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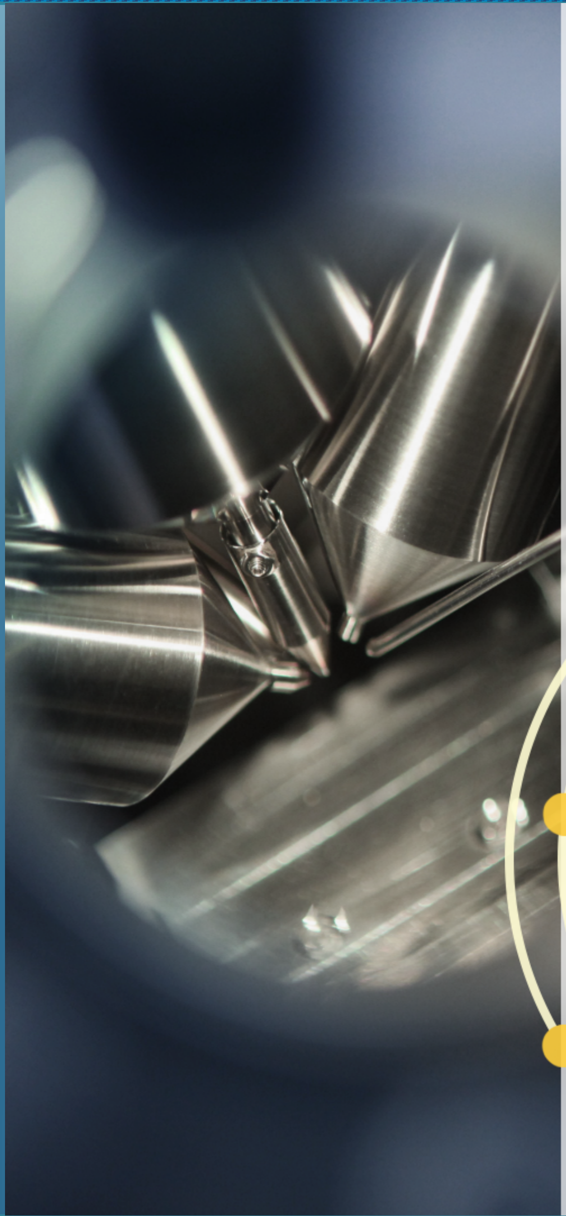

XPS - UPS - ISS

Surface Spectroscopic Techniques for Chemical Analysis

Roland Barbosa, PhD

June 11, 2020 11am PDT

COVALENT ACADEMY

EPISODE 10

RSVP at:
https://bit.ly/covalent10

Covalent Metrology

- **Founded 2016**
- Testing, measurement & characterization **Platform**
- **30 team members** (13 PhDs)
- **9,500 ft^2 lab in Sunnyvale, CA**
- **1-Stop-Shop Source for Answers**
  - 30 instruments in-house
  - 6 partnerships with instrument manufacturers
  - 11 partner labs
  - 6 corporate “tool shares”
- **More than 275 customers** (80 % repeat)

Covalent Technical Groups and Organization

COVALENT METROLOGY

hello@covalentmetrology.com

408-498-4611

Electron & Scanning Probe Microscopy

SEM / TEM, AFM, EDS, EELS, Nanoindentation, Acoustic Microscopy

Surface Analysis

XPS, Auger, TOF-SIMS, d-SIMS

Optical Microscopy & Spectroscopy

Laser Confocal, White Light, Chromatic Aberration, Spectral Ellipsometry, UV-Vis-Nir Spectroscopy

Materials / PC Board Failure Analysis

Cross Sections, Inspections, Dye & Pry Testing

X-Ray Characterization

XRD / XRR, XRF, µCT

Chemical Analysis

ICPMS, GCMS, FTIR, Raman Spectroscopy, NMR

Nanoparticle Analysis

DLS, PSA, Particle Zeta Potential

Bulk Properties Characterization

DSC, TGA, DMA, Rheometry, Tensile Testing, Pencil Test, Surface Zeta Potential

Dr Roland Barbosa, Manager, Surface Chemical Analysis

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- PhD Chemistry, *University of Houston*
- BS Chemistry, *University of the Philippines*

- Over 15 years of academic and industry-based research experience focused in characterizing and developing new materials in the areas of catalysis, tribology, semiconductor, energy production and advance manufacturing.

- Extensive experience utilizing various analytical techniques including XPS, TPD, HREELS, FTIR, AFM, XRD, TOFMS, UPS, TEM, etc working in different countries (Philippines, US, France, Germany, Belgium).

Episode 10 Overview

- **General introduction** - Surfaces

- **XPS**
- **UPS**
- **ISS**

- **Examples**
  - Composition, coverage and band gap analysis of ALD-grown ultra thin films
  - Combined XPS/UPS argon cluster depth profile of 10nm C_{60} film on CaF_2
  - Analysis of electrode materials for lithium ion batteries

- **Next Episode**
- **Question and Answer Session**

Nexsa Surface Analysis System

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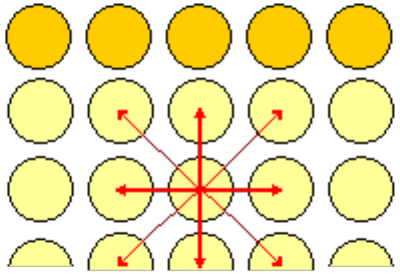
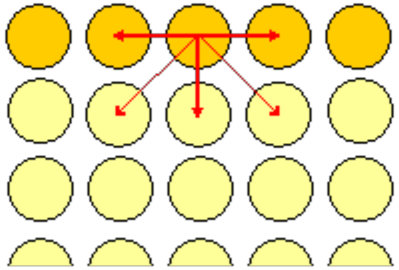
- X-ray Source Type: Monochromated, micro-focused, low power Al Kα
- X-ray spot size: 10μ-400 μm
- Depth profiling: *EX06* monatomic or *MAGCIS* dual mode ion source
- Vacuum Transfer Module: sample transfer without air exposure
- SnapMap™ : create high resolution, large area XPS images within minutes
- AvantageTM: instrument control, data acquisition, data processing and reporting
- Additional Features:
  - ISS: Ion scattering spectroscopy provides elemental composition information from the top atomic layer of the surface
  - UPS: UV photoelectron spectroscopy provides information from the valence electrons
  - reflected energy loss spectroscopy (REELS) and Raman - optional

Surfaces

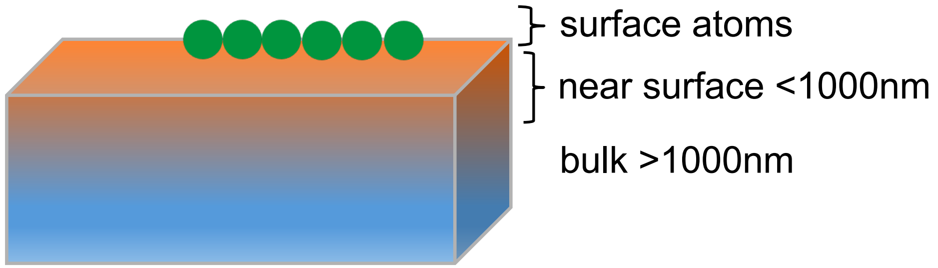
- Surface – boundary layer between a solid and a vacuum/gas/liquid



Bulk solid

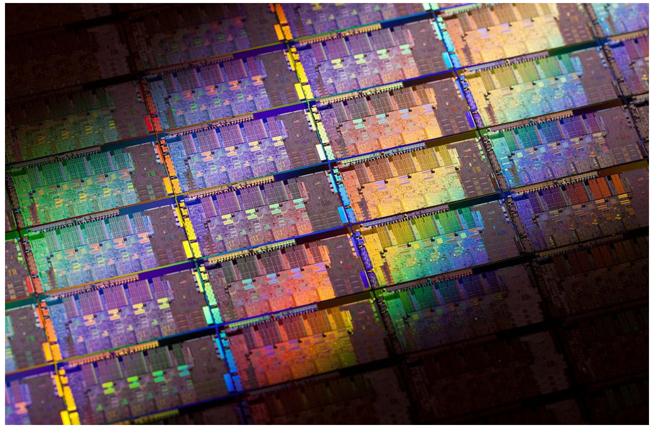


Bulk solid

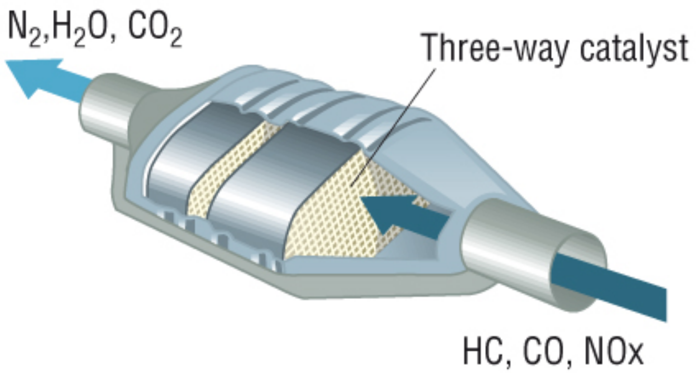


- Differs in geometrical and electronic structure

Surface Issues



Credit: Intel Free Press // creative commons



www.covingtonortho.com

How Do You Characterize a Surface?

Here are a few examples of how you can characterize a surface:

Mechanical

- Roughness
- Flatness
- Hardness
- Scratch resistance

Chemical

- Elemental Composition
- Chemical Bonding
- Contamination

Electrical

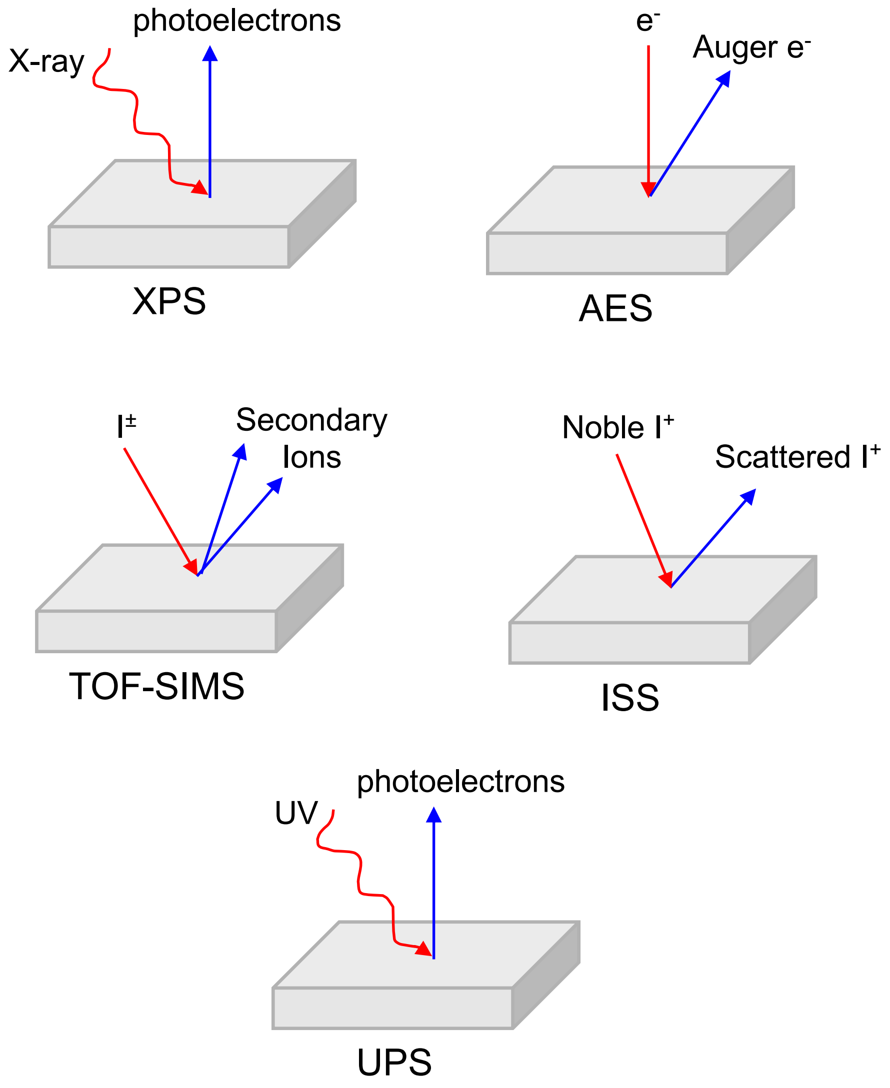
- Spreading Resistance

Physical

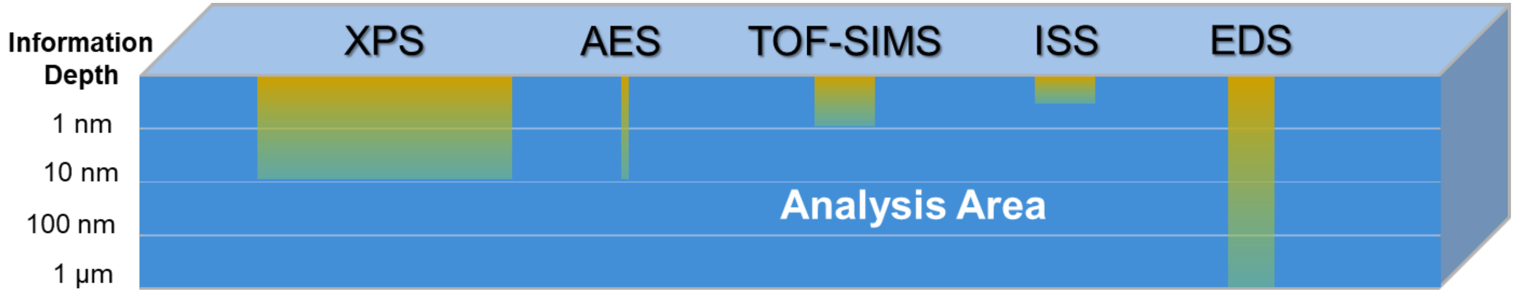
- Work Function
- Carrier Lifetime

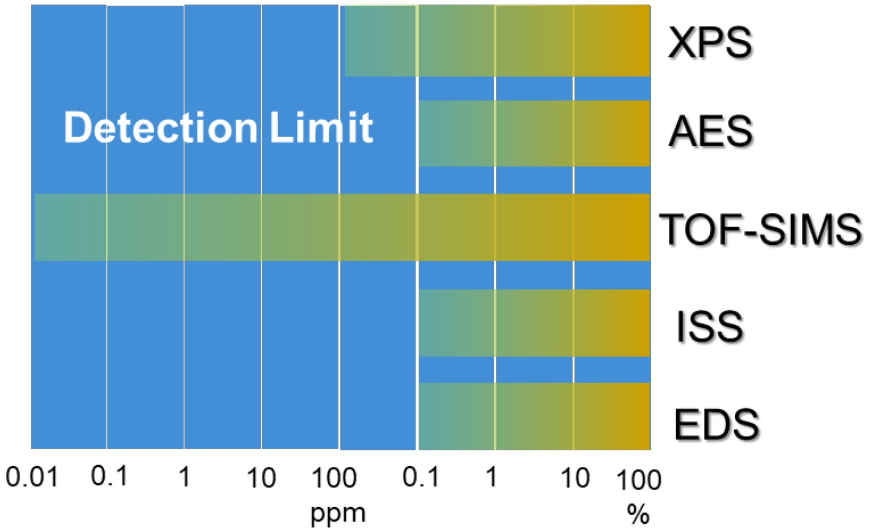
Surface Techniques

Techniques		Information Provided
X-ray Photoelectron Spectroscopy	XPS/ESCA	elemental and chemical state
Auger Electron Spectroscopy	AES/Auger	elemental and chemical state
Time-of-Flight Secondary Ion Mass Spectrocopy	TOF-SIMS	elemental, chemical state, molecular information
Ion Scattering Spectroscopy	ISS/LEIS	elemental
Ultraviolet Photoelectron Spectroscopy	UPS	valence band, workfunction



Surface Techniques





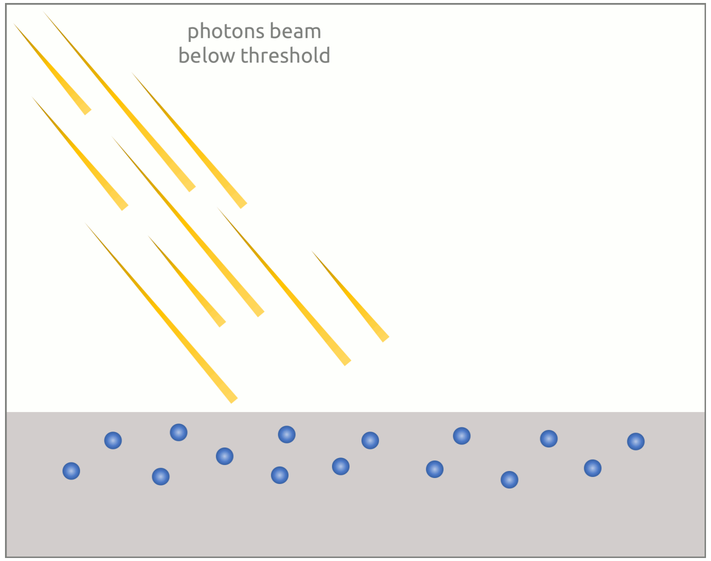
Photoelectric Effect

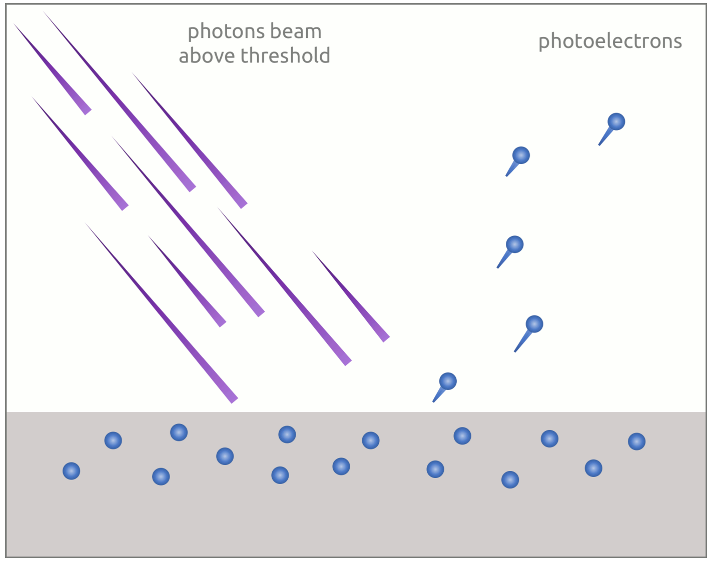
- Einstein's photoelectric effect (1905)
  – Nobel Prize in Physics (1921)

- Siegbahn developed the XPS technique (1960).
  – Nobel Prize in Physics (1981)

- XPS – X-ray
- UPS – Ultraviolet

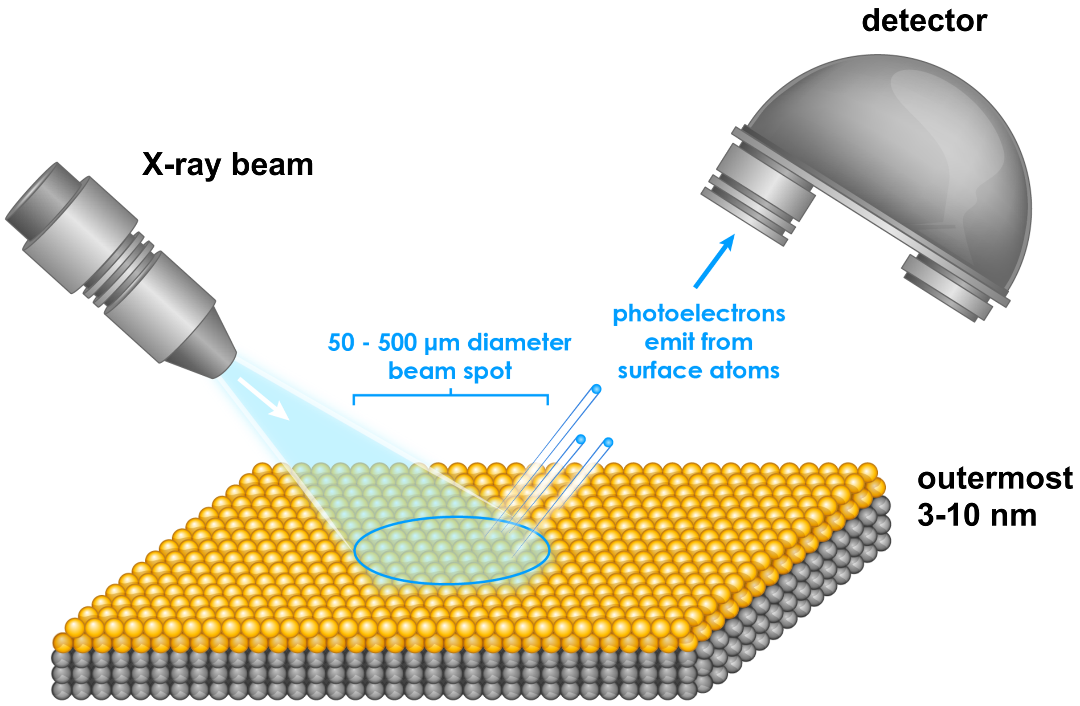
Photoelectron spectroscopy (PES)



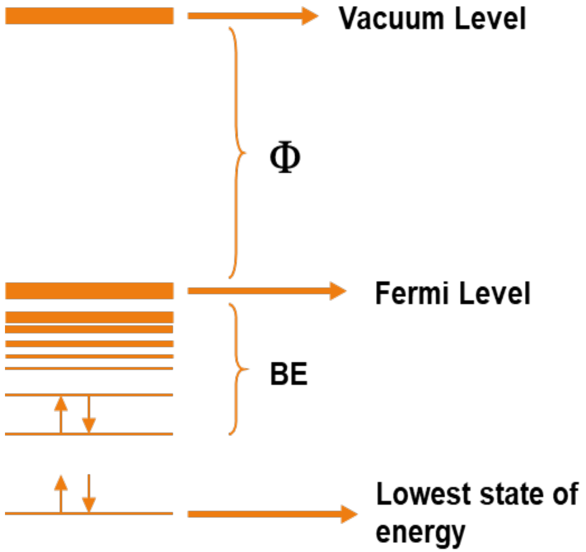


https://gsalvatovallverdu.gitlab.io/

Principles of Operation



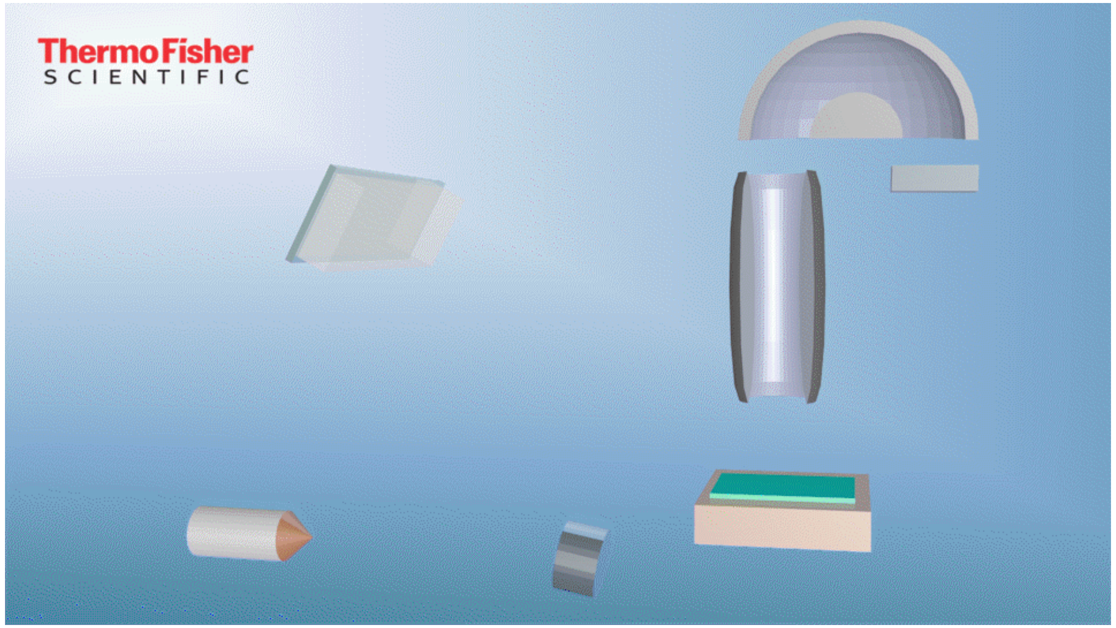
$$BE = h\nu - KE - \Phi$$



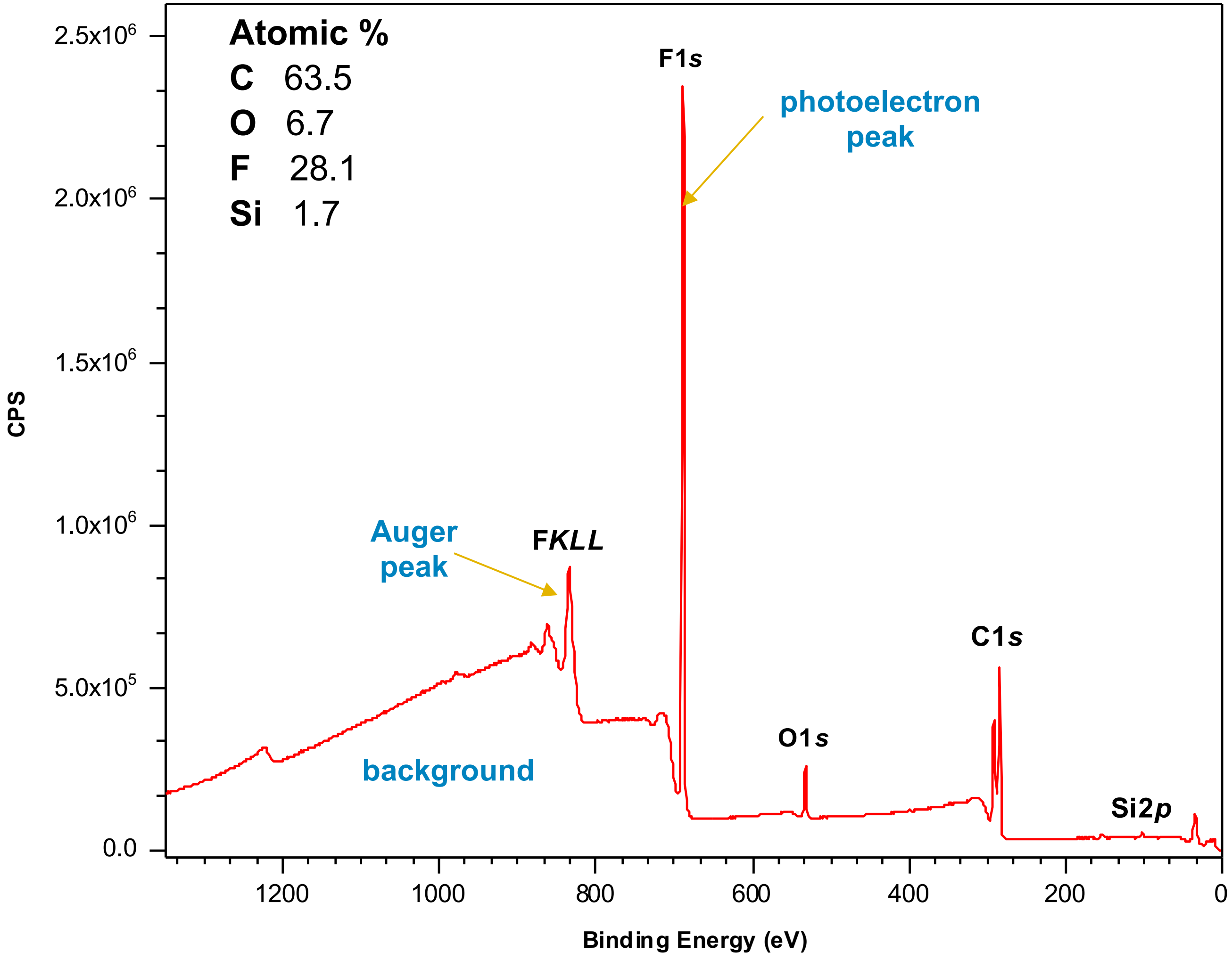
Where: **BE** = *Electron Binding Energy*
KE = *Electron Kinetic Energy*
Φ_{spec} = *Work Function*

Instrumentation

- X-ray sources
  - Mg Kα radiation : hv = 1253.6 eV
  - Al Kα radiation : hv = 1486.6 eV
- electron energy analyzer
- an ultra high vacuum environment
  - maintain sample surface integrity
  - minimize scattering of the photoelectrons
  - increase the mean free path for electrons, ions and photons.



Survey Spectrum



Quantification

For a Homogeneous sample:

$I = N\sigma DJL\lambda AT$

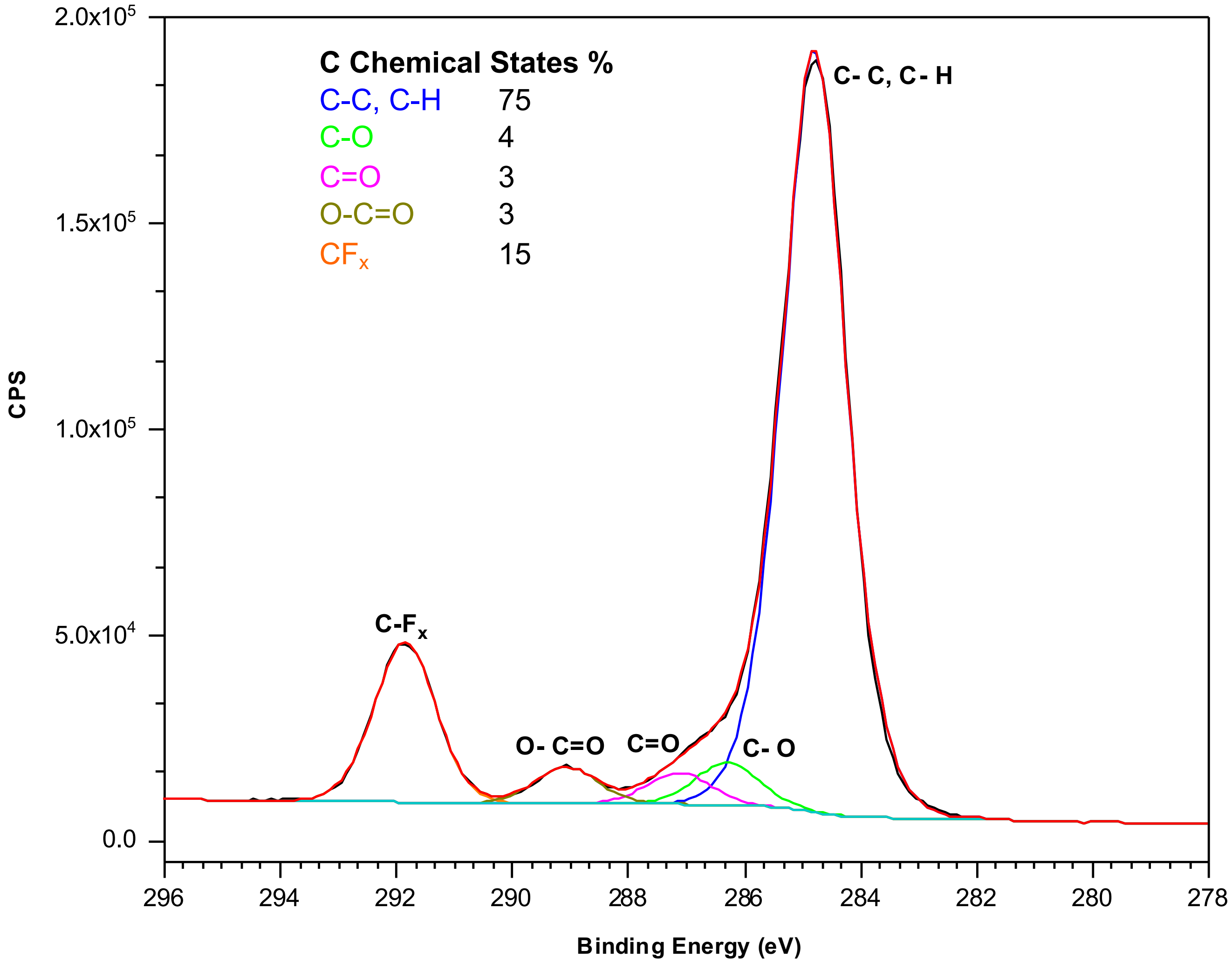
where: N = atoms/cm3
σ = photoelectric cross-section, cm2
D = detector efficiency
J = X-ray flux, photon/cm2-sec
L = orbital symmetry factor
λ = inelastic electron mean-free path, cm
A = analysis area, cm2
T = analyzer transmission efficiency

$N = I/\ \sigma DJL\lambda AT$
Let denominator = elemental sensitivity factor, S
$N = I / S$
Can describe Relative Concentration of observed elements as a number fraction by:

$$C_x = N_x / \Sigma N_i$$
$$C_x = I_x/S_x / \Sigma\ I_i/S_i$$

The values of S are based on empirical data.

Chemical State

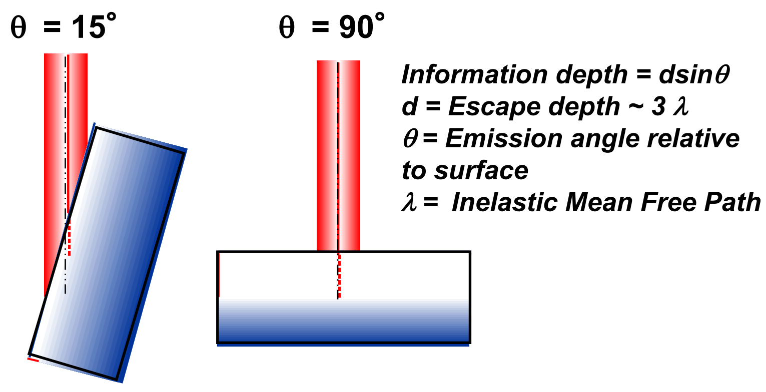


- Chemical shift – increase charge, increase BE
  - number of substituents
  - electronegativity of substituents
  - oxidation state
- BE increases with more bonds with electronegative atoms
- BE increases with oxidation state

Depth Profile

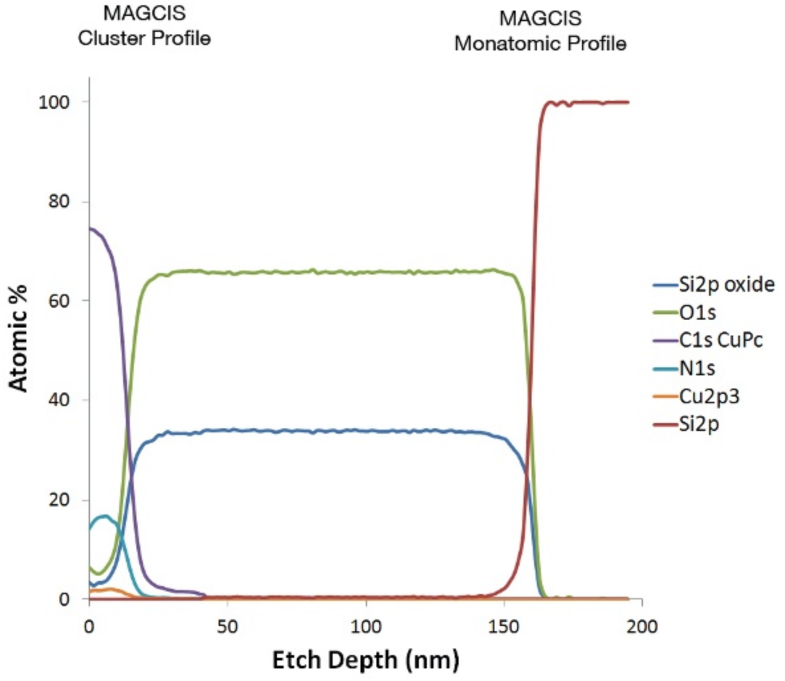
Angle-Resolved XPS

- depth profiling can be done by rotating the sample.
- mean free path changes depth from which photoelectrons are detected.



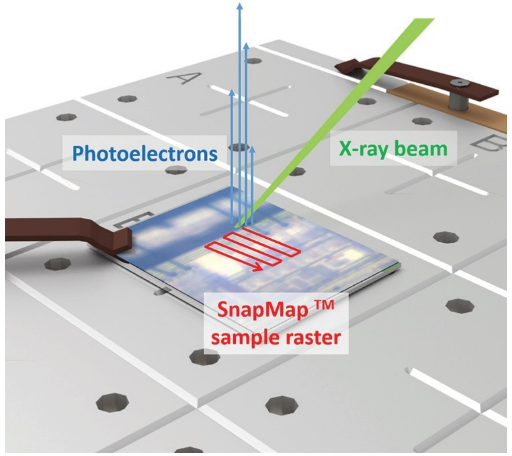
Sputter Ion XPS Depth Profile

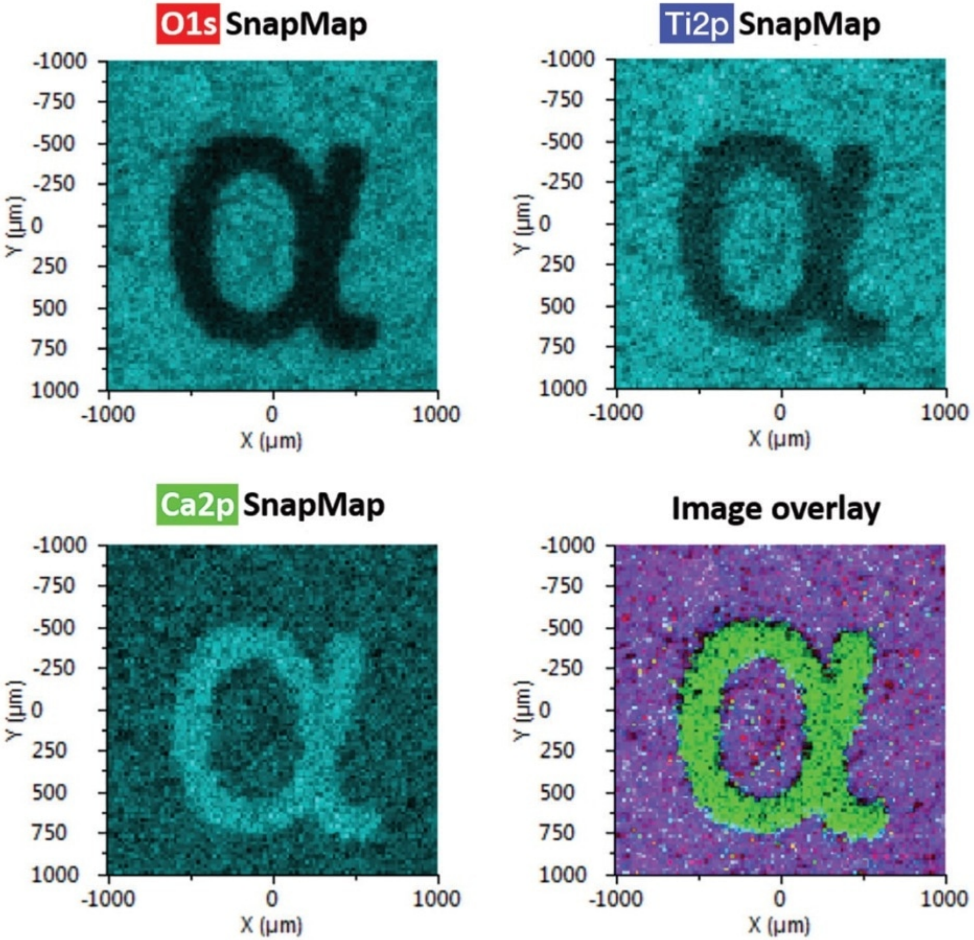
- combining a sequence of ion gun etch cycles with XPS analyses



Paul Mack and Andy Wright, AN52476, Thermo Fisher Scientific Inc.

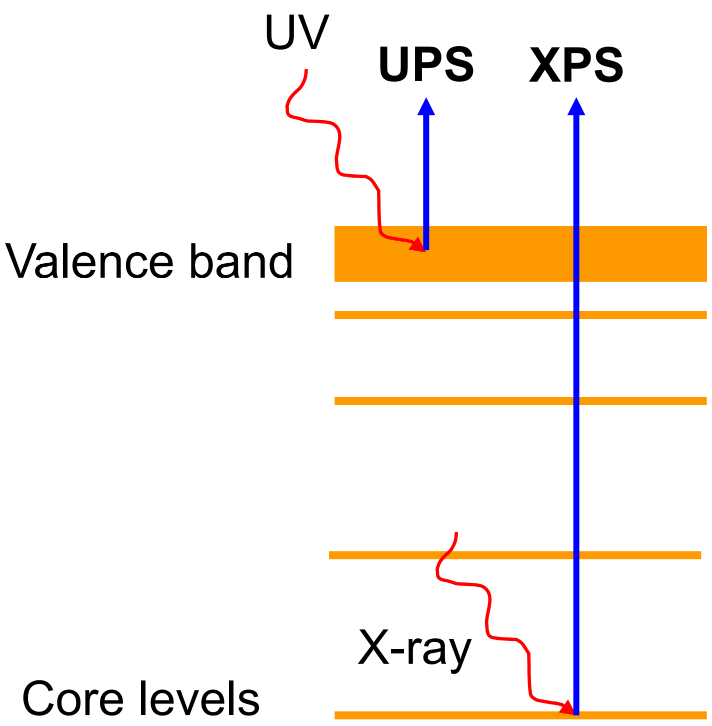
XPS Imaging





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

Ultraviolet photoelectron spectroscopy (UPS)

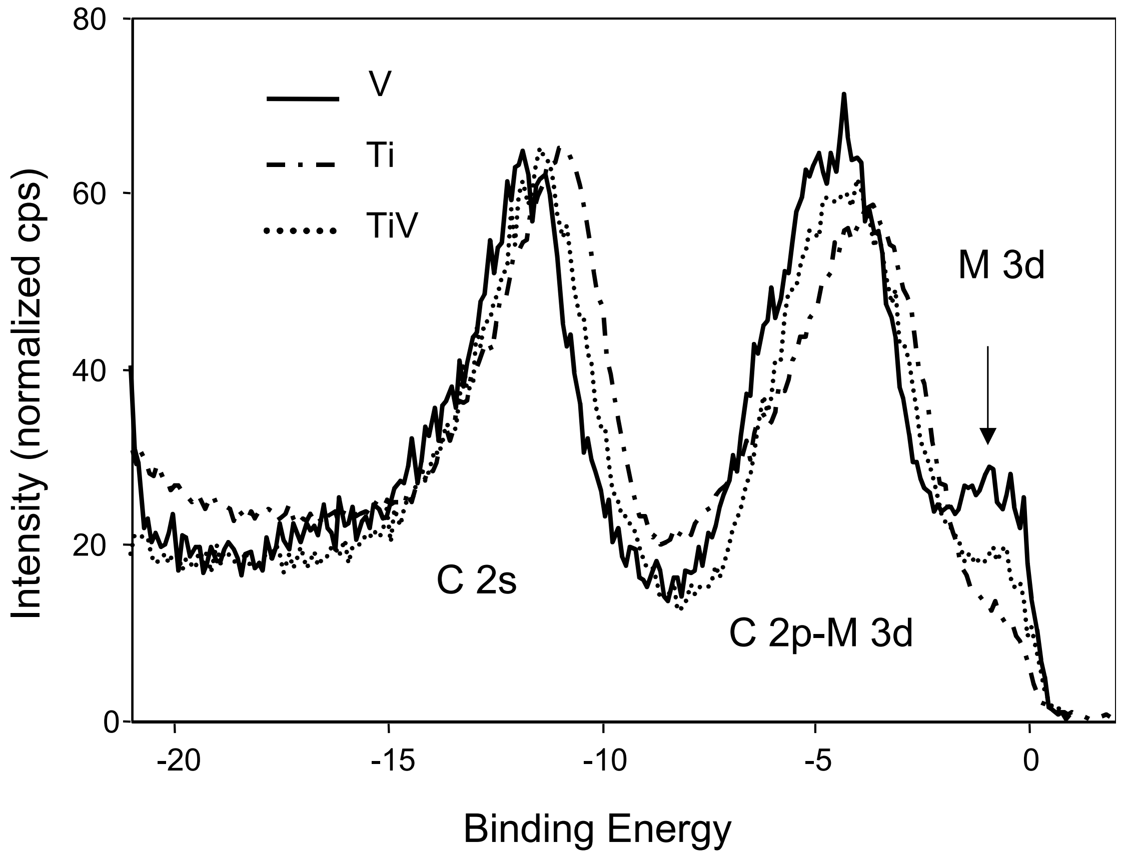


- like XPS with lower incident energy
  - He(I) = 21.2 eV
  - He (II) = 40.8 eV
- density and occupancy of electronic states in the valence band
- work function determination
- surface sensitive – low mean escape depth

Valence Band

- information about the density and occupancy of electronic states
  - hybridization
  - typically require theoretical modeling

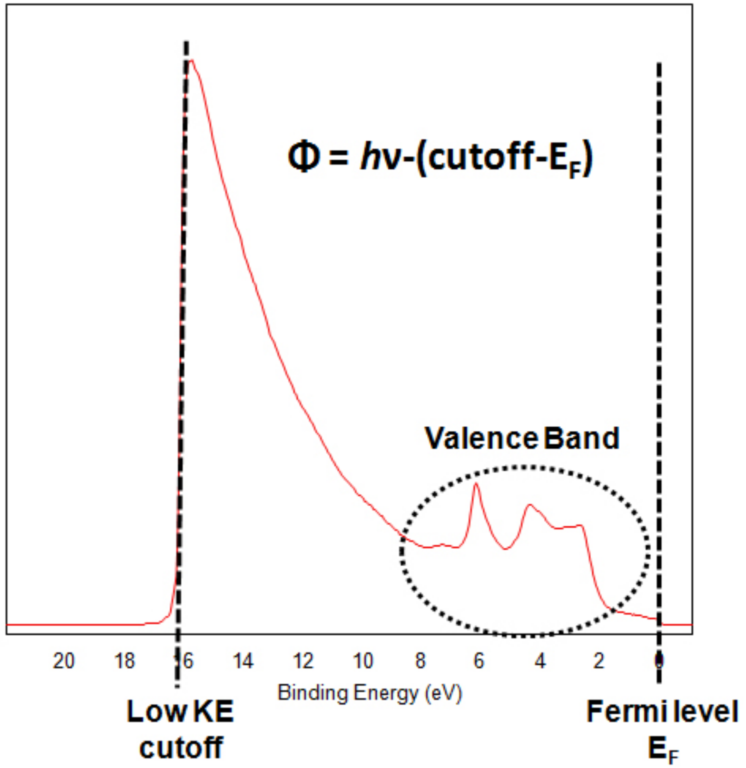
- valence spectra of TiC, VC, TiVC
  - VC is electronically different from TiC
  - Interfacial chemical reactions (CO and benzene on the surfaces).



Work Function

- work function - energy needed to remove an electron from the surface of a material to the vacuum state
- Work Function Determination
  - Sensitive to surface contamination or adsorbed layers
  - Incident photon energy –(cutoff-EF)

UPS spectrum of Au surface

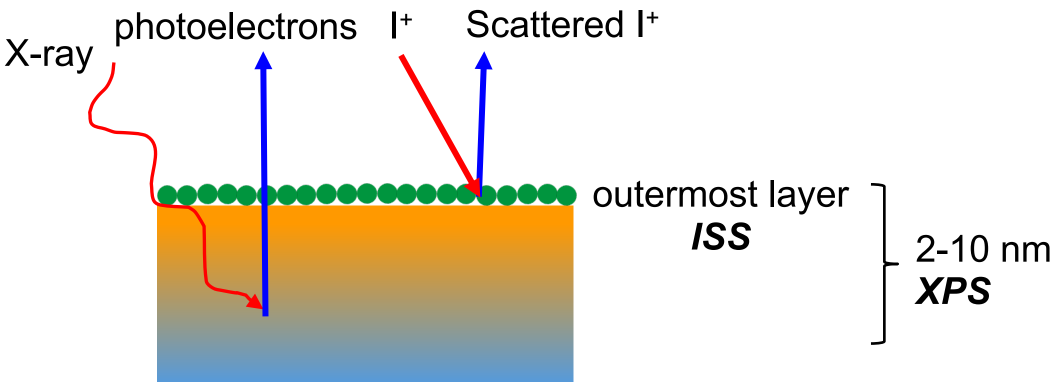


xpssimplified.com

Work Function = 21.21-15.9 = 5.3 eV

Ion Scattering Spectroscopy (ISS)

- Quantitative elemental composition of the outermost atomic layer
- Low-energy ion scattering spectroscopy (LEIS)
  - MEIS
  - RBS
- Ion energy 0.1 eV to 3 keV
  - Interaction distance short (<10 Å)
  - sensitive to the outermost atomic layer

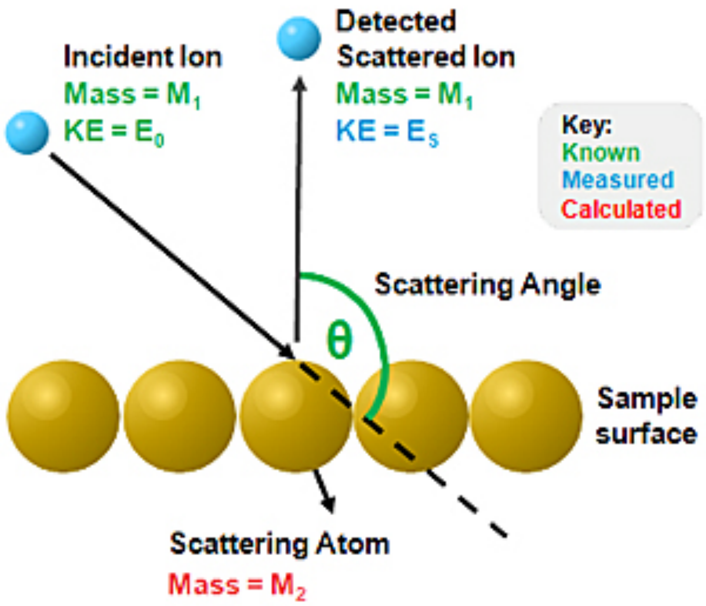


Principles of Operation

$$\frac{E_S}{E_0} = \left[\cos\theta \ \pm \left[\left(\frac{M_2}{M_1}\right)^2 - \sin^2\theta\right]^2 / 1 + \left(\frac{M_2}{M_1}\right)\right]$$

E_S = Kinetic energy of the scattered ion
M_1 = Relative atomic mass of the scattered ion
E_0 = Kinetic energy of the primary ion beam
M_2 = Relative atomic mass of the scattering surface atom
θ = Scattering angle

$\frac{M_2}{M_1} \geq 1$



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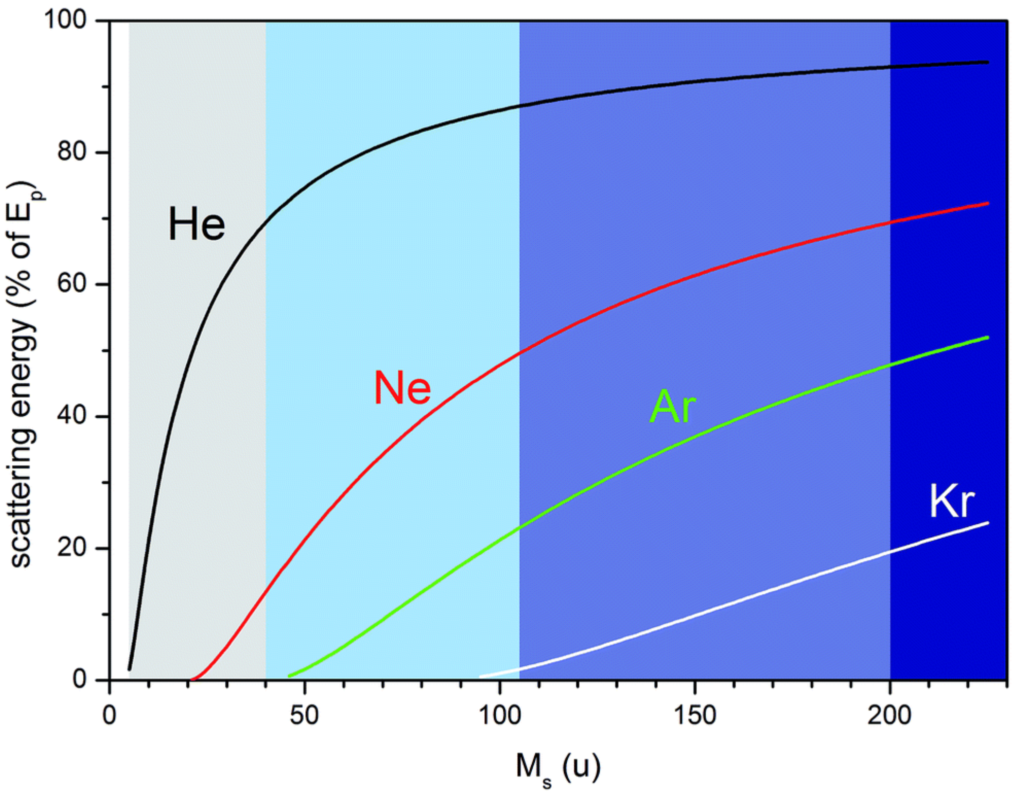
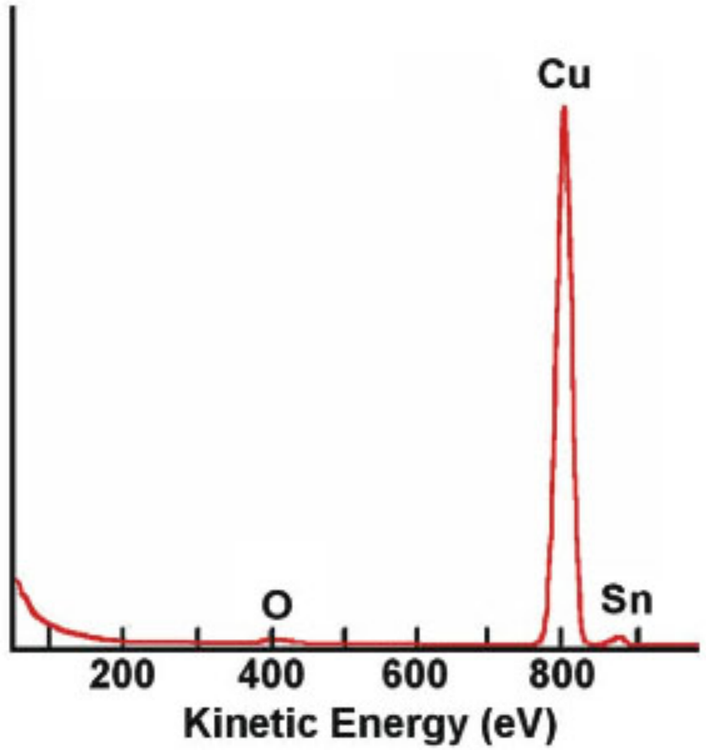
ISS Spectra

% of Energy Scattered as a Function of M_S



Cushman, et.al., Vacuum Technology & Coating April 2015, 26.

ISS Spectrum of a phosphor-bronze sample



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Analysis of ALD-grown ultra thin films

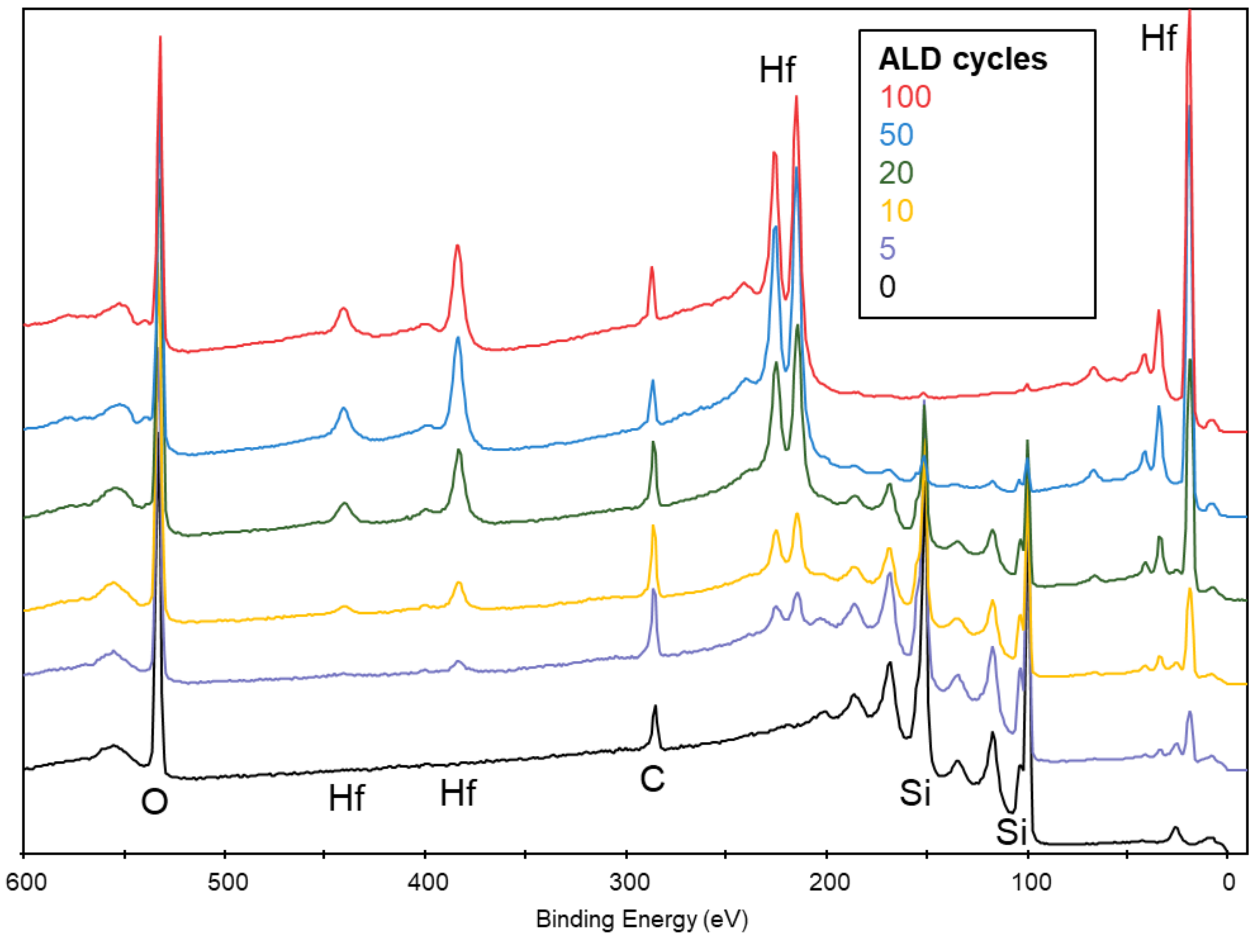
Schematic of high-k stack

- Gate dielectric materials
  - ALD of HfO_2 on SiO_2/Si
    - XPS for measuring amount of hafnium deposited
    - XPS for high-k and interfacial film thickness
      - Does interfacial layer thickness change with ALD cycles?
    - Ion Scattering Spectroscopy to determine how many cycles of ALD it takes to make full coverage
    - Cannot use XPS for band gap measurement for HfO_2
      - Use REELS to measure band gap of high-k film

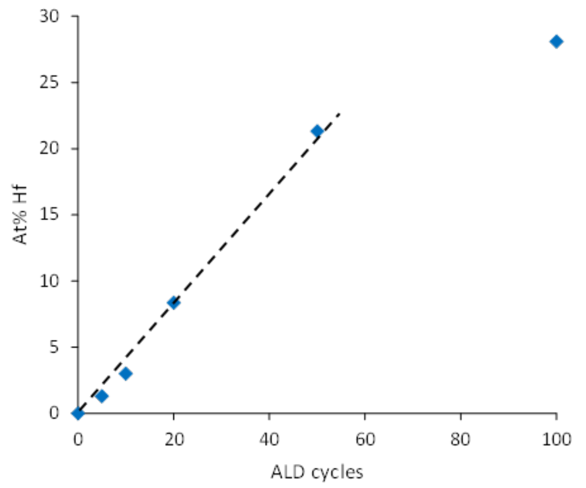
Paul Mack and Robin Simpson, AN52344, Thermo Fisher Scientific Inc.

ALD HfO_2 on SiO_2/Si

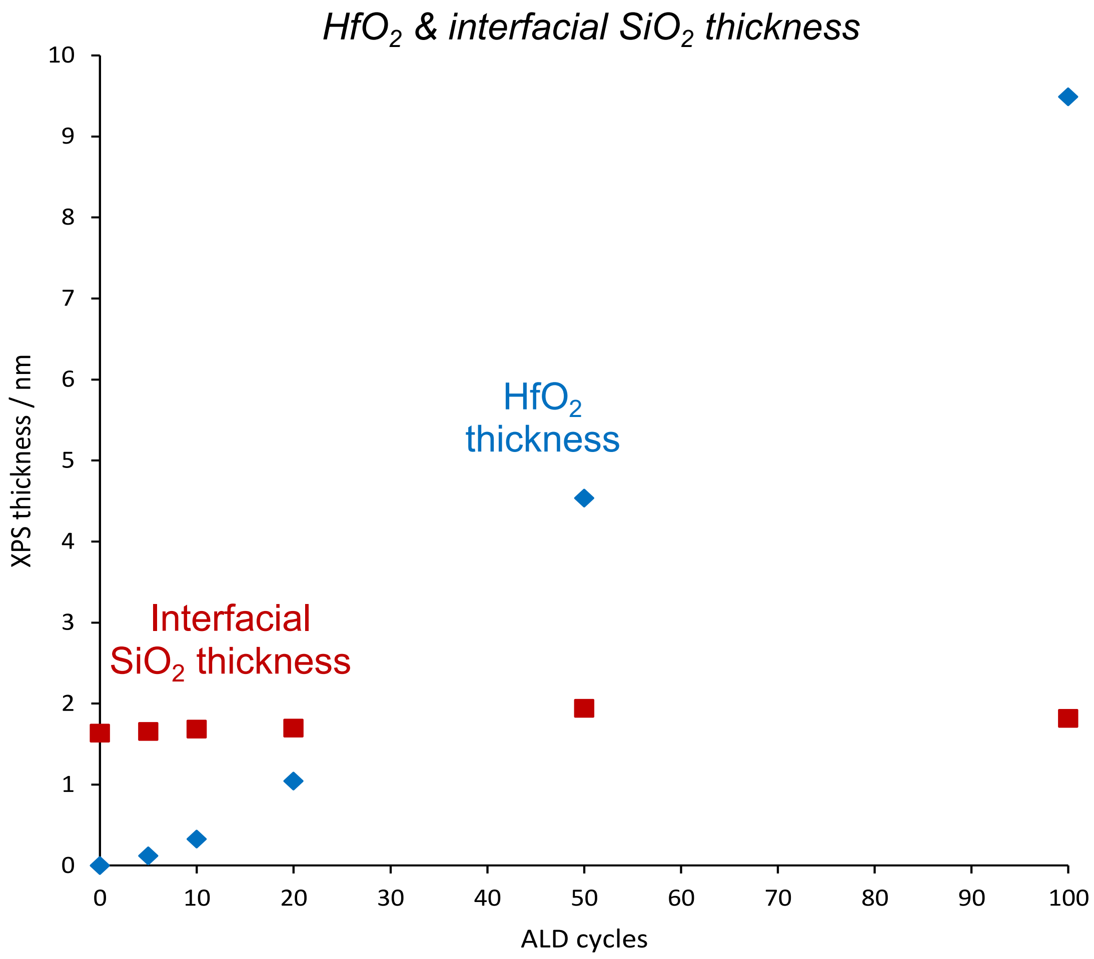
XPS survey spectra as a function of ALD cycles



Quantification of Hf as a function of ALD cycles



ALD HfO_2 on SiO_2/Si



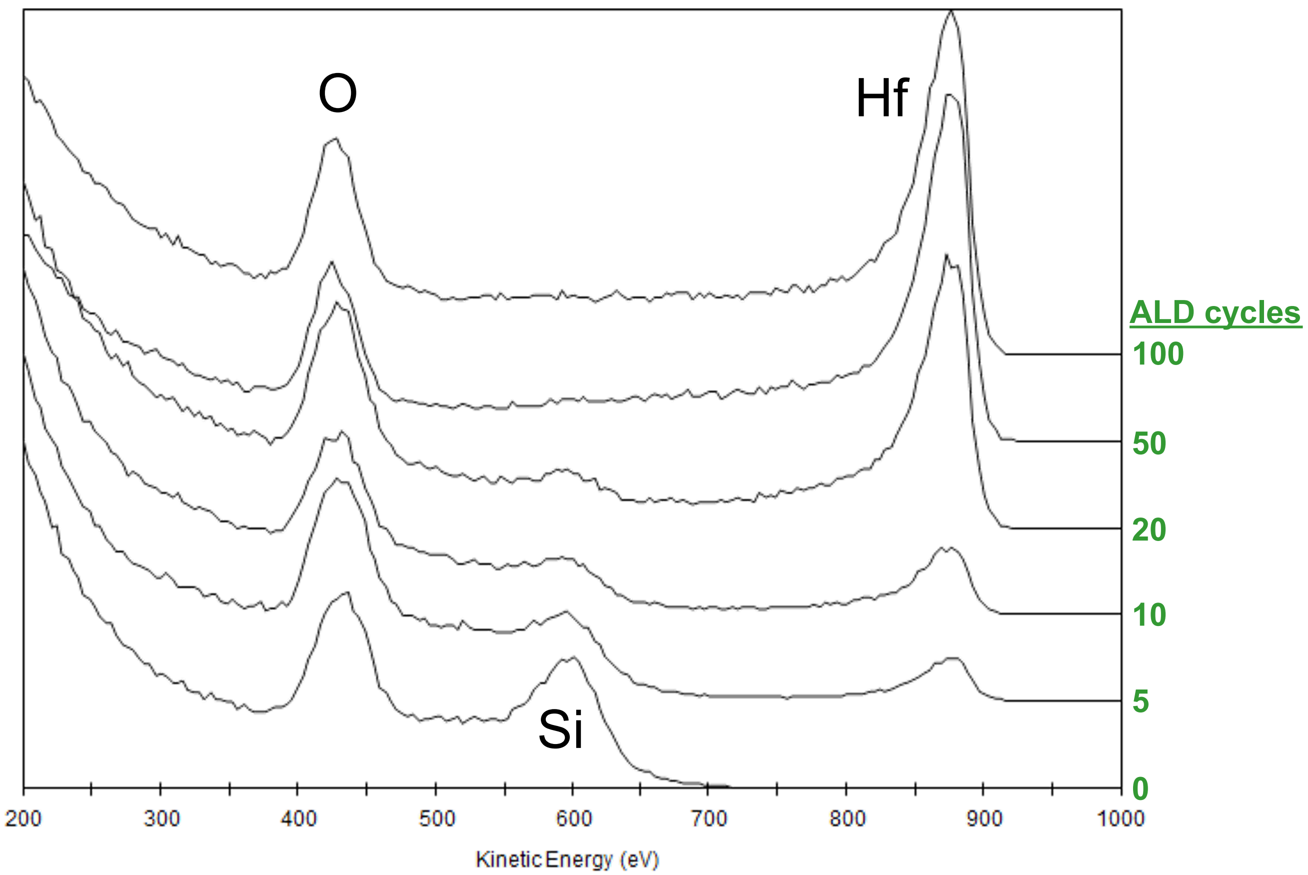
Method

- Assume uniform & complete coverage of high-k film on SiO_2/Si
- Acquire Hf and Si XPS data

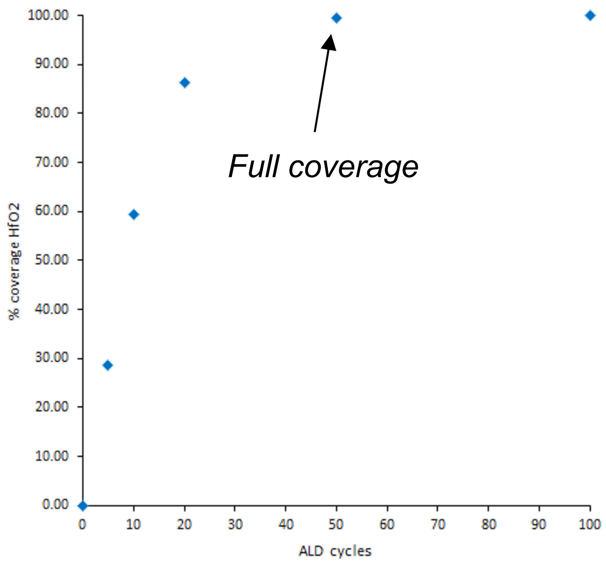
Results

- Interfacial layer thickness not significantly affected by HfO_2 deposition
- Under model assumptions, some thickness measurements are unrealistically thin, e.g. 0.1nm at 5 ALD cycles

ALD HfO_2 on SiO_2/Si



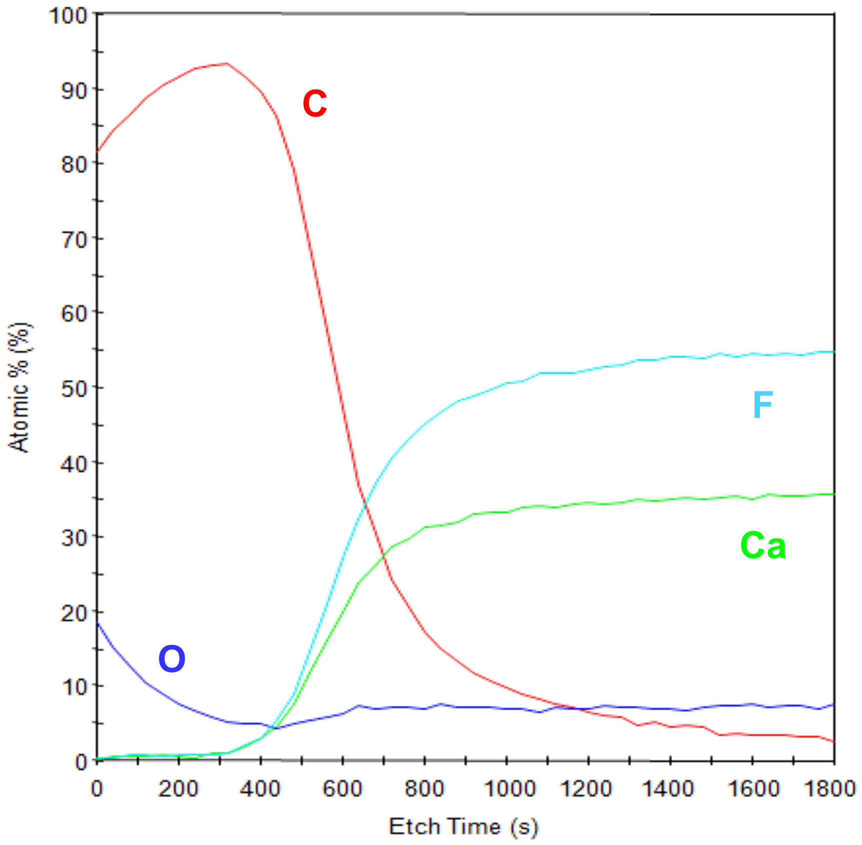
ISS spectra as a function of ALD cycles



HfO_2 coverage from ISS

Combined XPS/UPS depth profile of 10nm C_{60} film on CaF_2

Argon cluster (4keV Ar_{2000}^{+}) profiling of C_{60} on CaF_2



- C60 film on 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

Paul Mack and Robin Simpson, Thermo Fisher Scientific Inc.

Combined XPS/UPS depth profile of 10nm C_{60} film on CaF_2

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C1s spectrum (0s, as received surface)

Adventitious carbon (contamination) was observed on top of the C_{60} layer

C_{60}

$C_{adventitious}$

294 292 290 288 286 284 282 280

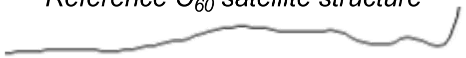
Binding Energy (eV)

C1s spectrum (240s etch time)

Argon clusters allow the adventitious carbon to be sputtered away without damaging the underlying C_{60} chemistry

C_{60}

Reference C_{60} satellite structure

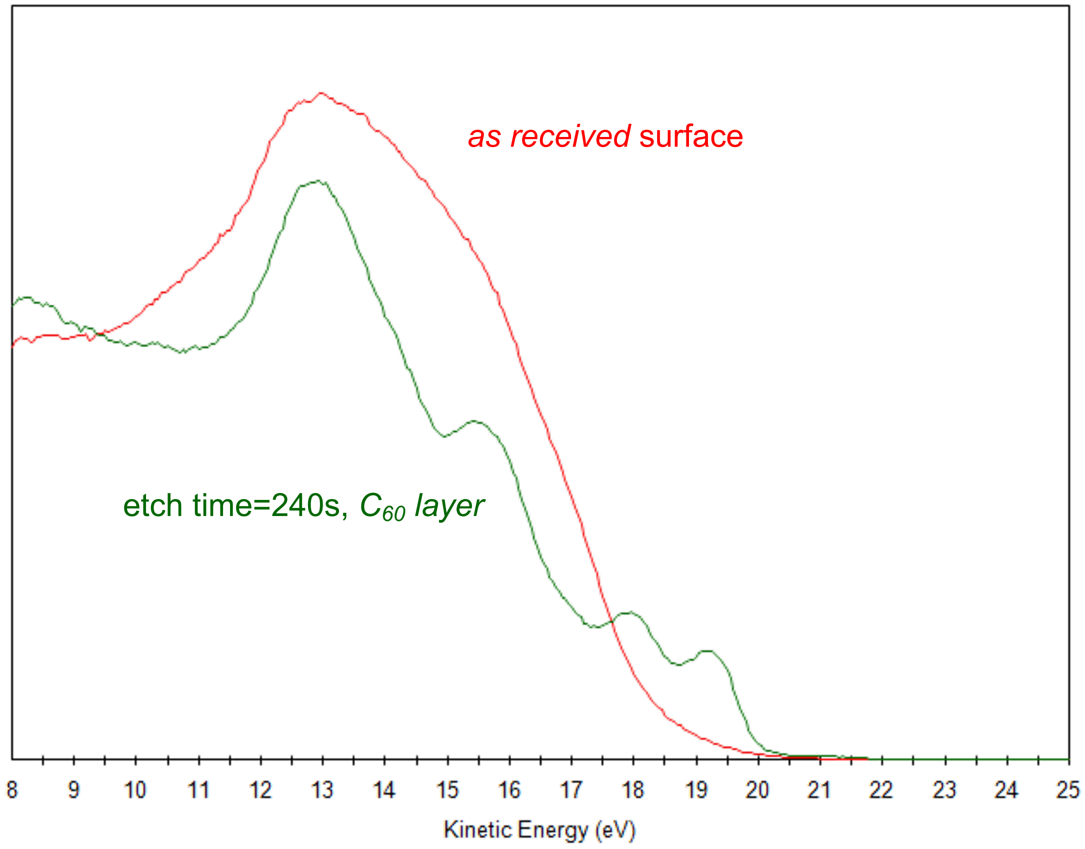


294 292 290 288 286 284 282 280

Binding Energy (eV)

Combined XPS/UPS depth profile of 10nm C_{60} film on CaF_2

He(I) UPS spectra from two different etch times during depth profile



- UPS spectra from the as received surface and C_{60} layer have different structure
  - amorphous carbon contamination
- After cleaning the surface with clusters, the contamination is removed
  - UPS layer confirms the C_{60} valence electronic structure is also preserved

Combined XPS/UPS depth profile of 10nm C_{60} film on CaF_2

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Carbon spectra at different depths

The satellite structure is NOT like that of C_{60}

294 292 290 288 286 284 282 280

Binding Energy (eV)

C1s spectrum (600s, as received surface)

The carbon chemistry completely changes when well into the CaF_2 substrate

C-C

CF_2

294 292 290 288 286 284 282 280

Binding Energy (eV)

C1s spectrum (960s etch time)

Combined XPS/UPS depth profile of 10nm C_{60} film on CaF_2

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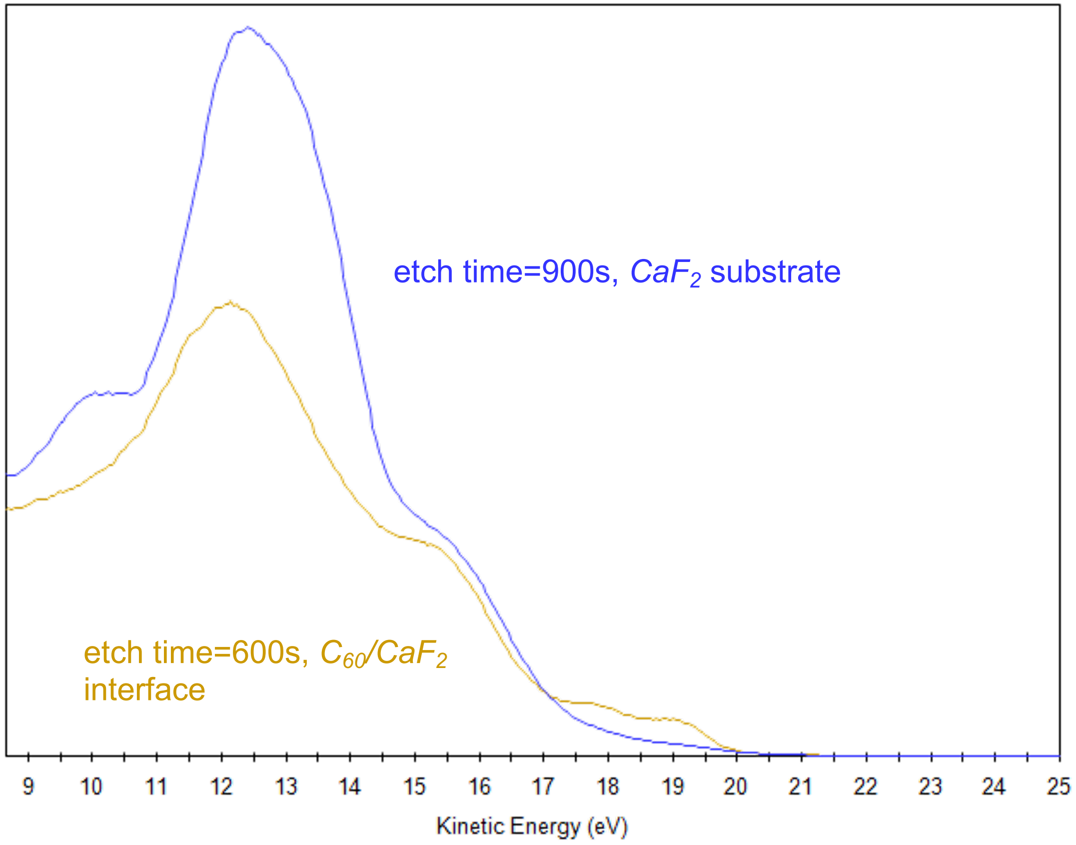
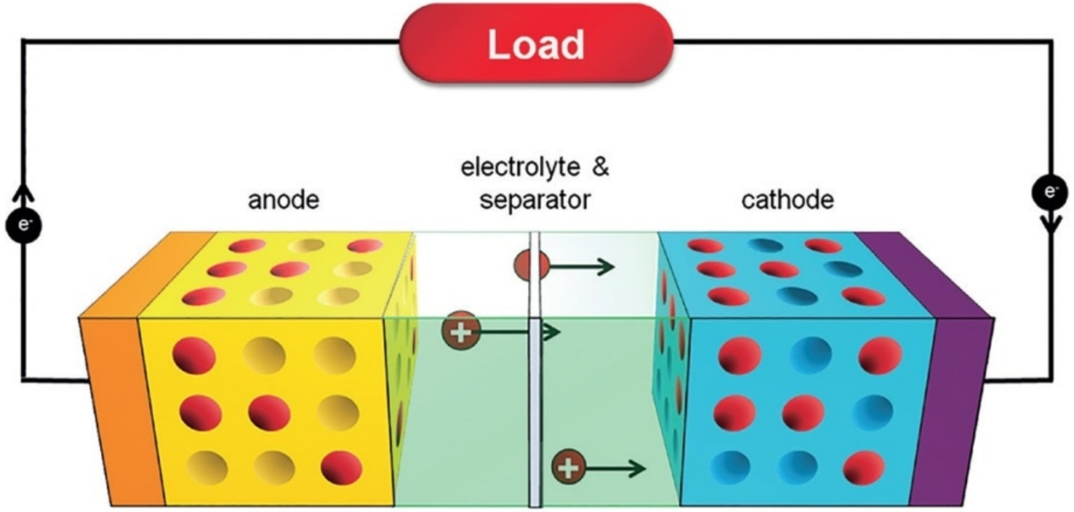


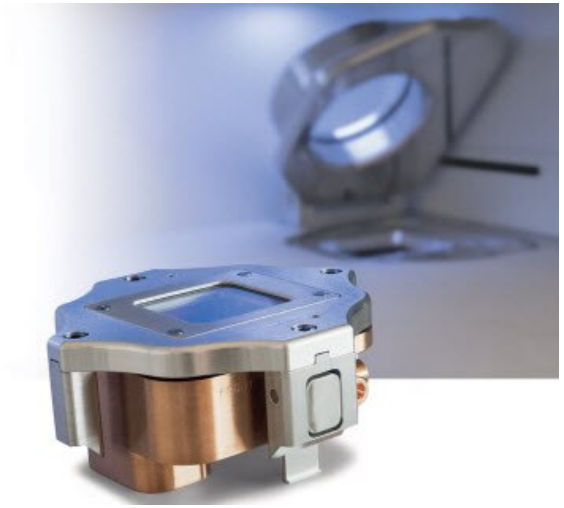
He(I) UPS spectra from two different etch times during depth profile

- XPS analysis at the C_{60}/CaF_2 interface indicates carbon is no longer present as C_{60}
- He(I) UPS analysis confirms that the valence electronic structure of the film is no longer like that of the C_{60} layer

Analysis of Electrode Materials for Lithium Ion Batteries

Li-ion cell in operation





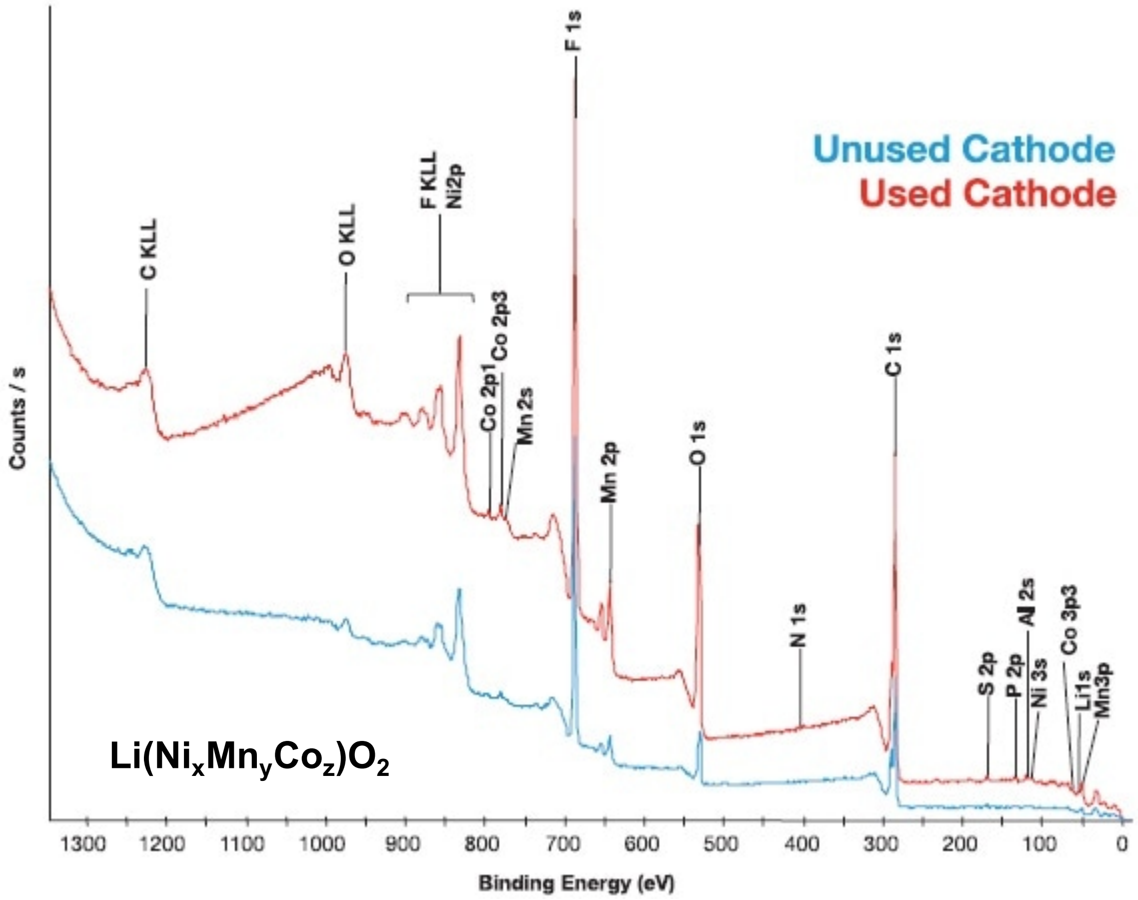
Vacuum Transfer Module (VTM)

- Solid-electrolyte interphase (SEI) – contributes to failure of the cell
- Lithium is very sensitive to air and moisture

Tim Nunney, AN52344, Thermo Fisher Scientific Inc.

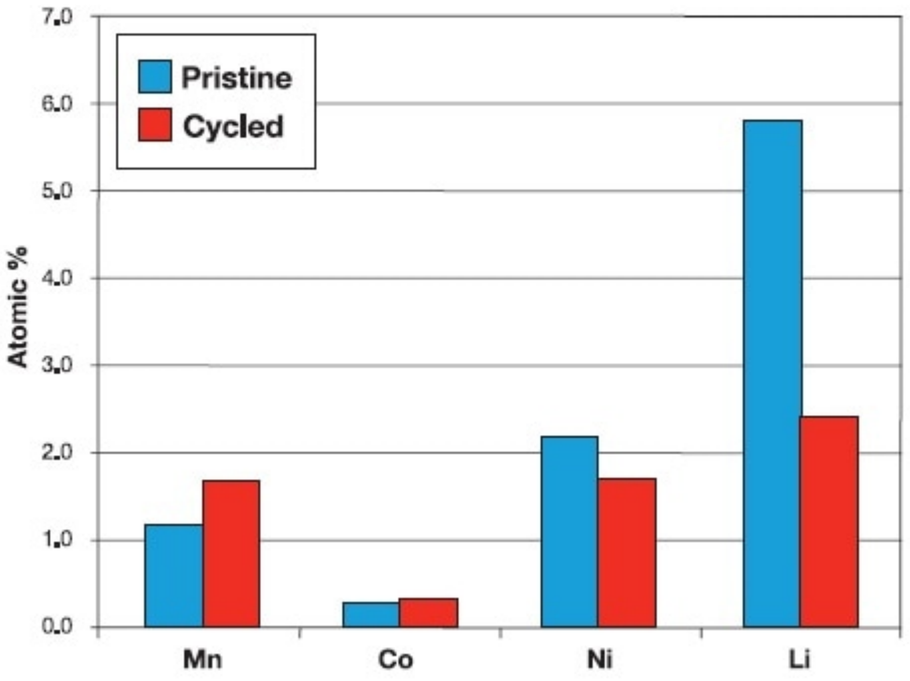
Analysis of Electrode Materials for Lithium Ion Batteries

Survey spectra from pristine cathode and cycled cathode samples



Analysis of Electrode Materials for Lithium Ion Batteries

Composition variation for the NMC components



Pricing for Surface Chemical Characterization

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Surface Analysis Capabilities				
Technique	**Information Provided**	**Info Depth, LOD**	**Make/Model**	**Pricing**
XPS	quantitative elemental and chemical state, depth profile, film thickness, mapping	2-10nm, 0.1-1%	*Thermo Scientific Nexsa* *Phi Quantera* *Thermo Scientific ESCALAB 250* *PHI VersaProbe III*	*$730/sple (hi-res)*
UPS	valence band, work function	1-3nm	*Thermo Scientific Nexsa*	*$548/sple (valence band)*
ISS	elemental	monolayer, >0.1 at% for heavy elements and >10 at% for light elements.	*Thermo Scientific Nexsa*	*$548/sple*
Auger	quantitative elemental and chemical state, depth profile, mapping	2-8nm, 0.1-1%	*Perkin Elmer Model 600* *PHI 710 Scanning Auger Nanoprobe*	*$335/hr* *$650/hr (high-end)*
TOFSIMS	elemental and chemical state, molecular information, depth profile, mapping	1-5nm, ppm-ppb	*IONTOF Model IV* *PHI NanoTOF II*	*$800/hr*

Summary

- XPS, ISS and UPS – complimentary surface chemical analysis
  - XPS – elemental and chemical composition, ~3-10nm region
  - ISS – elemental composition, topmost layer
  - UPS – valence band, topmost layer

- The Nexsa XPS system
  - XPS, ISS, UPS
  - MAGCIS dual mode ion source
  - Vacuum Transfer Module

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SOLID SURFACE ZETA POTENTIAL: INDUSTRIAL APPLICATIONS, CHALLENGES, AND SOLUTIONS

GUEST SPEAKER:

Dr. Christine Körner
Product Specialist,
Materials Characterization

June 25, 2020 11am PDT

COVALENT METROLOGY

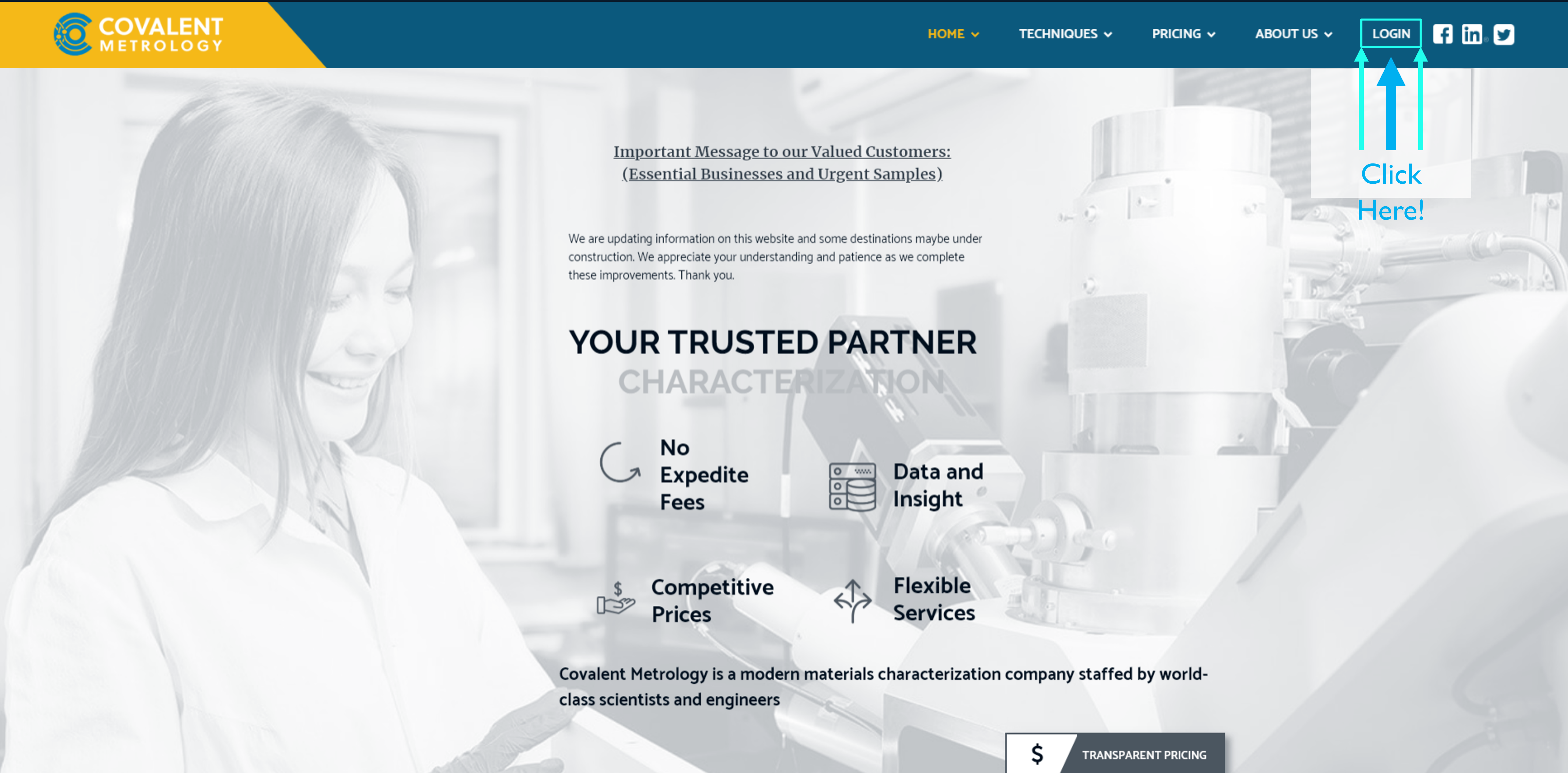
Anton Paar

COVALENT ACADEMY

Advancements in Instrumentation Series

RSVP at:
https://bit.ly/covalent11

Covalent Community



Covalent Community

Data Portal

Customer Access to Data & Community Content

The DATA PORTAL is used by Customers and Lab Partners for uploading and downloading data. It requires two-factor authentication and advanced password protection. Data Portal users have complete access through their home page on the portal to all Community content, and do not require a separate Community account.

Covalent Community

All Other Users

The COVALENT COMMUNITY PORTAL requires password entry. It contains webinar and other metrology and characterization-related content that we believe would be useful and educational for the materials science innovation community. It does not provide access to any customer data and should only be used by individuals that are not Covalent customers or lab partners.

Thank You

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