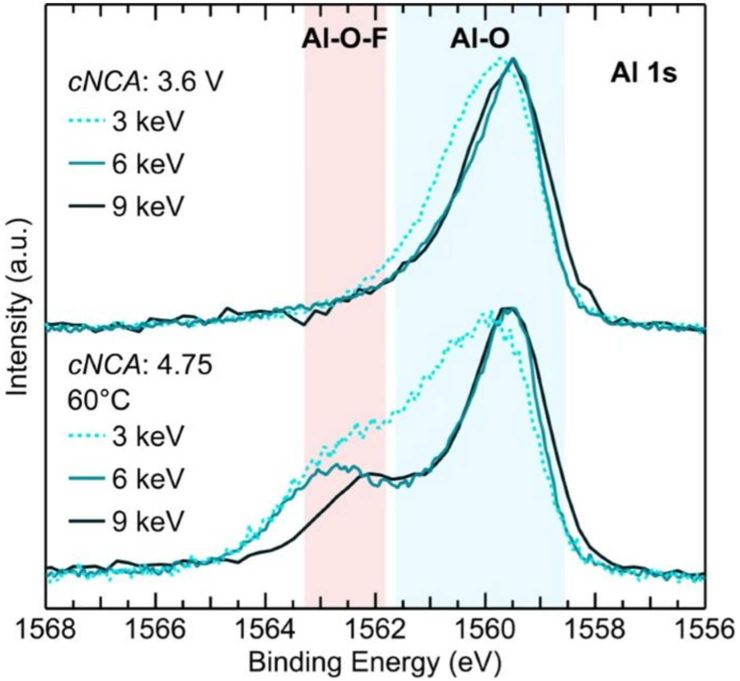
Example – *Probing Evolution of Al in Li-ion Battery Cathodes*

The HAXPES-Lab's Ga-Kα source enables investigations of Al-containing compounds.

The Al 1s region is accessible with HAXPES and can be crucial for understanding many Li-ion battery materials like NCA and NMC.



Comparison of photon energies provides info on surface versus sub-surface compounds.

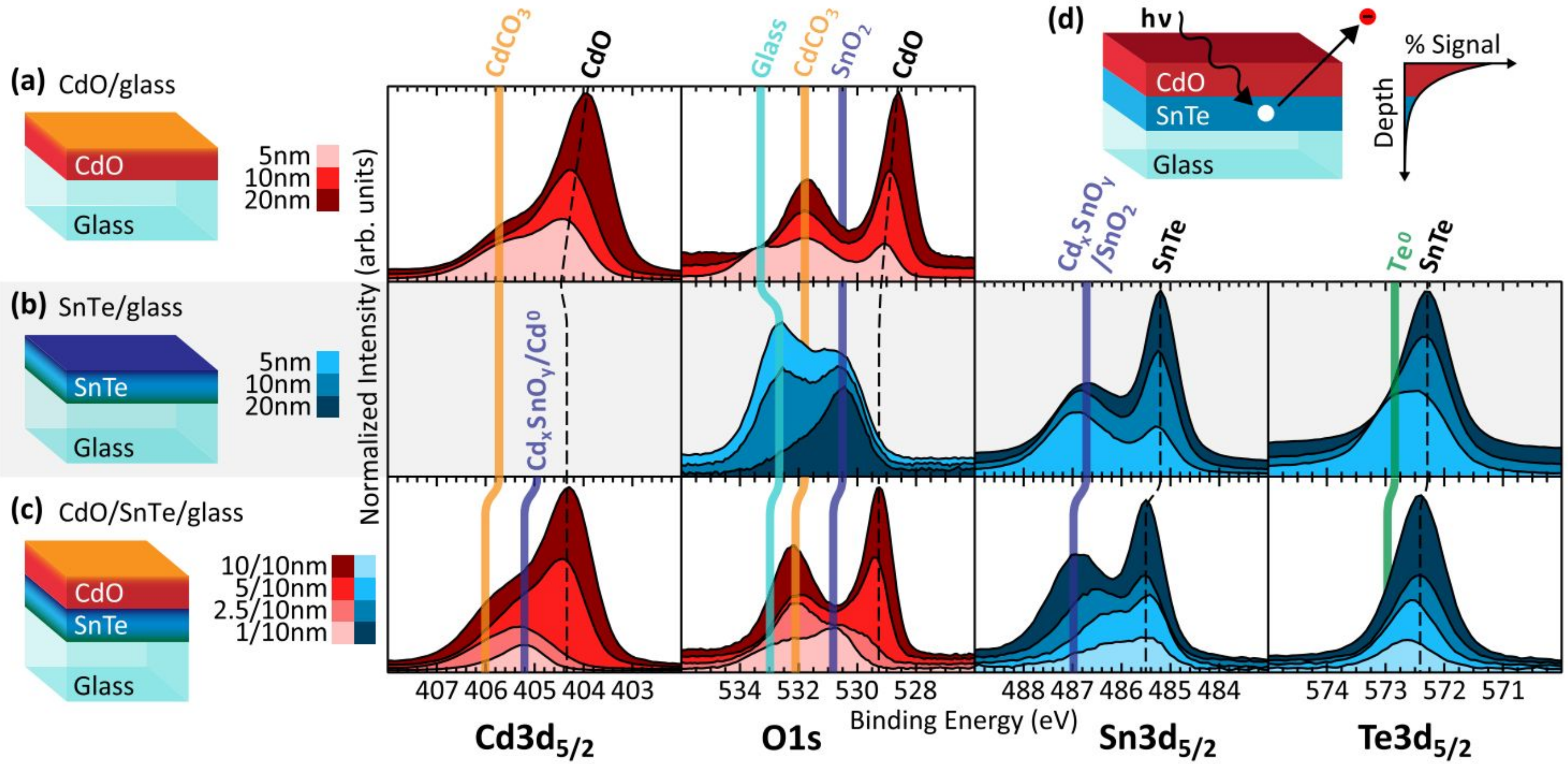


Lebens-Higgins, Z.W., *et al.* Surface Chemistry Dependence on Aluminum Doping in Ni-rich $LiNi_{0.8}Co_{0.2-y}Al_yO_2$ Cathodes. *Sci Rep* **9,** 17720 (2019).

**6 & 3 keV HAXPES data from synchrotron beamline (Diamond I09) with comparable capabilities.*

Example – *Determining Interfacial Compounds (HAXPES)*

The deep probing depth of HAXPES enables non-destructive buried interface studies.



Using multiple layered samples with a single HAXPES energy, the location of different interfacial compounds within the stack were determined.

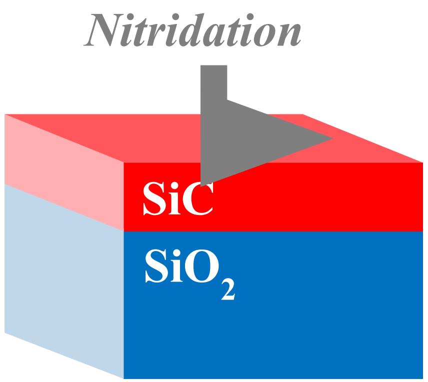
Wahila, M. J. et al. Evidence of extreme type-III band offset at buried n-type CdO / p-type SnTe interfaces. *Phys. Rev. B* 91, 205307 (2015).

**4 keV HAXPES from synchrotron beamline (NSLS X24A) with comparable capabilities.*

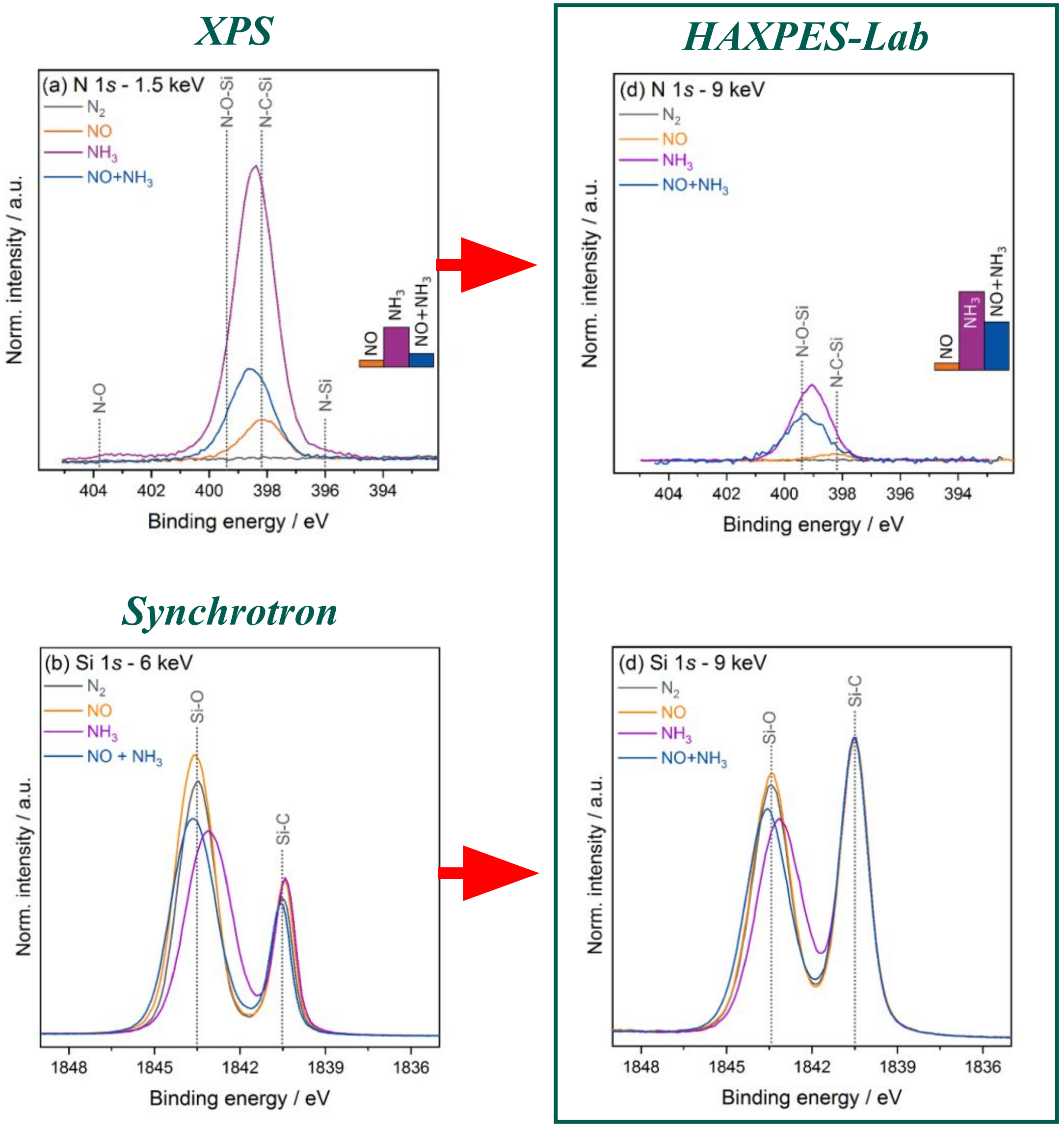
Example – *Determining Interfacial Compounds (XPS + HAXPES)*

The combination of XPS and HAXPES enables non-destructive depth studies on individual samples.

Using multiple X-ray energies, the effects of different nitridation processes on the SiC and SiO_2 interface were tracked.



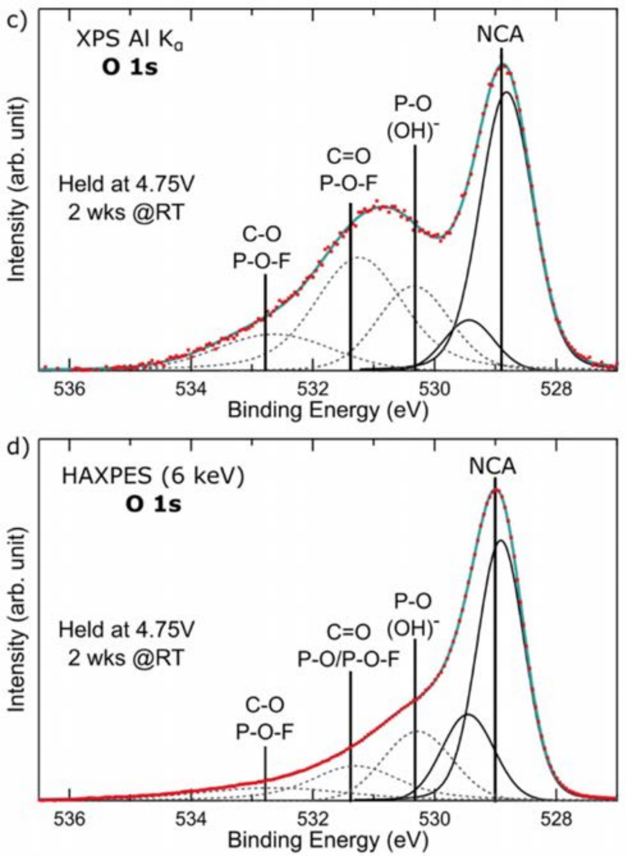
Berens, J. et al. Effects of nitridation on SiC/SiO_2 structures studied by hard X-ray photoelectron spectroscopy. *J. Phys. Energy* 2, 035001 (2020).



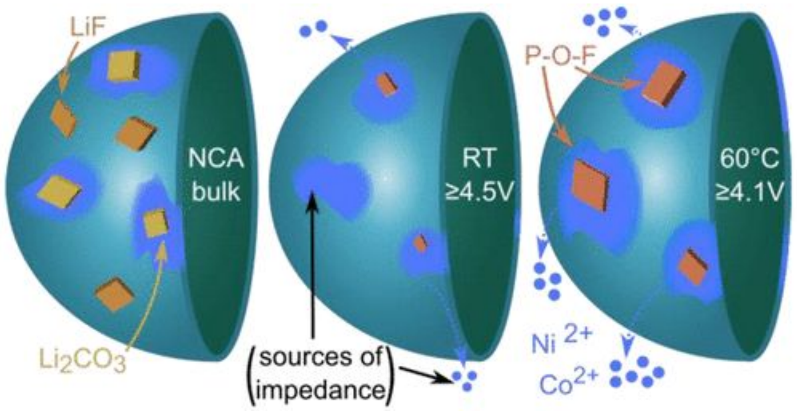
**6 keV HAXPES from synchrotron beamline (Diamond I09) with comparable capabilities.*

Example – *Probing Evolution of Surface Compounds in Li-ion Batteries*

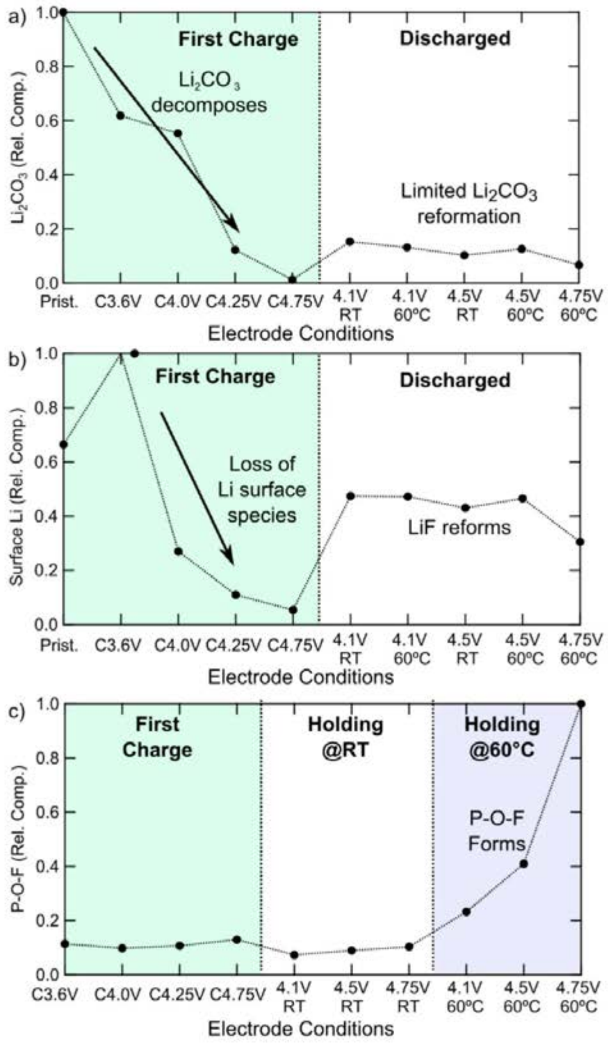
The combination of XPS and HAXPES enables comparison of surface *vs* bulk of battery cathodes & other materials.



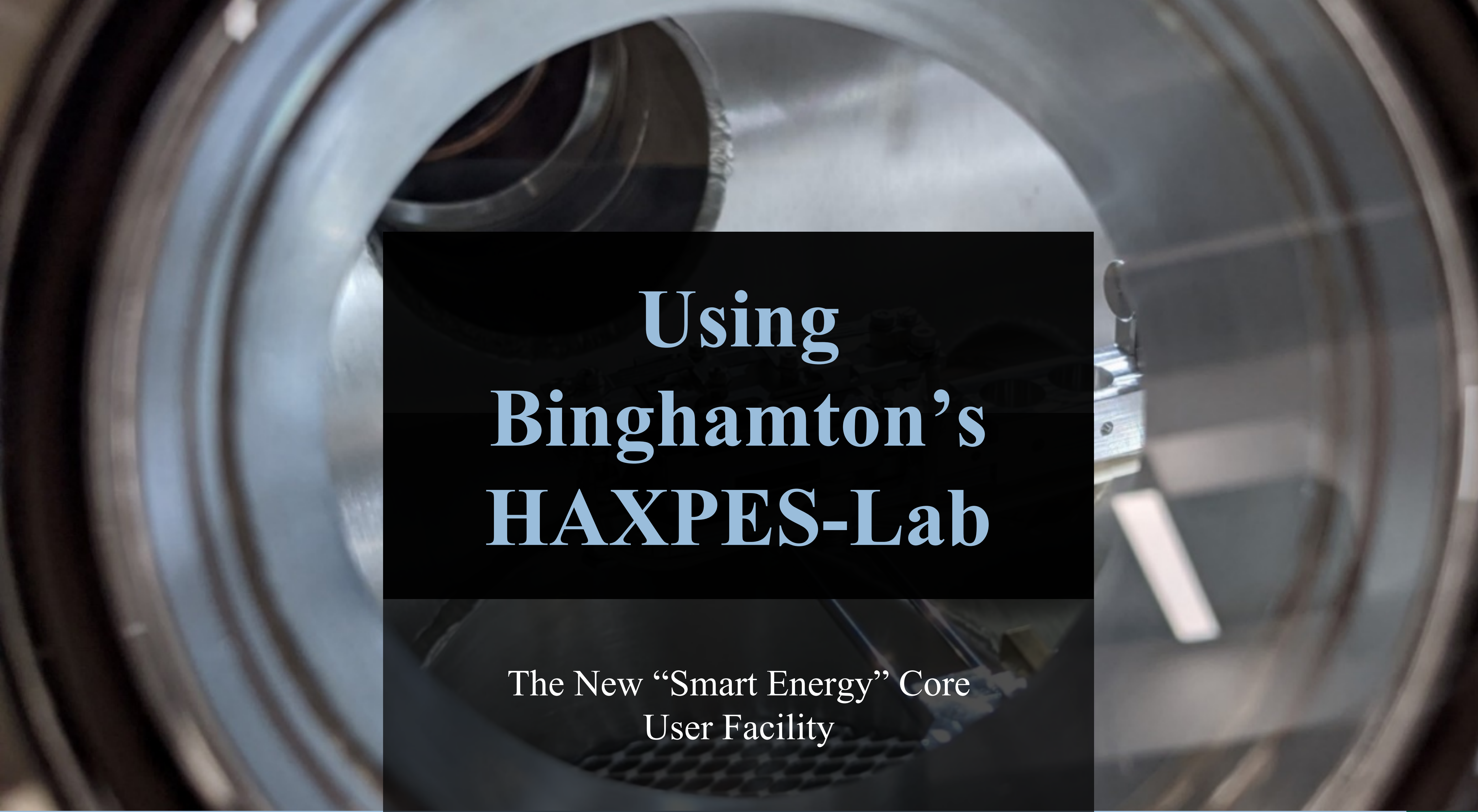
Multiple photon energies provide information on the evolution of compounds formed at different depths during Li-ion battery cycling.



Lebens-Higgins, Z.W., *et al.* Evolution of the Electrode-Electrolyte Interface of $LiNi_{0.8}Co_{0.15}Al_{0.05}O_2$ Electrodes Due to Electrochemical and Thermal Stress. *Chem Mater* **30**, 3, 958–969 (2018).



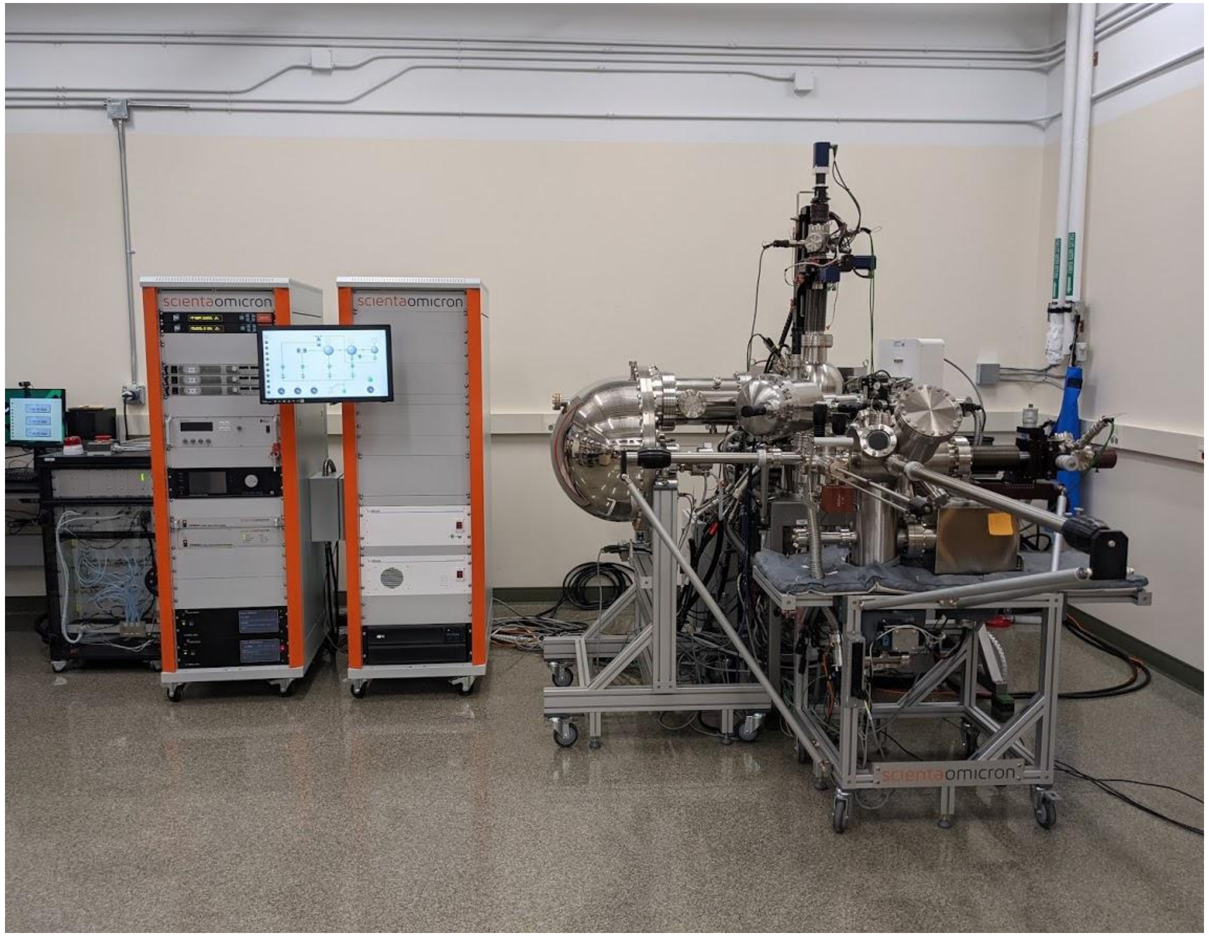
**6 keV HAXPES from synchrotron beamline (Diamond I09) with comparable capabilities.*



Using Binghamton's HAXPES-Lab

The New "Smart Energy" Core User Facility

Using the HAXPES-Lab at Binghamton University



HAXPES-Lab is a part of Binghamton University's core user facilities.

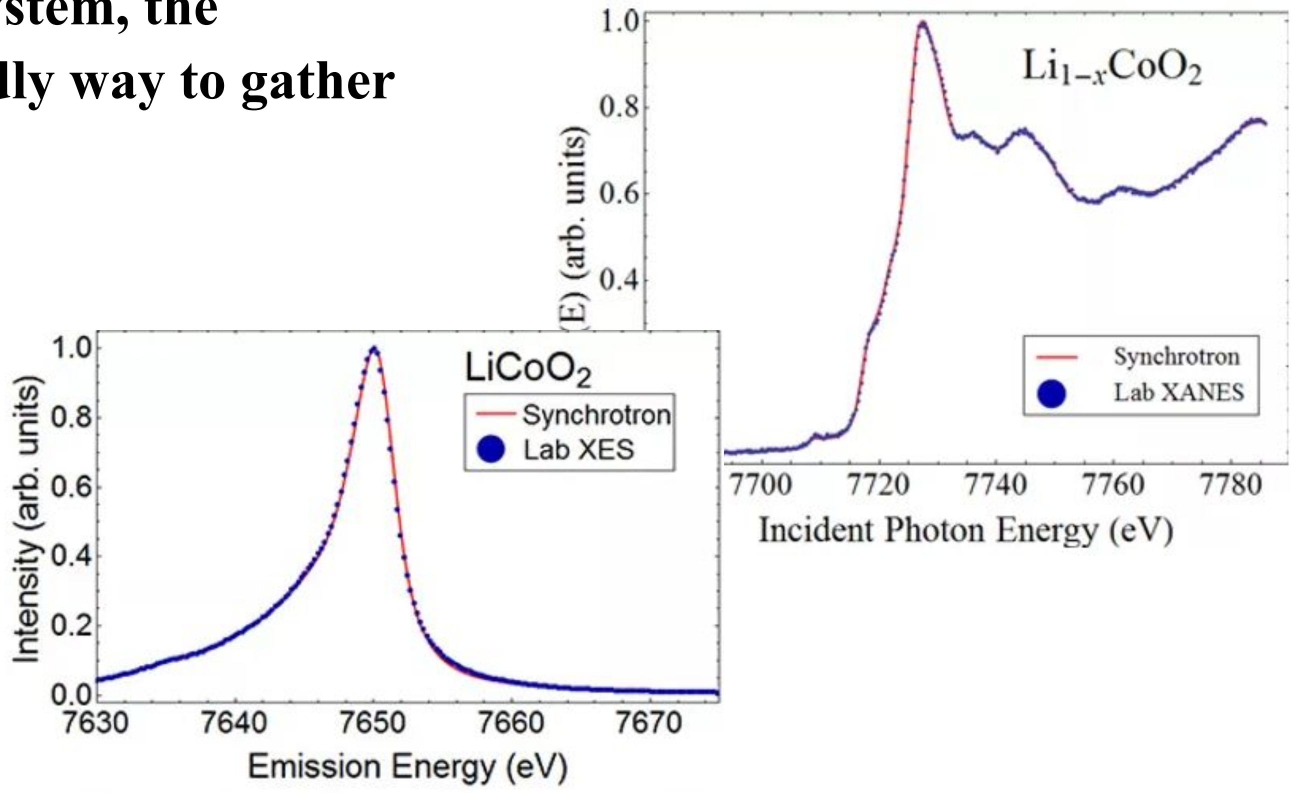
External users can gain access via the Analytical & Diagnostics Laboratory, part of the S3IP Center of Excellence.

S3IP
A New York State Center of Excellence
BINGHAMTON UNIVERSITY

To become a user, email **Dr. In-Tae Bae** (itbae@binghamton.edu).

Complementary User Equipment at BU – *easyXES150*

Located across form our HAXPES-Lab system, the easyXES150 system provides a user-friendly way to gather synchrotron-comparable XAS/XES data.



BINGHAMTON
UNIVERSITY
STATE UNIVERSITY OF NEW YORK

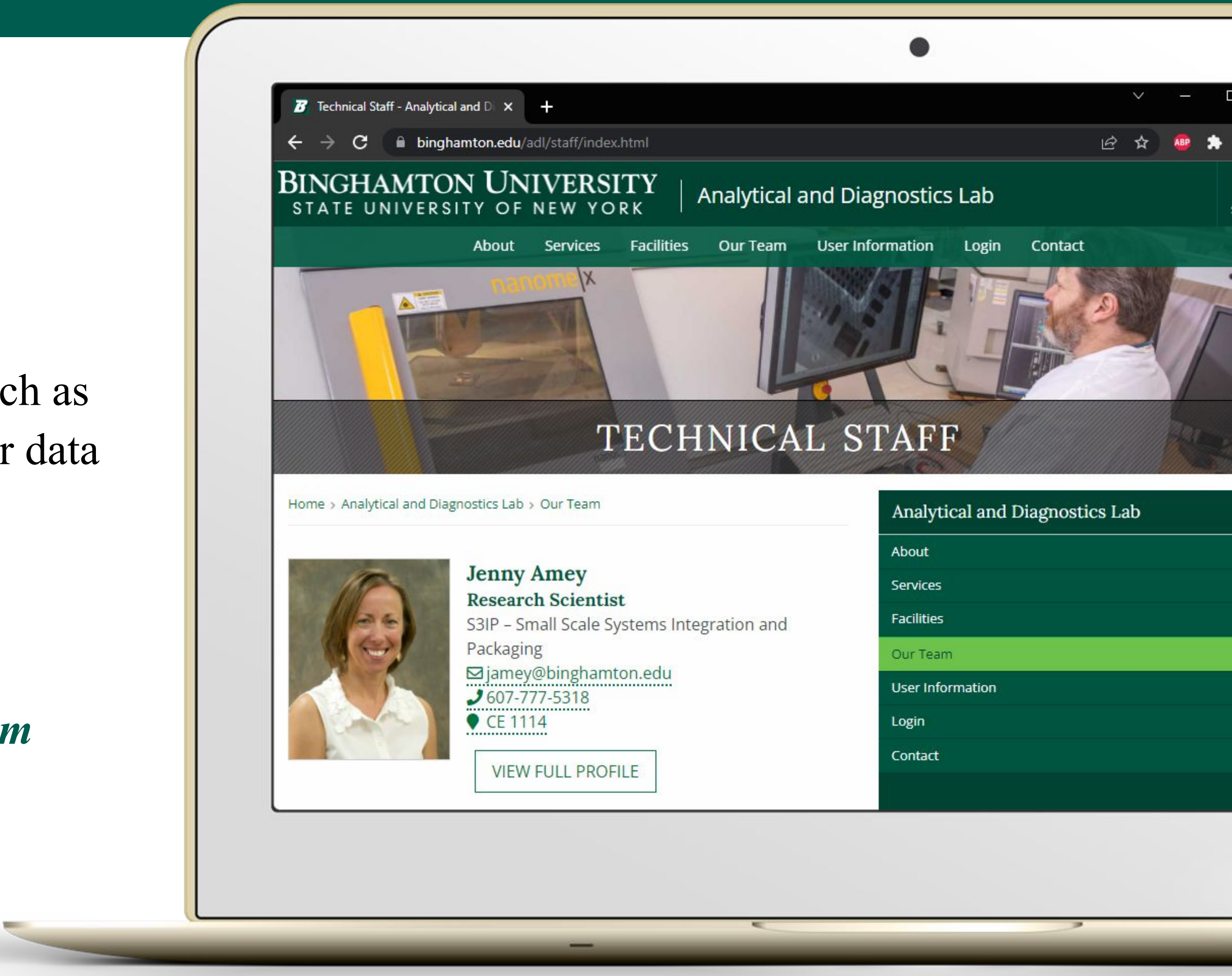
In addition, XAFS analysis can provide atomic bond length info for structural characterization.

ADL Staff Scientists

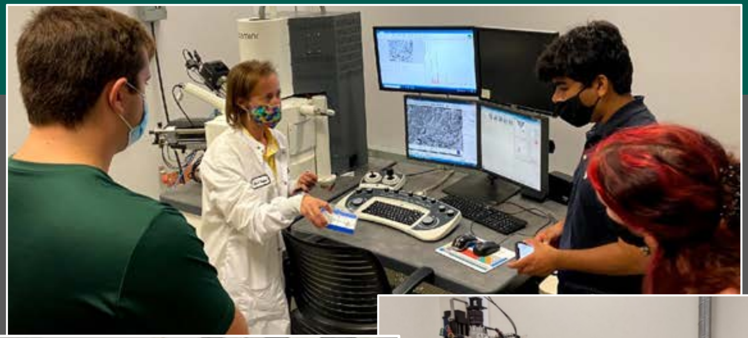
The ADL staff are experienced PhD scientists that train and assist users.

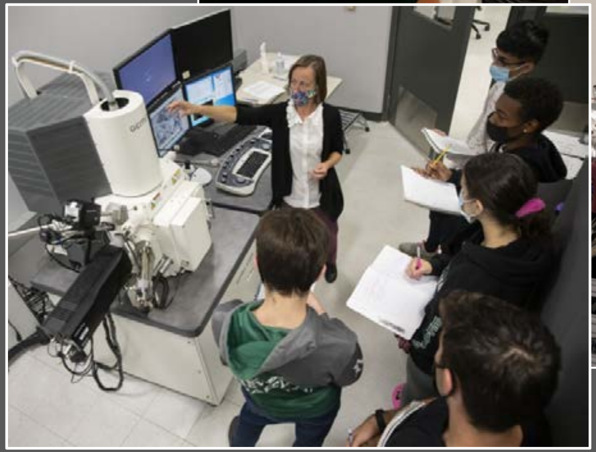
We can consult on technical matters, such as appropriate techniques for your needs or data analysis.

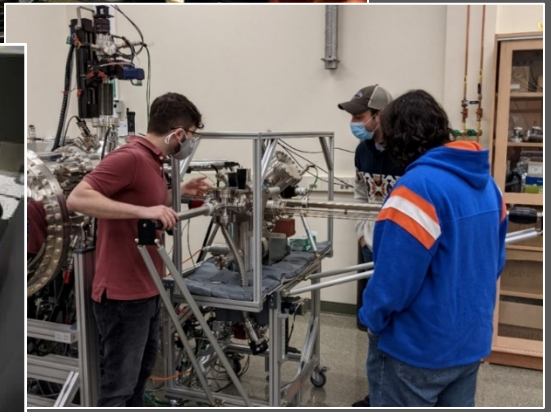
Staff scientists are also available to collaborate on long-term and short-term projects on product, process, and materials R&D.



Webinar Summary







What is HAXPES?

What is the HAXPES-Lab?

What can you do with the HAXPES-Lab?

Using the HAXPES-Lab at Binghamton University.

QUESTIONS?

THANK YOU

Dr. Matt Wahila

Binghamton University

+1 (607) 237-4462

mwahila@binghamton.edu

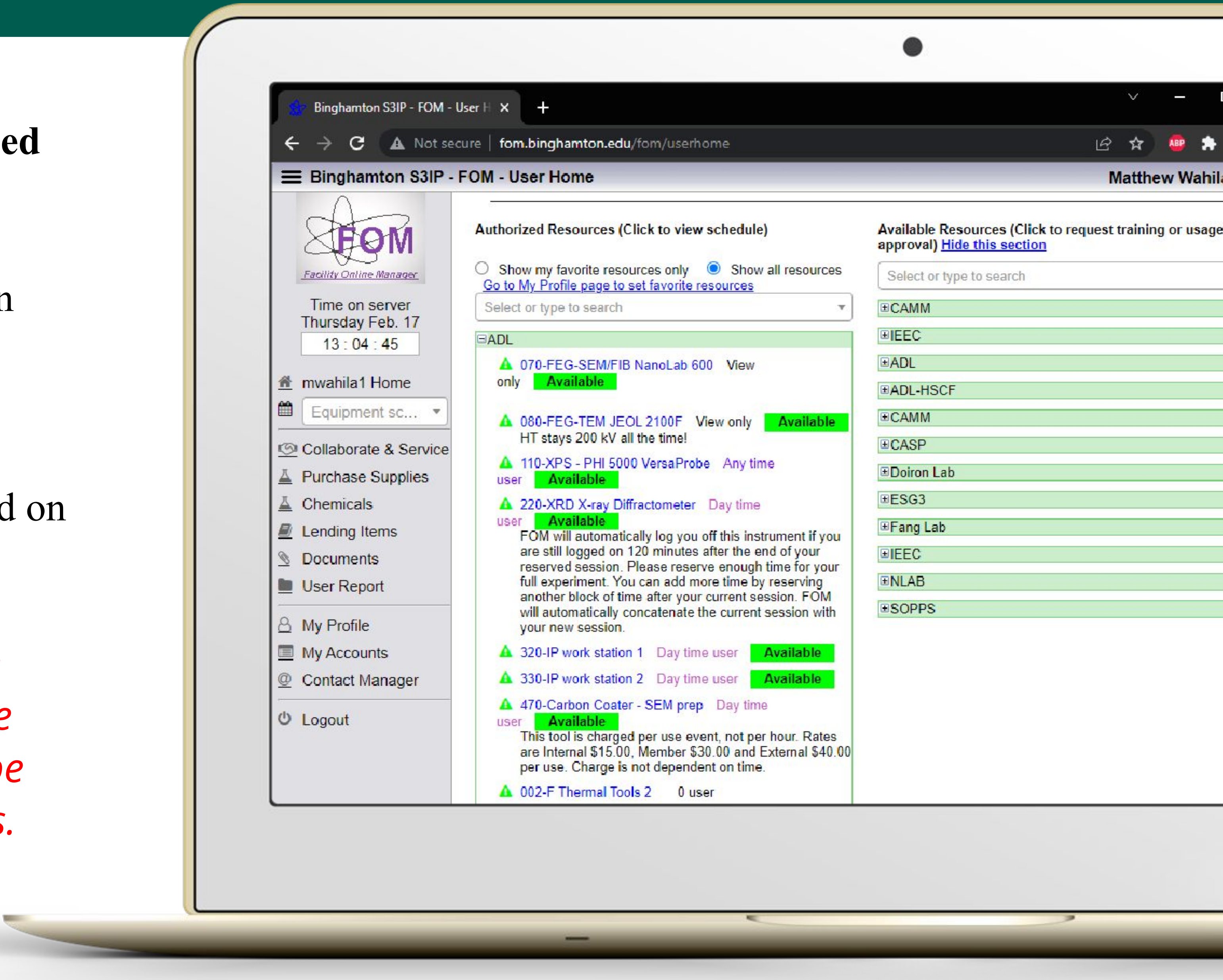
Facility Online Manager

Access to ADL user equipment is managed via our FOM system.

Through FOM users can request training on specific pieces of equipment, reserve equipment time, etc.

Most ADL equipment is reserved and billed on an hourly basis.

**Billing policies for the HAXPES-Lab are still being determined as it is a far more complex system and experiments can be more time-intensive than other systems.*



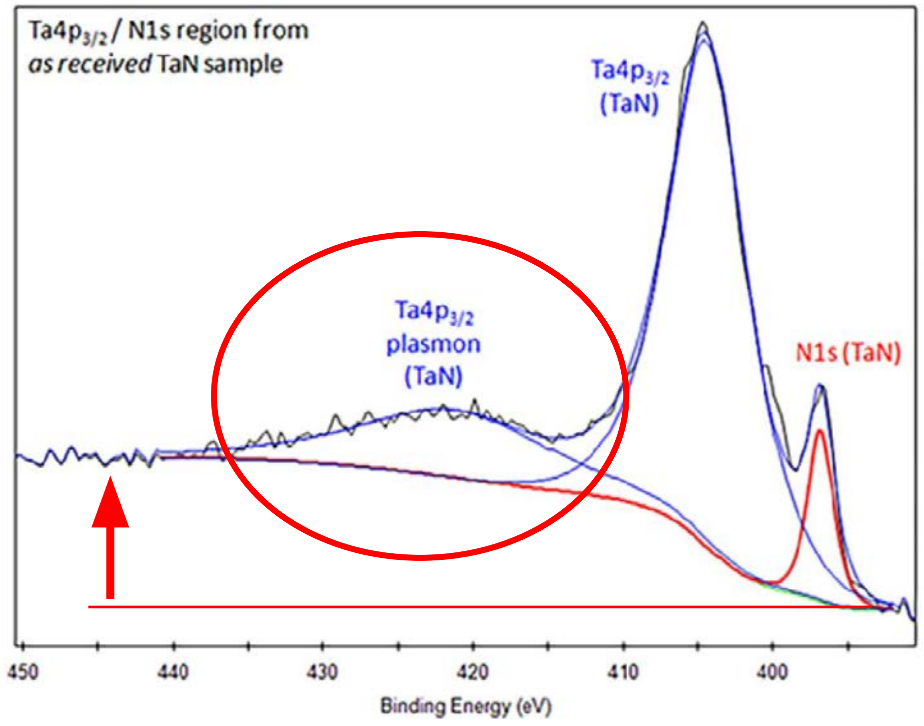
Backgrounds & Plasmons

Electrons emitted within a sample may undergo inelastic collisions that alter the final energy of the electron.

This generates a **background** determined by the probability distribution for electrons with a given KE undergoing some modification to their initial value.

If this probability distribution also exhibits a resonance type structure, the convolution of a photoelectric peak with this bias in the energy loss distribution may give rise to *peak-like* "**plasmon**" structures considered a part of the background.

**i.e., peaks may appear in XPS that are extrinsic rather than intrinsic to the photo-excitation mechanism.*



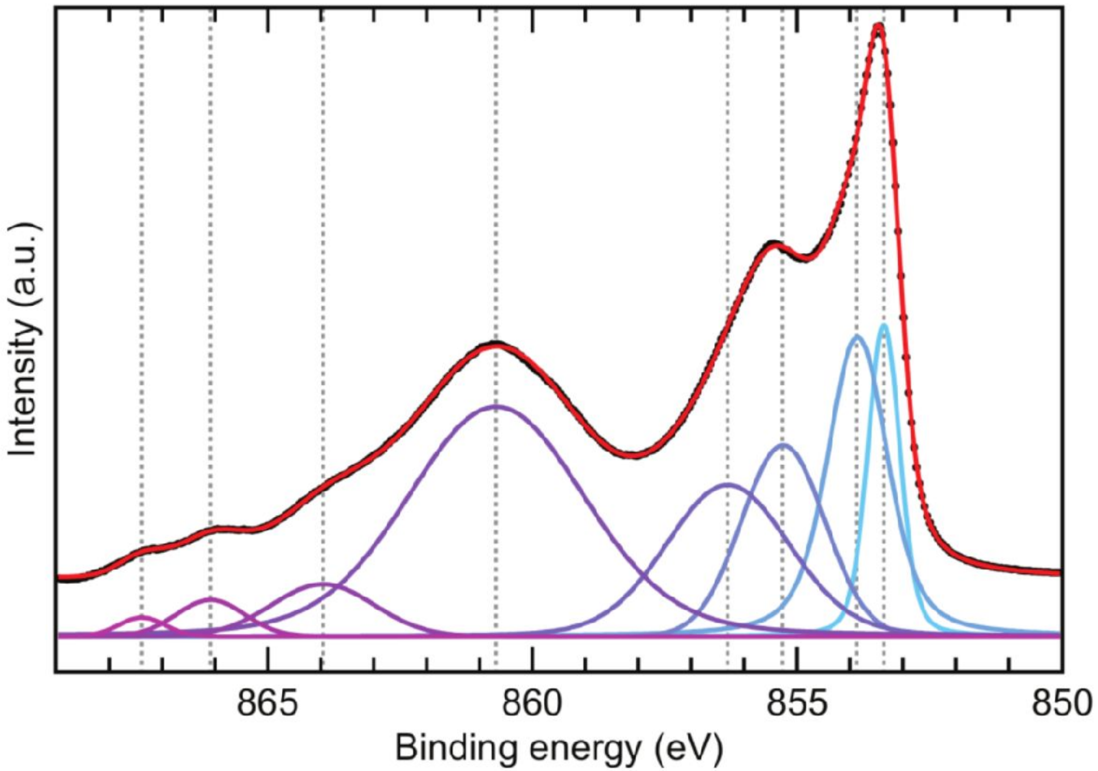
The background **increases towards higher BE**, until BE approaches the initial X-ray energy, at which point the photoelectron signal ceases.

Shake-Up/Shake-Off Features

Shake-up peaks appear at energies characteristic of the ***excited states*** for an element with respect to the state measured by the zero loss intensity.

Some of the photon energy is used to excite the ion out of the zero loss state whilst at the same instant ejecting the photoelectron with the remaining photon energy.

Similarly, **Shake-off** events, ***where more than one electron is ejected at the time of photo-ionization***, may result in broad structures to high binding energies.



Due to spin-splitting, asymmetry, the background, plasmons, shake-ups, shake-offs, and the potential for multiple elemental charge states, some XPS core levels can become quite complex to peak fit and analyze.