



eBook

# Surface Spectroscopic Techniques for Chemical Analysis

A snap-shot comparison and analysis of XPS, UPS and ISS

Excerpts of Covalent Academy's Webinar (Episode 10) Presented by, Roland Barbosa, Phd Chemistry

- 03 Introduction
- 04 Techniques
  - 05 X-ray Photoelectron Spectroscopy (XPS)
  - 06 Ultraviolet Photoelectron Spectroscopy (UPS)
  - 07 Ion Scattering Spectroscopy (ISS)
- 08 Overview Snapshot
- 09 Case Studies
- 12 Summary
- 13 Vetting a Materials Characterization Partner

*For most materials, surfaces are the point of interaction with the world,*

and, as scientists and engineers, understanding the physical and chemical properties of surfaces can give light to many of the issues with, and opportunities to improve, modern materials. In industries where the surface interactivity is vital - including semiconductors, photovoltaics, adhesives, display technologies, plastics, protective coatings, medical devices, and many more - understanding the surface composition becomes crucial. All materials are composed of atoms, with the most stably bonded atoms located deep within the bulk of the material.

**However, on the surface there are atoms that are exposed and have increased binding potential.**

By understanding the composition and arrangement of the surface atoms, conclusions can be drawn about the conductivity, biocompatibility, catalytic properties, extent of corrosion, and many other material properties appropriate to the material itself.

# Characterization Techniques

Much of the focus of surface analysis revolves around the characterization of the material in question. Depending on the material, the purpose of the characterization may vary, but each technique looks to address the same few questions. The first question is, “what is on the surface?” which ranges from contamination surveys, to selective atom mapping, and leads in the second question, “how much of each material is on the surface?” Once the composition of the surface is determined, it is important to investigate “what is the effect of the surface?” with variation in the effect type depending on the specific intent of the material. With these questions in mind for each planned analysis, it becomes easier to narrow down the preferred technique.

## Available Techniques and How/When to Leverage Them

Each technique provides a different range of information, for varying depths and resolutions, and it becomes important while designing an experiment to understand and identify the strengths and limitations of each technique. Oftentimes multiple techniques are required in order to fully characterize a material.

*What is on the surface?*

*How much of each material is on the surface?*

*What is the effect of the surface?*

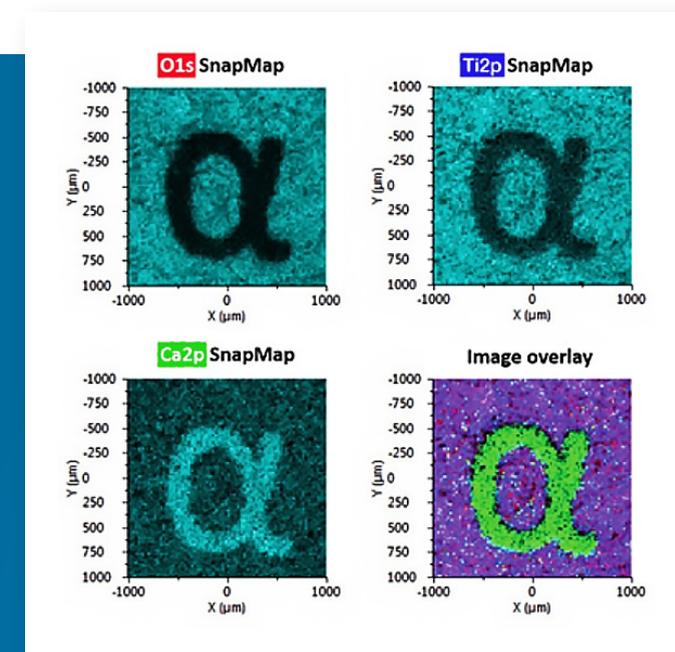
# X-ray Photoelectron Spectroscopy (XPS)

XPS is one of the most common and powerful surface analysis methods. This method utilizes the photoelectric effect, which was identified by Einstein in 1905, before being utilized in 1960 to develop the XPS technique by Siegbahn. The photoelectric effect is a phenomenon where electrically charged particles are ejected from a material after being exposed to electromagnetic radiation. This is often seen in the release of electrons from metal when light above a threshold energy is focused on it. The electrons that are released have a characteristic energy due to the material-dependent threshold energy and the material-dependent energy required to free the electron from the metal itself, also called the metal's work function.

Within the XPS instrument the 'light source' is an x-ray beam which can be sourced from electron excited metallic anodes, allowing for a clean radiation source. The X-ray beam is angled at the materials surface, exciting and ejecting electrons from the outermost three to ten nanometers of the surface, which are then caught and processed by a detector which determines the electron kinetic energy. The entire apparatus is enclosed in an ultra-high vacuum environment which helps to maintain sample surface integrity, minimize scattering of the photoelectrons, and increase the mean free path for electrons, ions, and photons. With a little bit of calculation\*, the instrument produces an energy spectrum of intensity versus binding energy, which can then be read for characterization information. Both XPS and Ultraviolet photoelectron spectroscopy (UPS) utilize the photoelectric effect with minor variations that change the analysis and characterization that is produced.

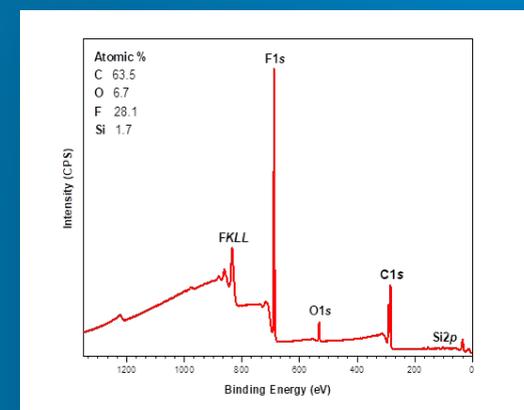
\*The energy of the escaping electrons is given by  $E_e = h\nu - E_b$  where  $E_e$  is the kinetic energy of the escaping electron,  $h\nu$  is the x-ray photon energy and  $E_b$  is the binding energy of the electron in the material.

If the incident x-ray energy is known and the escaping electron energy is measured, the original binding energy of the electron can be calculated. Since each element has a unique set of binding energies, the binding energy of the electron determines the element from which the electron came. So, this is the first use of XPS – determining elemental composition.

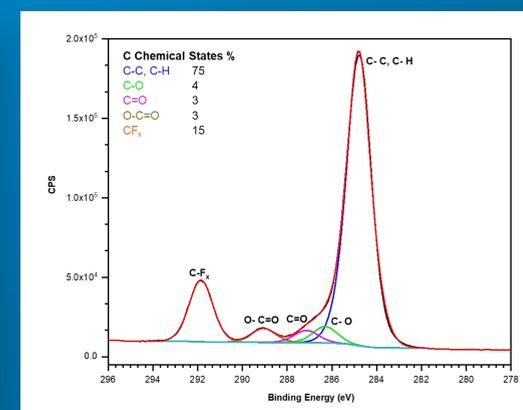


XPS imaging applications:

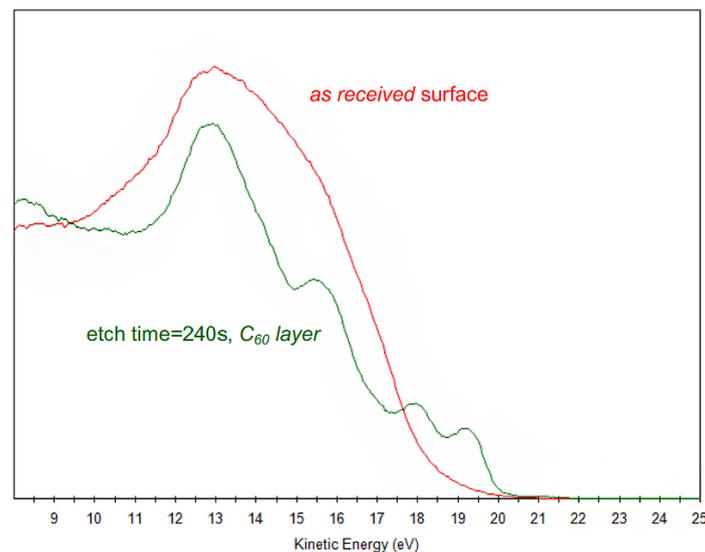
- distribution of chemistries across a surface
- finding the limits of contamination
- examining the thickness variation of an ultra-thin coating.



Example survey scan identifying fluorocarbon film on a Si wafer.

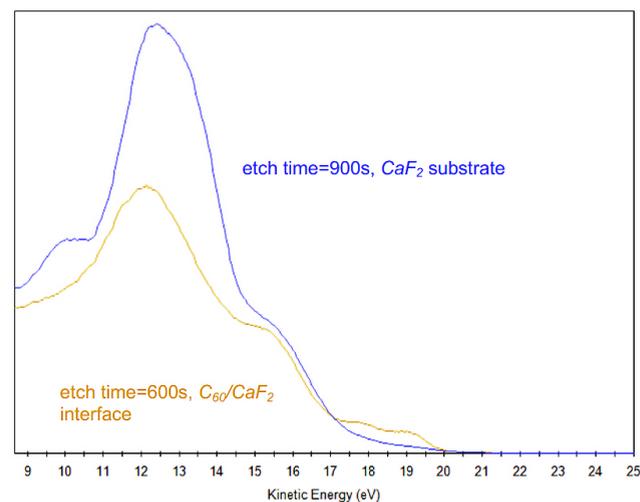


High resolution C1s spectrum showing Carbon-Oxygen and Fluorocarbon bonding states.



*He(I) UPS spectra from 10 nm fullerene ( $C_{60}$ ) film on  $CaF_2$  substrate before any surface cleaning (by ion cluster etch), and after initial surface cleaning. As received, the sample showed overlaying amorphous carbon contamination that obscured measurement of the  $C_{60}$  film.*

*He(I) UPS spectra from 10 nm fullerene ( $C_{60}$ ) film on  $CaF_2$  substrate at 2 more etch times. After 900 second etch, the valence electron structure has shifted away from the  $C_{60}$  bonding configuration (shown above).*



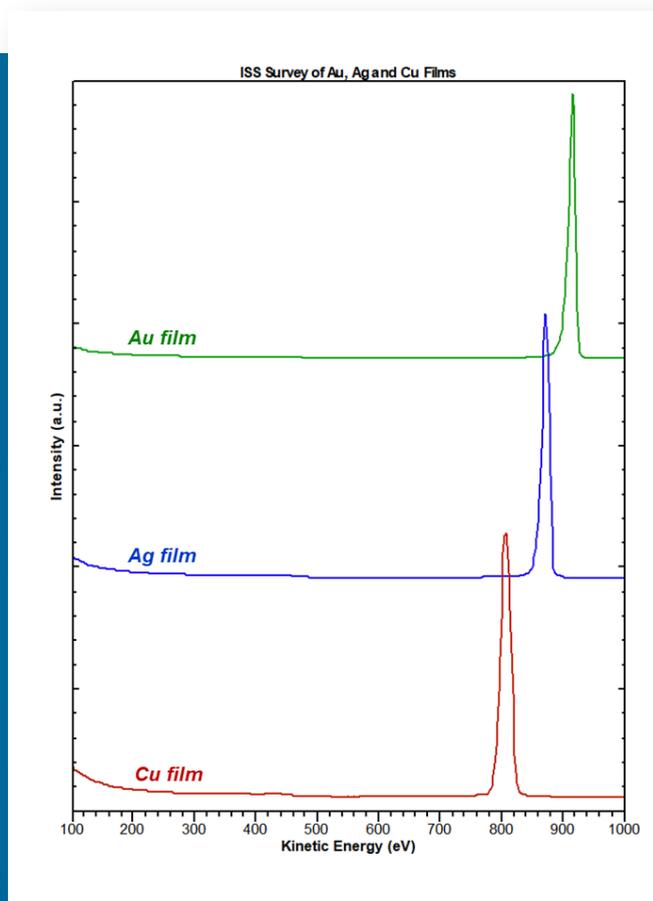
## Ultraviolet Photoelectron Spectroscopy (UPS)

UPS is similar to XPS in that it also utilizes the photoelectric effect to analyze materials, but there are a few important differences that change the ideal uses of UPS. While the XPS X-ray radiation energy is about 1253.6eV (MgK) or 1486.6eV (AlK), the UPS sources has much lower energy, with common sources being 21.2eV (He(I)) or 40.8eV (He(II)). The reduction in source energy reduces the probe depth of the measurement, from about ten nanometers to about 2.5 nanometers, allowing for specific focus on the surface.

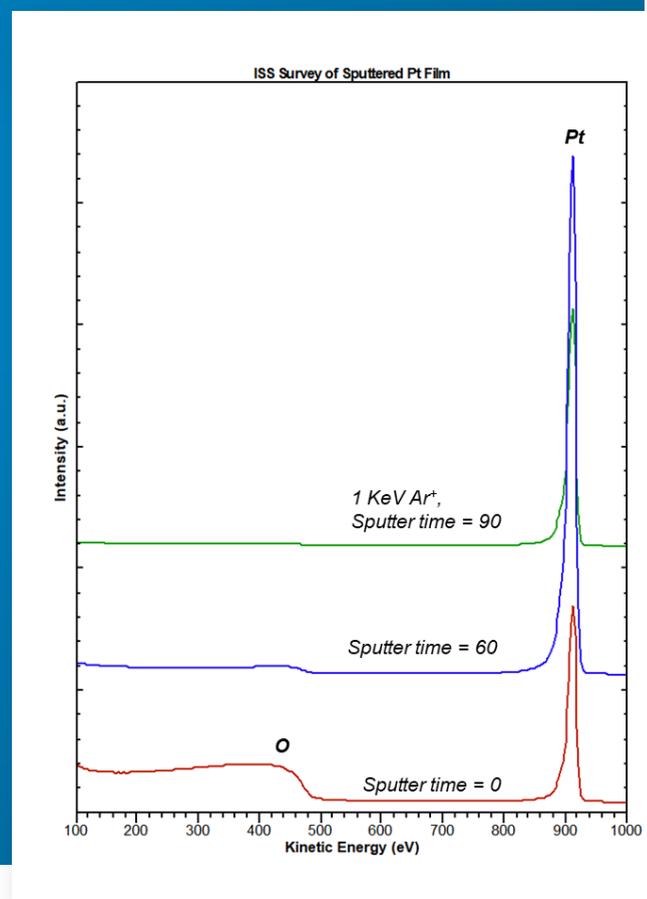
UPS has a higher resolution, allowing for investigation of components that XPS could not resolve. This resolution allows for investigation of the valence bands, finding information on the density and occupancy of electronic states in the valence band, as well as information about the work function of the material. The work function describes the energy need to remove an electron from the surface of a material in a vacuum state, and while the work function determination is sensitive to surface contamination as well as adsorbed layers, this information can help refine and calibrate other measurements.

# Ion Scattering Spectroscopy (ISS)

ISS is different from both XPS and UPS in that it is not derived from the photoelectric effect, but uses similar principals. Instead of X-ray beam radiation, ISS utilizes positively charged ions which scatter against only the outermost layer of the material. ISS is focused on quantizing the elemental composition of the outermost atomic layer, and while is more narrowed in scope, can be used to corroborate data from XPS. Due to the investigation of only the topmost layer of the surface, ISS is vulnerable to surface contamination, but if the surface is known to be clean, can map compositional segregations of a material.



(Left) Overlay of 3 ISS survey scans taken on 3 different film species, showing peak separation for Copper (Cu), Silver (Ag), and Gold (Au)



(Right) Overlay of 3 ISS survey scans of a sputtered Platinum (Pt) film, captured after 3 sputtering segments: at 0 seconds (before sputtering), an oxide layer is present; after 60 seconds of sputtering, the O peak is nearly extinguished, and the Pt signal is very strong; after 90 seconds of sputtering, the O peak is fully eliminated

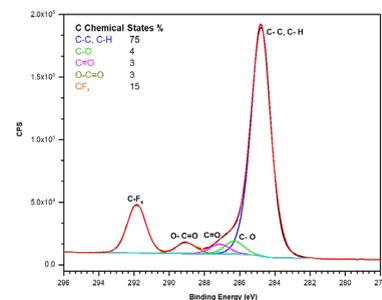
Example Output

Strengths

Limitations

Sample Requirements

XPS

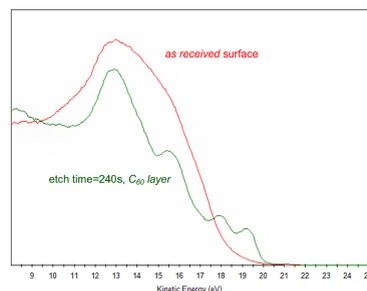


- Quick and easy sample preparation
- Rapid data acquisition
- Accurate quantitative elemental composition in the near-surface region (2-10 nm)
- Charge neutralization is possible for non-conducting materials

- Lateral resolution limited to about 10 microns
- Sputter depth profiling to assay chemical changes with depth can lead to artifacts and sample damage

- **Phase:** Solid
- **Stability:** Stable under ultra-high vacuum conditions
- **Maximum Sample Dimensions:** 60mm (L) x 60mm (W) x 20mm (T)
- *Flatter topographies improve signal detection*

UPS

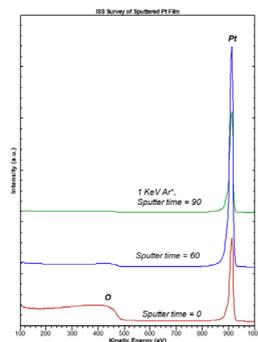


- **Very high surface specificity:** information depth 2-4nm
- Highly accurate spectral fingerprinting
- **Selective valence-band signal:** bonding orbital properties
- Reliable work function measurements possible

- **UPS peaks are not used for elemental quantification:** degree of hybridization and extent of BE-shift is too substantial
- Robust density of electronic states / orbital occupancy typically requires Advanced Modeling

- **Phase:** Solid
- **Stability:** Stable under ultra-high vacuum conditions
- **Maximum Sample Dimensions:** 60mm (L) x 60mm (W) x 20mm (T)

ISS



- **Maximally surface-selective:** signal isolated from outermost atomic monolayer
- Highly sensitive, quantitative elemental composition
- No calibration standards required for quantification
- Nondestructive analysis
- Can measure buried interfaces via depth profiling

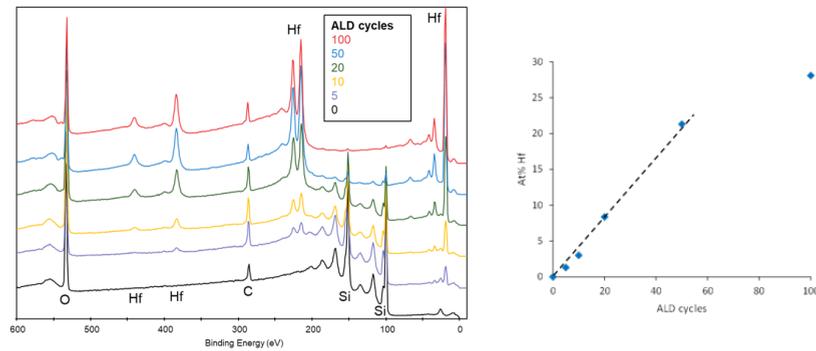
- Difficult to accurately measure light-element films over heavy-element substrates
- Surfaces must be clean to get good results

- **Phase:** Solid
- **Stability:** Stable under ultra-high vacuum conditions
- **Maximum Sample Dimensions:** 60mm (L) x 60mm (W) x 20mm (T)

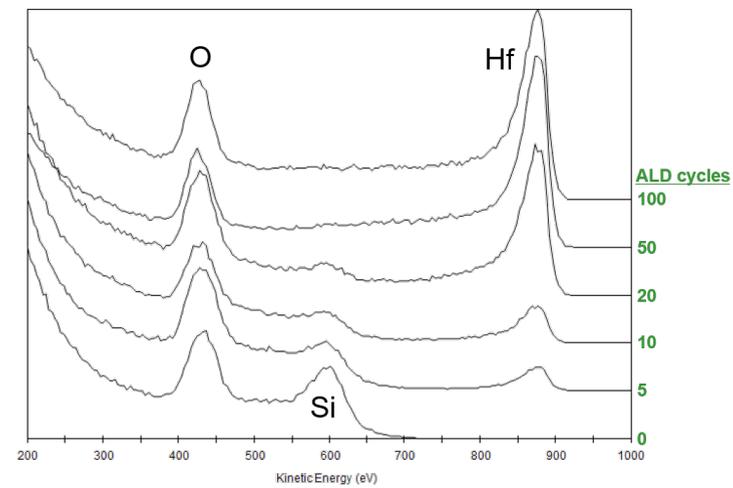
Instrument Technical Specs  
Thermo Scientific Nexsa



- **Spot Size:** 1mm
- **Sensitivity:** ppm
- **X-ray Source:** monochromated, micro-focused, high-efficiency Al K $\alpha$  X-ray Anode



(Left) Overlay of XPS survey spectra collected over 100 Hf ALD cycles on Si / SiO<sub>x</sub> layer stack. (Right) Quantified Hf concentration (At.%) as a function of ALD cycles, measured using XPS.



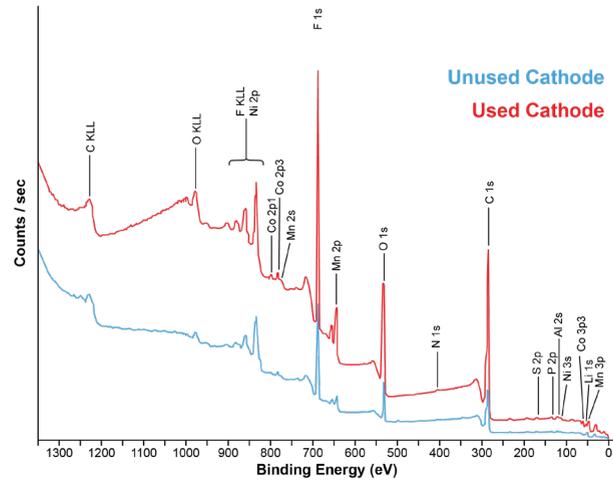
The ISS spectra collected after each round of ALD cycles show increasing completeness of Hf surface coverage. Extinction of the Si peak after 50 cycles indicates complete Hf coverage.

## Case Study 1

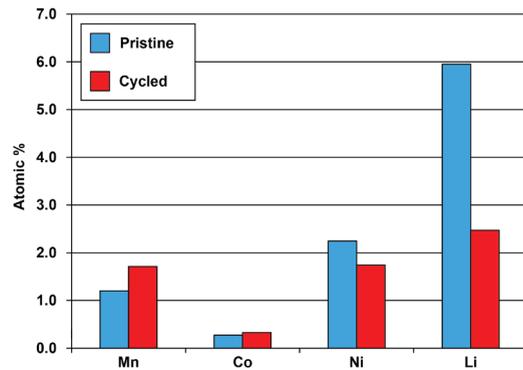
# Analysis of Atomic Layer Deposition Grown Ultra-Thin Films

Hafnium is deposited on a Silicon Oxide and silicon layered film using atomic layer deposition (ALD) to build up a full layer. The surface needs to be characterized to determine the amount of Hafnium that is deposited, the thickness of the Silicon Oxide interfacial layer, and how many cycles of ALD it takes to make a full surface of Hafnium.

1. In order to measure the amount of Hafnium deposited over multiple cycles, XPS Survey Spectra can be used over the course of the ALD cycles to take a cohesive look at the composition of the film. In the spectra, peaks for the Hafnium will appear, and as the number of cycles increase, the amount of Hafnium will also increase.
2. Using the depth probing XPS methods, the thickness of the Silicon Oxide interfacial layer can be determined over the course of ALD cycles and the increasing Hafnium thickness can be compared to the changes (or lack thereof) in the interfacial layer.
3. To find the number of cycles where there is a complete Hafnium layer, ISS can be used. As the numbers of ALD cycles increase and the coverage of the Silicon Oxide layer becomes more cohesive, the peaks associated with the Silicon Oxide interfacial layer disappear as a growing Hafnium peak is formed. When there are no peaks for the layer that should be completely covered, then it can be inferred that the Hafnium layer is full.



XPS Survey Spectra collected on the cathode before (“Unused” / pristine) and after (“Used”) cycling. While both scans show some contamination of Fluorine and Oxygen from the electrolyte, the used cathode shows increased contamination by these species.



Quantification of the active elements in the cathode ( $\text{Li}(\text{Ni}_x\text{Mn}_y\text{Co}_z)\text{O}_2$ ) show relative equivalence in Atomic % (At.%) of Mn, Co, and Ni between the pristine and cycled scans. Lithium concentration, however, is greatly reduced due to siphoning of  $\text{Li}^+$  ions to the anode during battery depletion.

## Case Study 2

# Analysis of Electrode Materials for Lithium Ion Batteries

A lithium ion cell is composed of an anode and a cathode separated by an electrolyte and a separator. The solid-electrolyte interphase (SEI) often contributes to the failure of the cell and analysis of the electrodes is necessary in cell development. In this situation the composition and contamination of the surface of the cathode before and after cycling is under investigation.

1. Using a vacuum chamber and vacuum transfer module to reduce the atmospheric contamination of the cell, the cathode can undergo XPS. Using XPS Survey spectra with the unused and used cathodes, the surface chemistries of the cathode can be investigated over the entire scope of binding energy. This will allow for a cohesive comparison of the atomic makeup and atomic percent of the cathode surface, depicting any buildup of contamination.



### Case Study 3

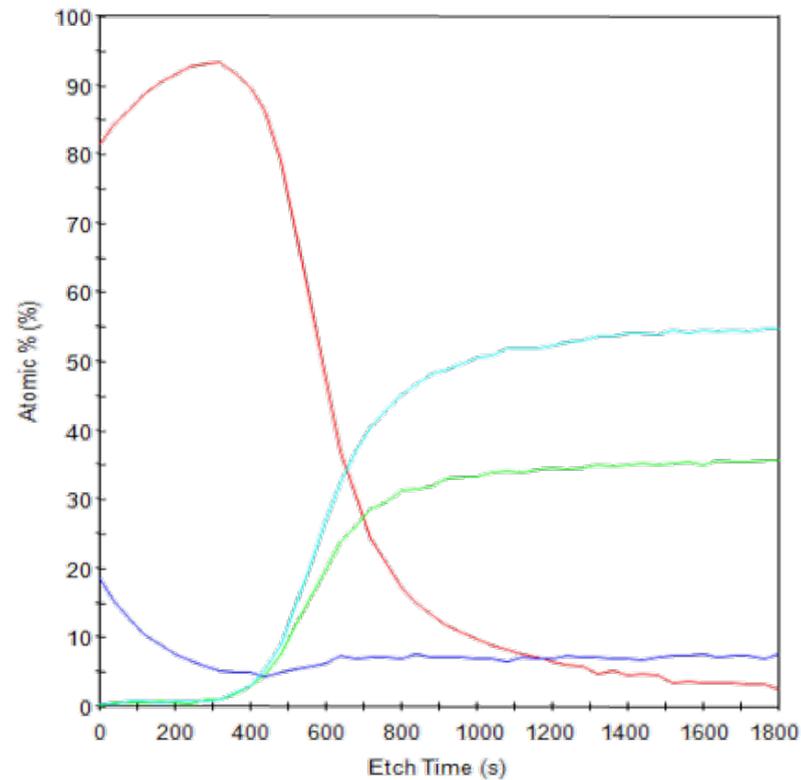
## Analysis of a 10nm Carbon 60 Film on Calcium Fluoride Layer

A thin carbon 60 film is cast onto a calcium fluoride base material. The film is assumed to be non-contaminated, and correctly laid on the calcium fluoride bulk material, but surface and depth profiling will need to be conducted to confirm both assumptions. While depth profiling is required, there may be concern that the final film structure would be physically damaged, so the electronic structure of the film will need to be monitored throughout the survey.

1. An initial survey of the chemical depth is conducted with XPS using the less invasive argon clusters which allows for the chemical profiling of elemental composition throughout the bulk of the film. The results will allow for elemental identification with the bulk of carbon separated from the appearance of calcium and fluorine in the base of the material, as well as contamination that may occur on the surface or throughout the film.
2. A more intense XPS survey can be conducted on the carbon spectrum individually. This will allow for a breakdown in the species of carbon present and can identify the presence of contamination or adventitious carbon. A UPS survey can also be taken before and after cleaning the surface with careful Argon cluster etching of the film to ensure the contamination is removed.
3. Investigation of the interface between the carbon and the  $\text{CaF}_2$  can be done using Argon cluster sputtering to the depth of the interface and consideration of the peaks at the depth. In cases where there are interactions between the two layers, the spectra will show a blend of peaks of the two layers, with further etching establishing the depth where the pure  $\text{CaF}_2$  layer begins.



XPS depth profile measurement of atomic percent (At.%)  $\text{CaF}_2$ , as a function of etch time (s).



- $\text{C}_{60}$  film on  $\text{CaF}_2$
- Sample profiled with MAGCIS: A beam of 4keV, 2000 atom argon clusters was used for profiling in this case
- Changes in carbon chemistry were observed during profile

*Surfaces are the location for many of the interactions that materials have with their surroundings*

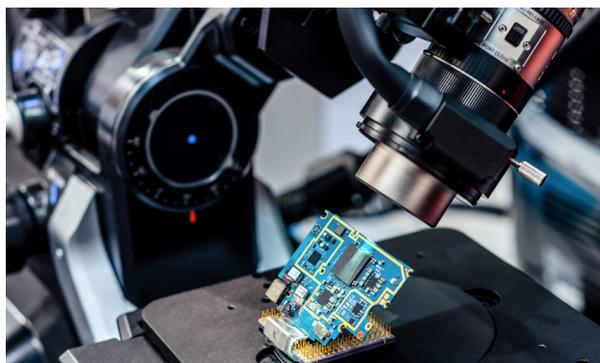
and they are one of the most important locations for a scientist or engineer to investigate and characterize to better understand the materials. Characterization specifics are dependent on the material, but the same thought process can be applied to all surface characterization:

**“What is on the surface, how much of each material is on the surface, what is the effect of the surface?”**

Mixing and matching these characterization techniques and others can give a comprehensive picture of the material, allowing for more informed and successful research to proceed.

# What to Look For in a Materials Characterization Partner

In the world of Materials Science and Characterization, there is no shortage of options when it comes to choosing a partner. But, when it comes right down to it, service labs can be slow, expensive and rigid in their approach, pricing and often fall flat when it comes to providing adequate data insights. There are a few questions that should be considered if you want a long-term, reliable and strategic partner for your R&D efforts. Do they offer:



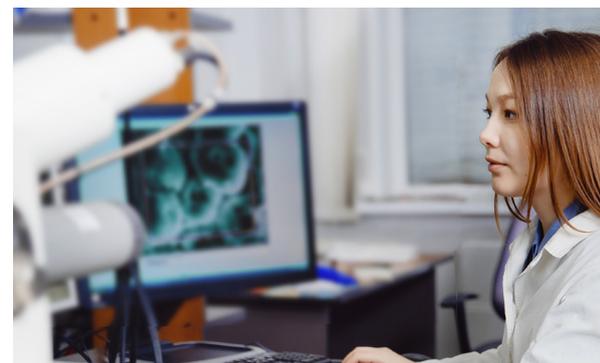
## A Comprehensive Solutions Stack

With diverse offering of techniques, instruments and expertise in advanced modeling, method development and analytical services.



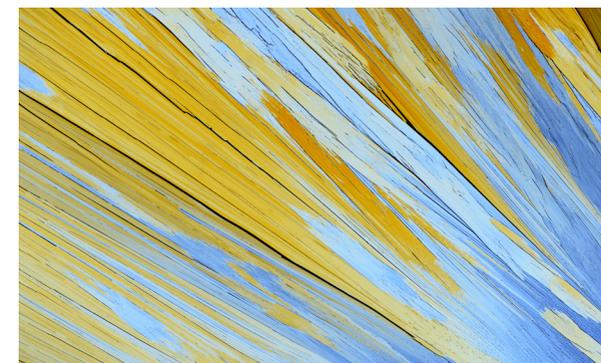
## A Flexible Business Model

With the ability to offer custom consulting and onsite support when needed, training and certification on instrumentation, tool-share capabilities.



## A Network of Partnerships

With expanded access to specialty labs, instrumentation and community learning.



## Speed and Access to Data

With fast turn-around times and secure portal for uploading, downloading and viewing data.

## About Covalent Metrology

Covalent Metrology is ready to serve you with our comprehensive platform of techniques and services, even during COVID 19. Reach out to our friendly team of experts to receive our answers to the above questions and to start a conversation about how we can help your team achieve your materials characterization goals.



W: [Covalentmetrology.com/contact](https://www.covalentmetrology.com/contact)