

# X-ray Photoelectron Spectroscopy (XPS)

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URBANA-CHAMPAIGN

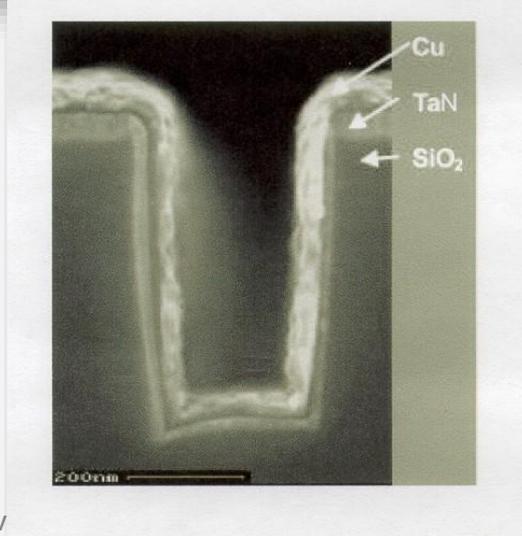
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**I** ILLINOIS

Materials Research Laboratory

GRAINGER COLLEGE OF ENGINEERING

# Surfaces and Interfaces





CHAMPAIGN-URBANA MASS TRANSIT DISTRICT

HYDROGEN FUEL CELL ELECTRIC

ZERO EMISSION

2102 MTD

TRANSFORM TO THRIVE

2102

22N ILLINI

2102

FLUTTERY FABULOUS

H2 ZERO EMISSION

CH2



*“God made the bulk; the surface was invented by  
the devil.”*

— Wolfgang Pauli

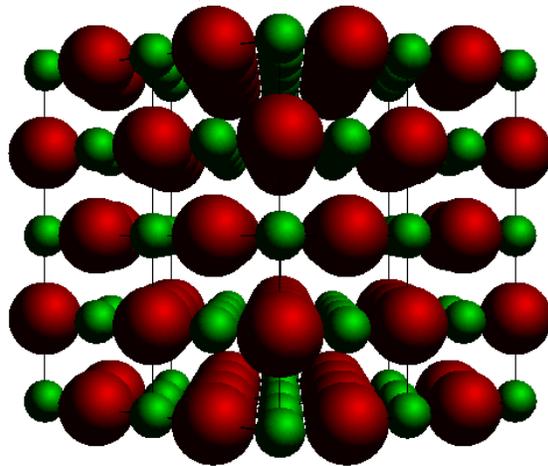
# Particle Surface Interactions

Primary beam  
(source)

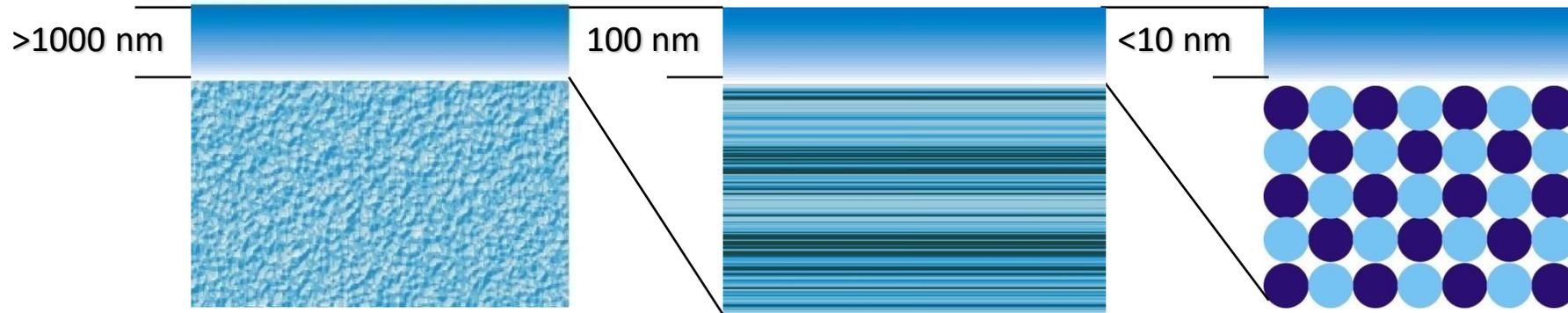
Ions  
Electrons  
Photons

Secondary beam  
(spectrometers, detectors)

Ions  
Electrons  
Photons



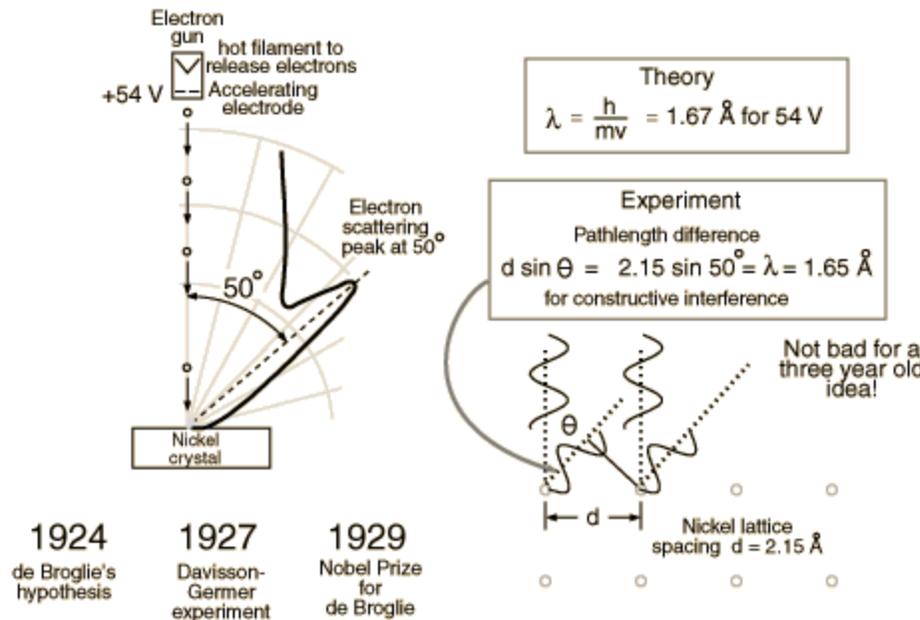
# What is the Surface?



Bulk Analysis

Thin-film Analysis

Surface Analysis



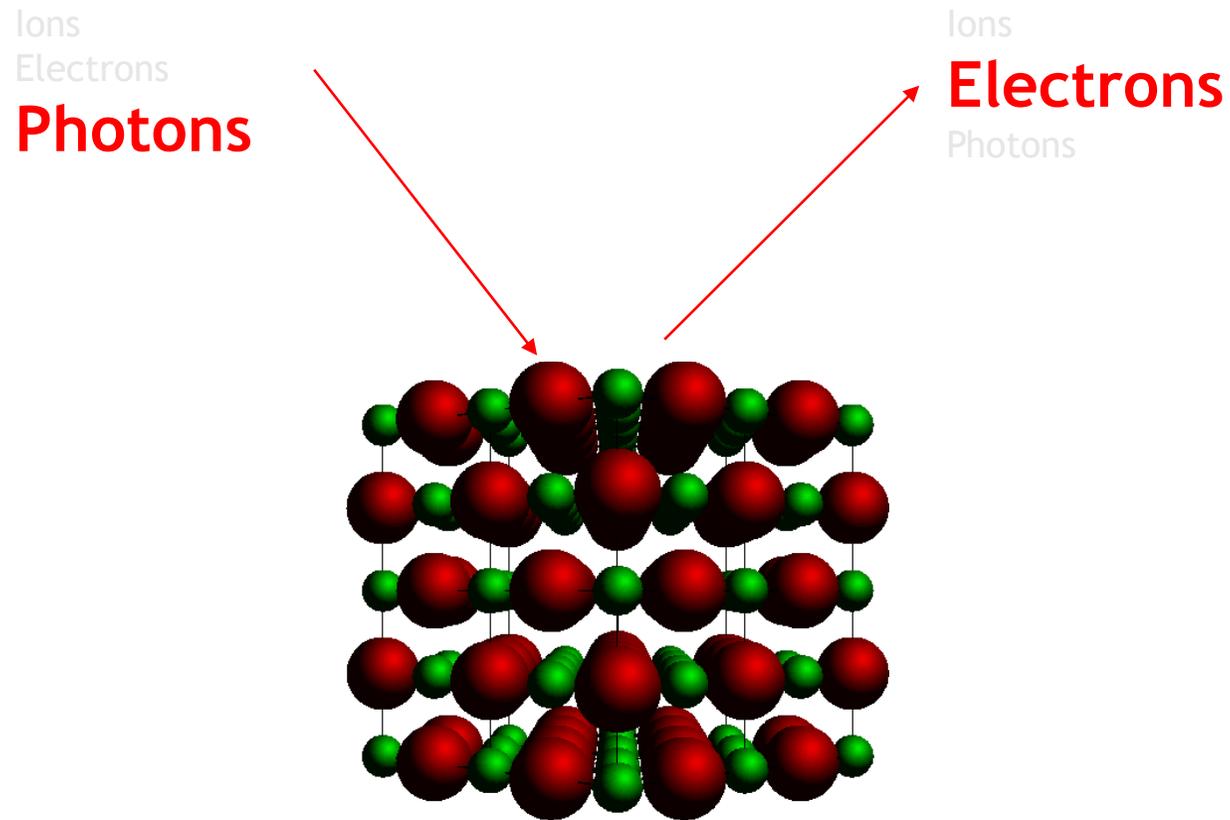
*For an electron* with KE = 1 eV and rest mass energy of 0.511 MeV, the de Broglie wavelength is **1.23 nm** (~1000X less than a 1 eV photon).

<http://hyperphysics.phy-astr.gsu.edu/hbase/davger.html#c1>



# Particle Surface Interactions

## Photoelectron Spectroscopy



Vacuum

# X-ray Photoelectron Spectroscopy (XPS)

**X-ray Photoelectron Spectroscopy (XPS)**, also known as **Electron Spectroscopy for Chemical Analysis (ESCA)** is a widely used technique to investigate the chemical composition of surfaces.

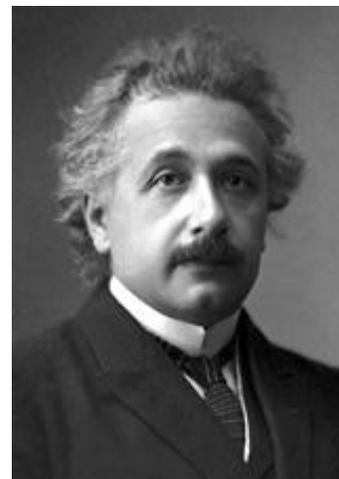
X-ray<sup>1</sup> Photoelectron spectroscopy, based on the photoelectric effect,<sup>2,3</sup> was developed in the mid-1960's as a practical technique by **Kai Siegbahn** and his research group at the University of Uppsala, Sweden.<sup>4</sup>



Wilhelm Conrad Röntgen



Heinrich Rudolf Hertz



Albert Einstein



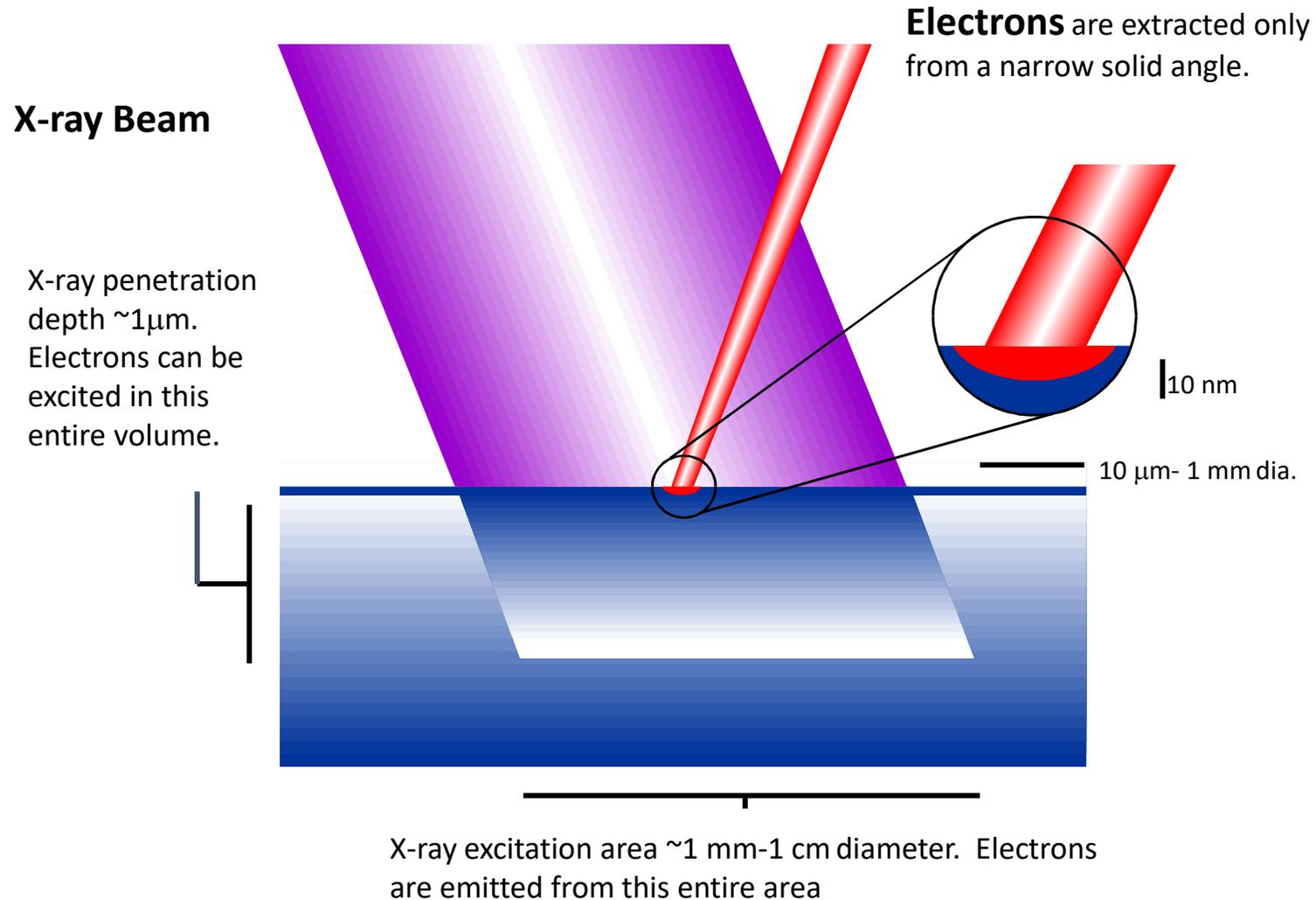
Kai M. Siegbahn



1. W. Röntgen, 1901 Nobel Prize in Physics "in recognition of the extraordinary services he has rendered by the discovery of the remarkable rays subsequently named after him."
2. H. Hertz, "Über einen Einfluss des ultravioletten Lichtes auf die elektrische Entladung," *Ann. Physik* **31**,983 (1887). The IEEE Heinrich Hertz Medal was established by the Board of Directors in 1987 "for outstanding achievements in Hertzian (radio) waves."
3. A. Einstein, "Über einen die Erzeugung und Verwandlung des Lichtes betreffenden heuristischen Gesichtspunkt," *Ann. Physik* **17**,132 (1905). 1921 Nobel Prize in Physics "for his services to Theoretical Physics, and especially for his discovery of the law of the photoelectric effect."
4. K. Siegbahn, *Et. Al., Nova Acta Regiae Soc.Sci.*, Ser. IV, Vol. 20 (1967). 1981 Nobel Prize in Physics "for his contribution to the development of high resolution electron spectroscopy."

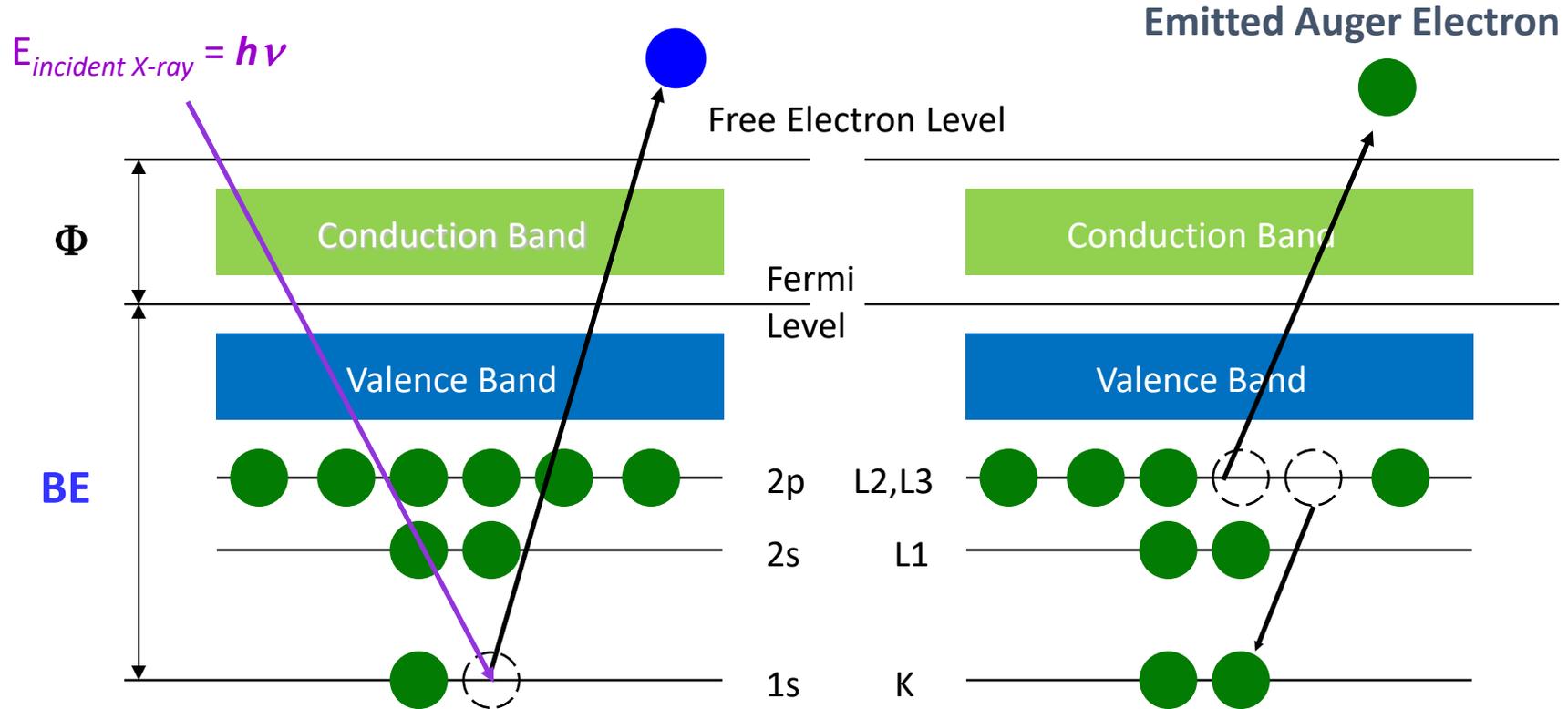


# X-ray Photoelectron Spectroscopy Small Area Detection



# Photoelectron and Auger Electron Emission

$$KE \text{ (measured)} = h\nu \text{ (known)} - BE - \Phi_{\text{spec}} \text{ (calibrated)}$$



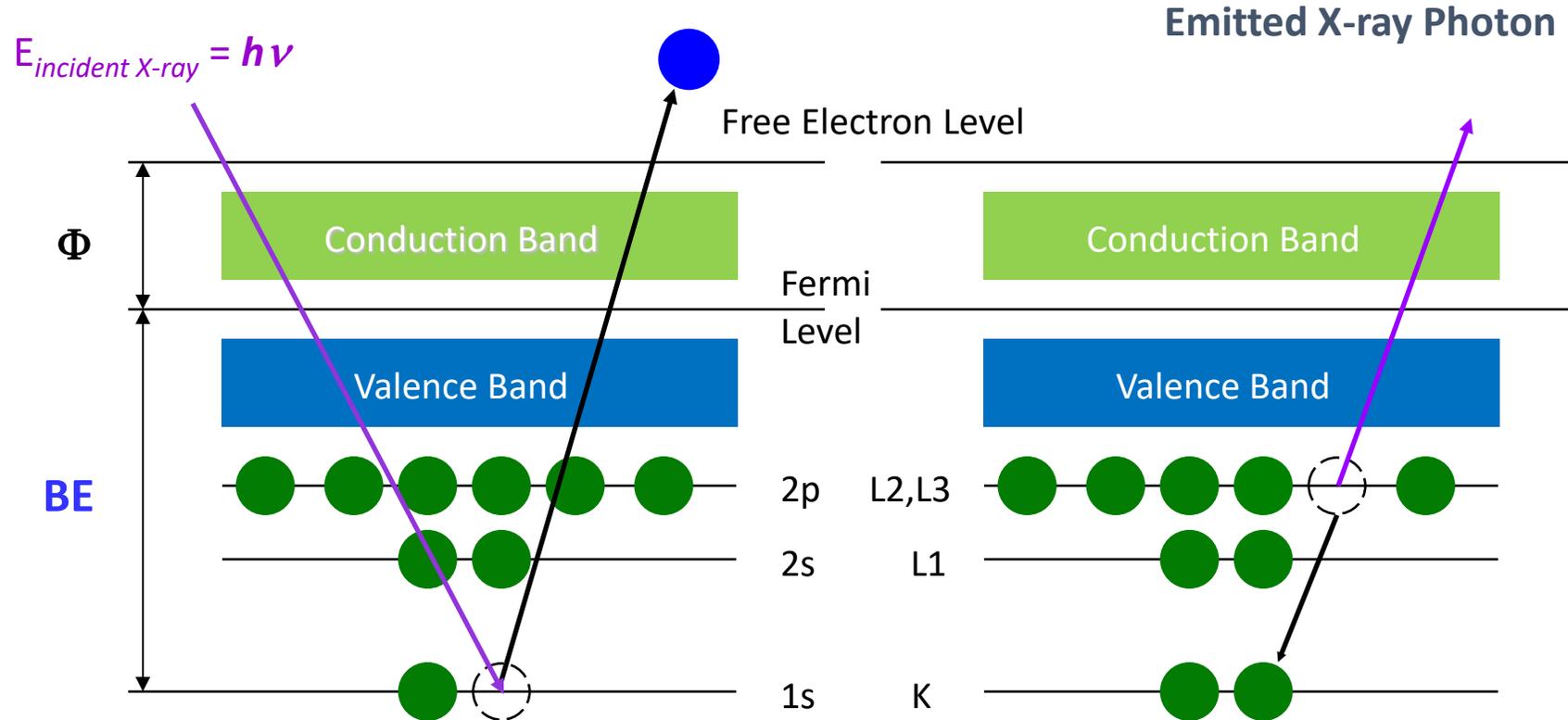
$$\text{Calculate: } BE = h\nu - KE - \Phi_{\text{spec}}$$

**BE – binding energy** depends on Z, i.e. characteristic for the element



# Photoelectron and Auger Electron Emission

$$KE \text{ (measured)} = h\nu \text{ (known)} - BE - \Phi_{\text{spec}} \text{ (calibrated)}$$



Calculate:  $BE = h\nu - KE - \Phi_{\text{spec}}$

**BE – binding energy** depends on Z, i.e. characteristic for the element



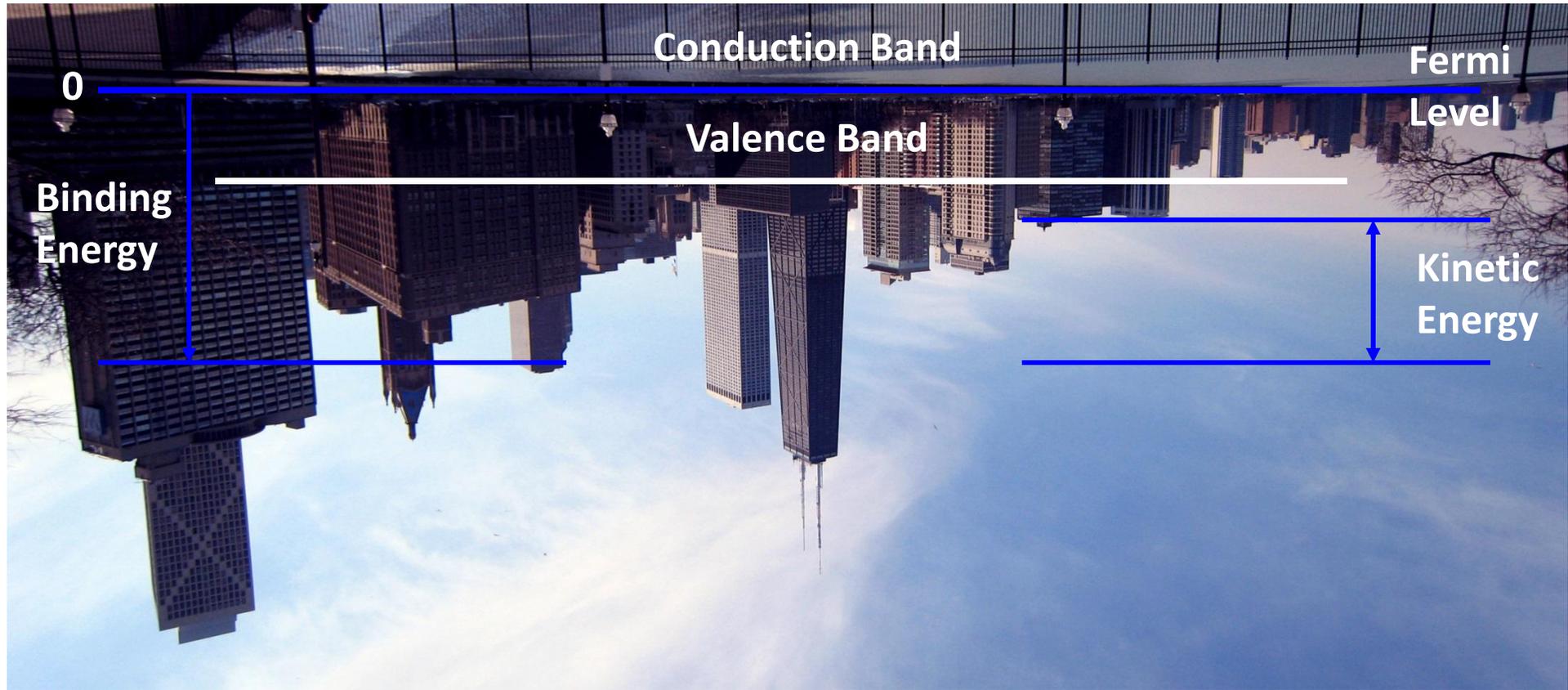
# Photoelectron and Auger Electron Emission



# Photoelectron and Auger Electron Emission



# Photoelectron and Auger Electron Emission



**Photoelectron Lines**

**Auger Electron Lines**



# Photoelectron and Auger Electron Emission

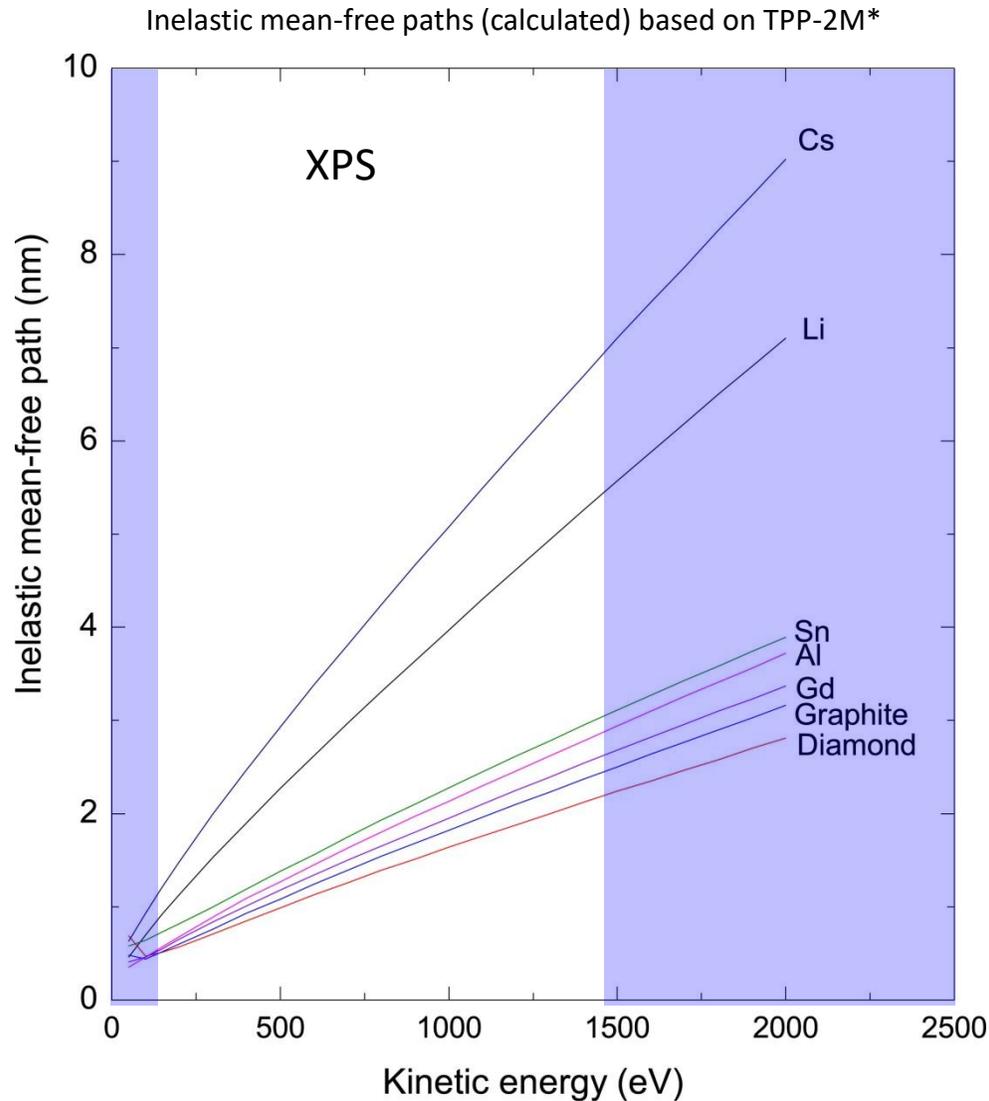


**XPS can probe all of the orbitals in only the light elements.**  
***e.g.* BE C 1s = 285 eV, Mg 1s = 1304 eV, Au 1s  $\approx$  81000 eV**



# Surface Sensitivity: Electron Spectroscopy

**Inelastic Mean-Free Path:** The mean distance an electron can travel between inelastic scattering events.



**Electrons travel only a few nanometers through solids.**

\*S. Tanuma, C. J. Powell, D. R. Penn, *Surface and Interface Analysis*, **36**, 1 (2004).



# Surface Sensitivity: Electron Spectroscopy

## Assuming Inelastic Scattering Only

### Beer-Lambert relationship:

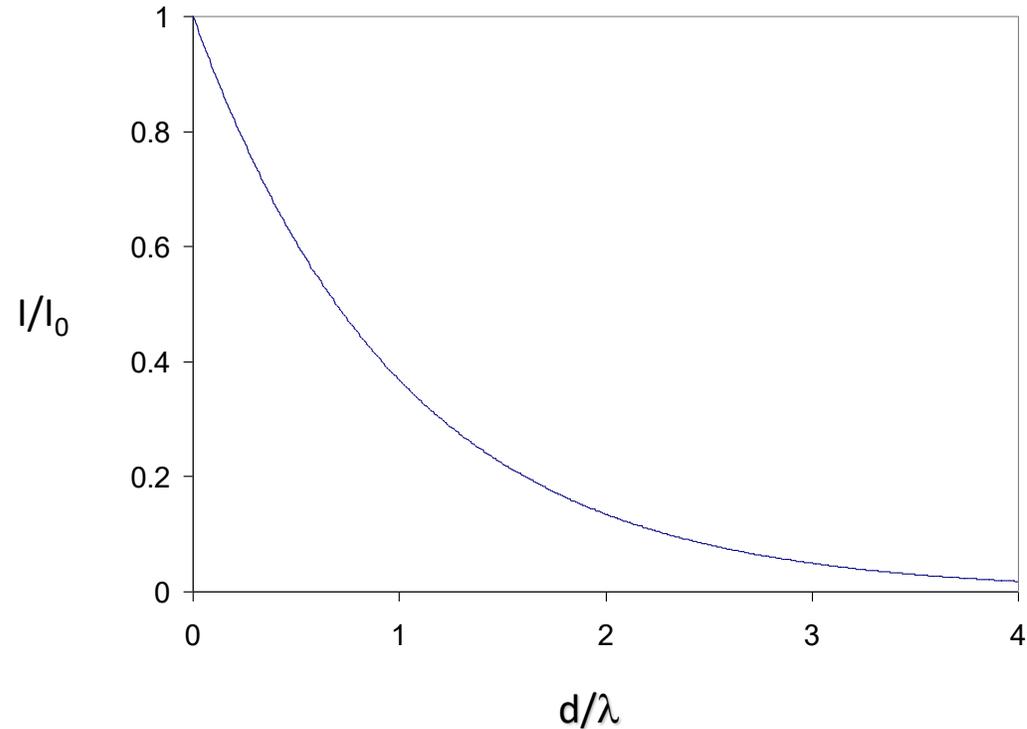
$$I = I_0 \exp(-d/\lambda \cos\theta)$$

where  $d$  = depth

$\lambda$  = Inelastic mean free path

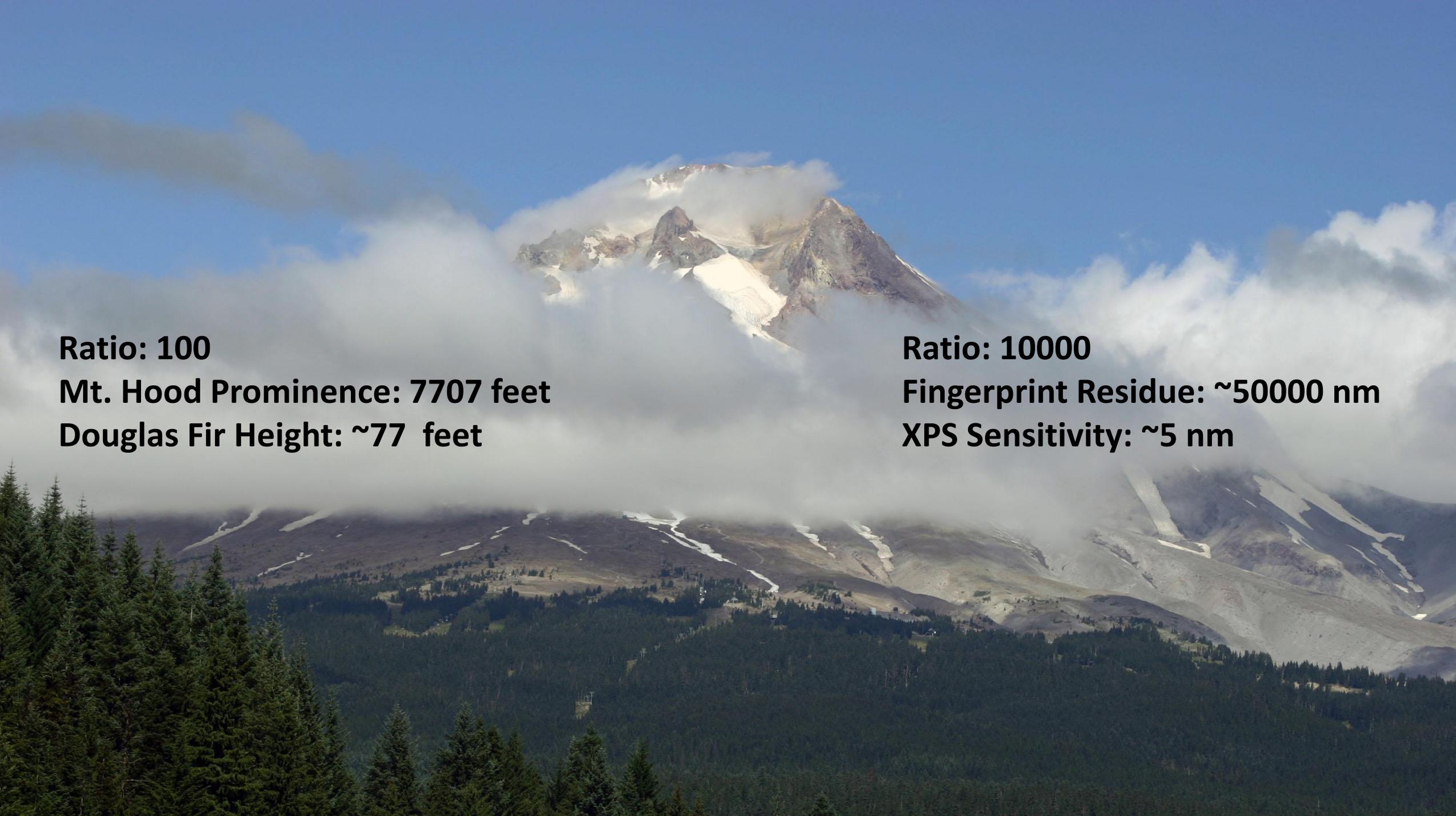
$$\text{at } 3\lambda, I/I_0 = 0.05$$

$$\text{at } 1000 \text{ eV, } \lambda \approx 1.6 \text{ nm}$$



**95% of the signal comes from within 5 nm of the surface or less!**





**Ratio: 100**

**Mt. Hood Prominence: 7707 feet**

**Douglas Fir Height: ~77 feet**

**Ratio: 10000**

**Fingerprint Residue: ~50000 nm**

**XPS Sensitivity: ~5 nm**

# Surface Sensitivity: Electron Spectroscopy

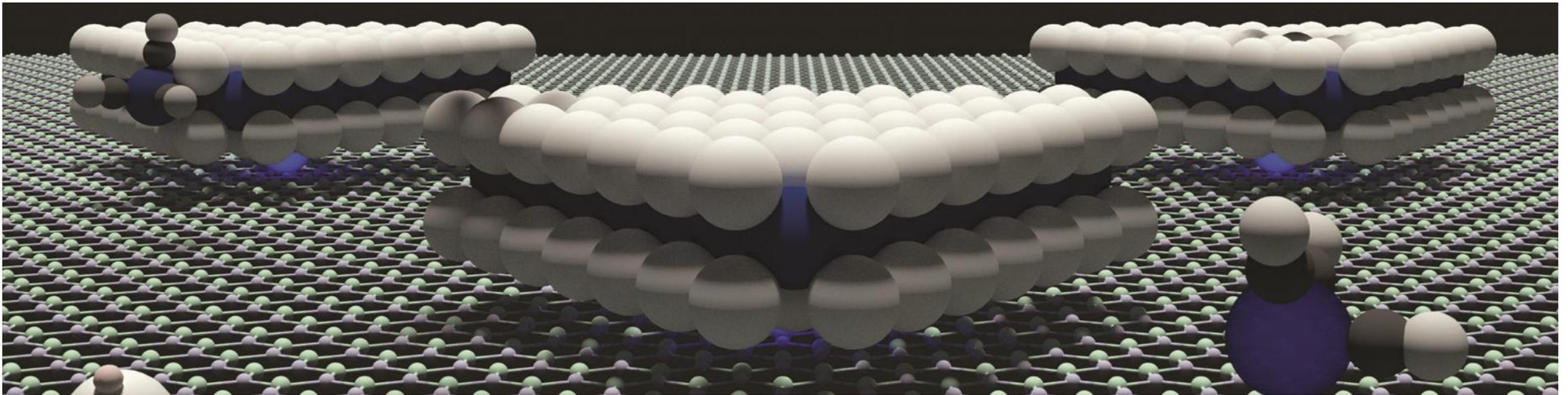
## X-ray Photoelectron Spectroscopy

### Advantage

Extremely surface sensitive!

### Disadvantage

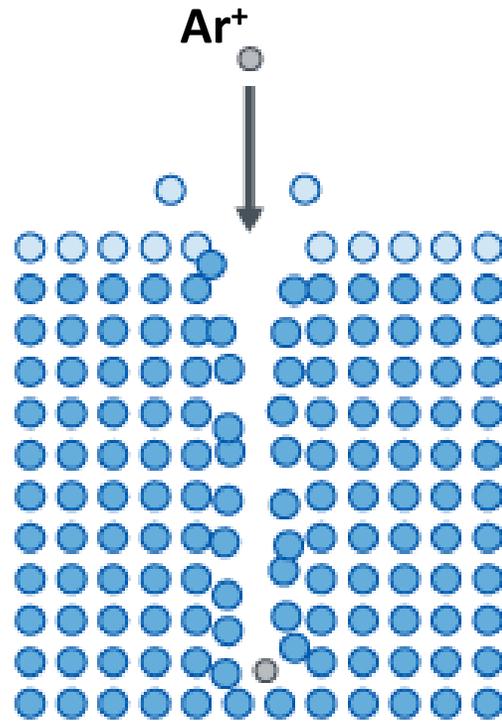
Extremely surface sensitive!



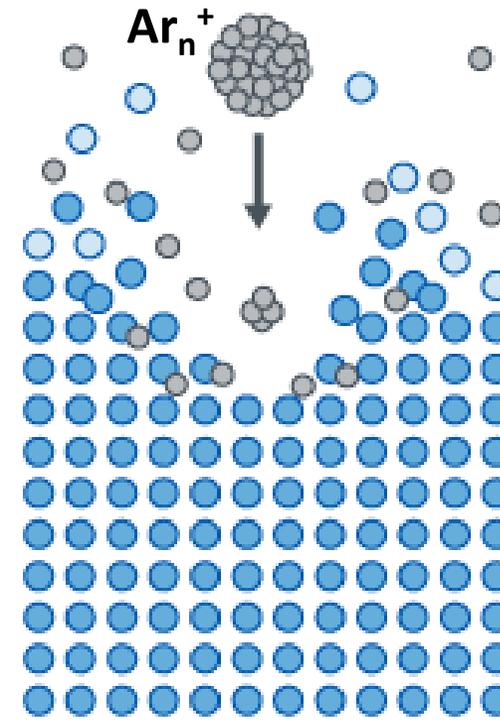
<https://phys.org/news/2019-05-substrate-defects-key-growth-d.html>

# Ion Sputtering

## Single atomic ion beam



## Cluster ion beam

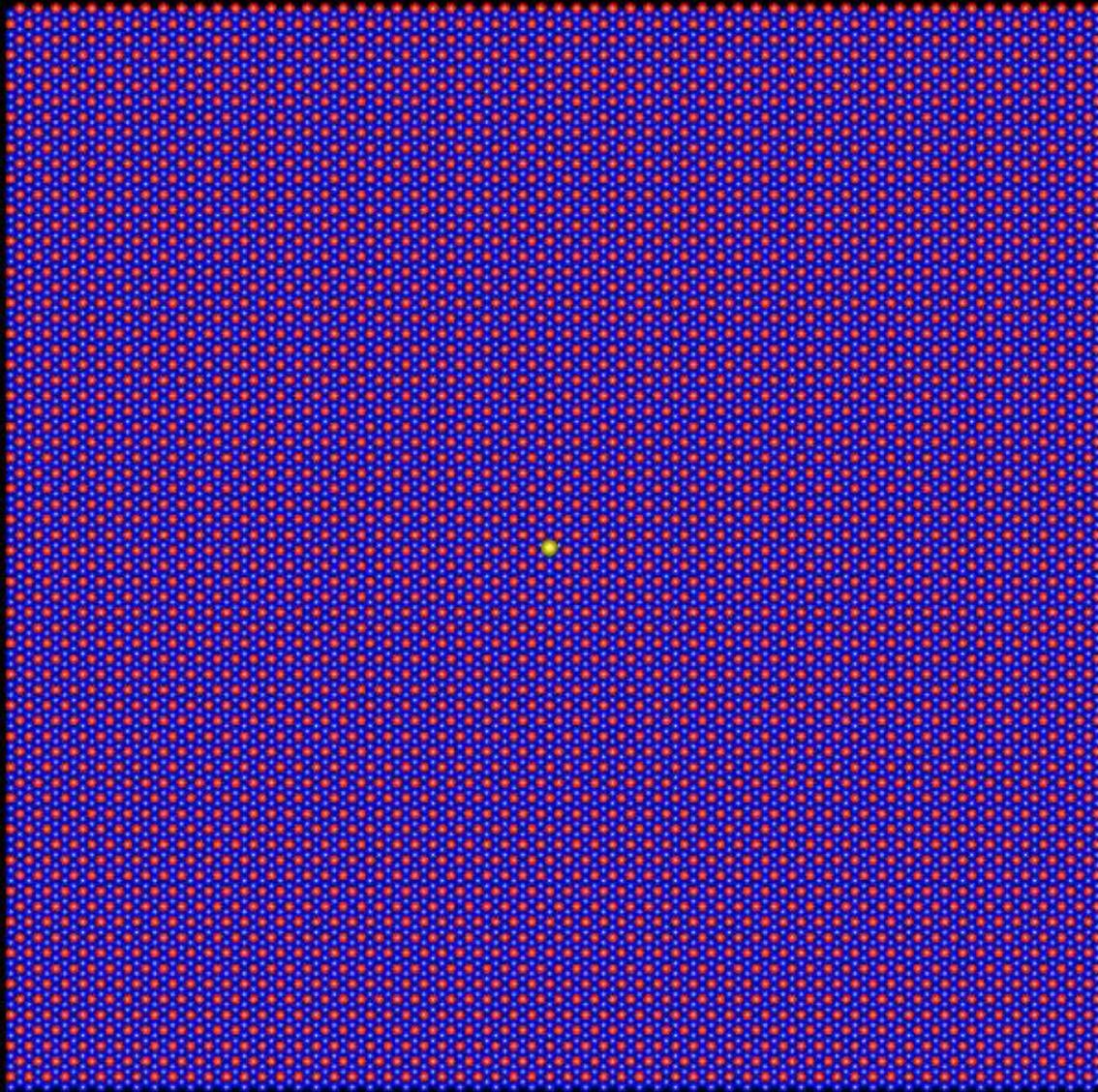


- Ions striking a surface interact with atoms in a series collisions.
- recoiled target atoms in turn collide with atom at rest generating a collision cascade.
- The initial ion energy and momentum are distributed among the target recoil atoms.
- When  $E_i > 1$  keV, the cascade is “linear,” *i.e.* approximated by a series of binary collisions in a stationary matrix.

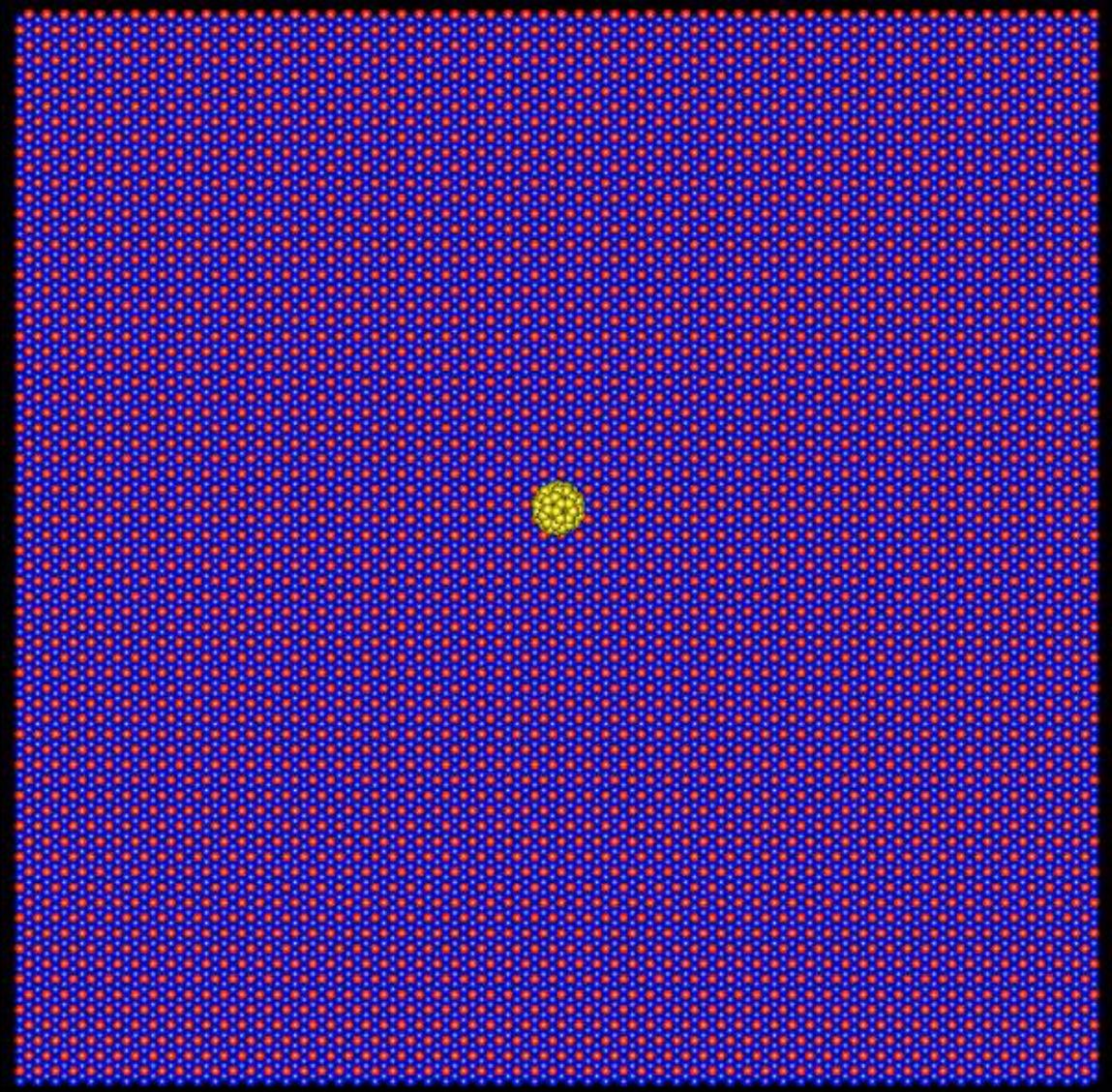


P. Sigmund, “Sputtering by ion bombardment: theoretical concepts,” in *Sputtering by particle bombardment I*, edited by R. Behrish, Springer-Verlag, 1981.  
Image credit: <https://ulvac-phi.com/>

15 KeV Ga<sup>+</sup>



15 KeV C<sub>60</sub><sup>+</sup>





# X-ray Photoelectron Spectrometer



- 1 Spherical mirror analyser
- 2 Hemispherical analyser
- 3 Delay-line detector
- 4 Electrostatic lens
- 5 Selected area aperture drive
- 6 Octopole scan plates
- 7 Variable iris drive
- 8 Charge neutraliser
- 9 Magnetic lens

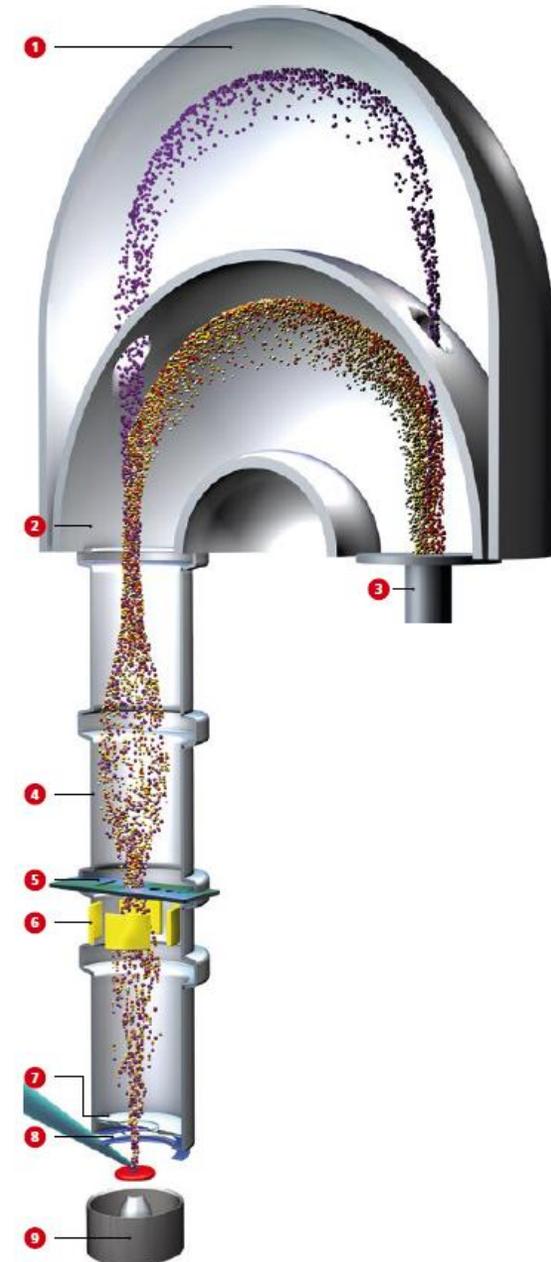
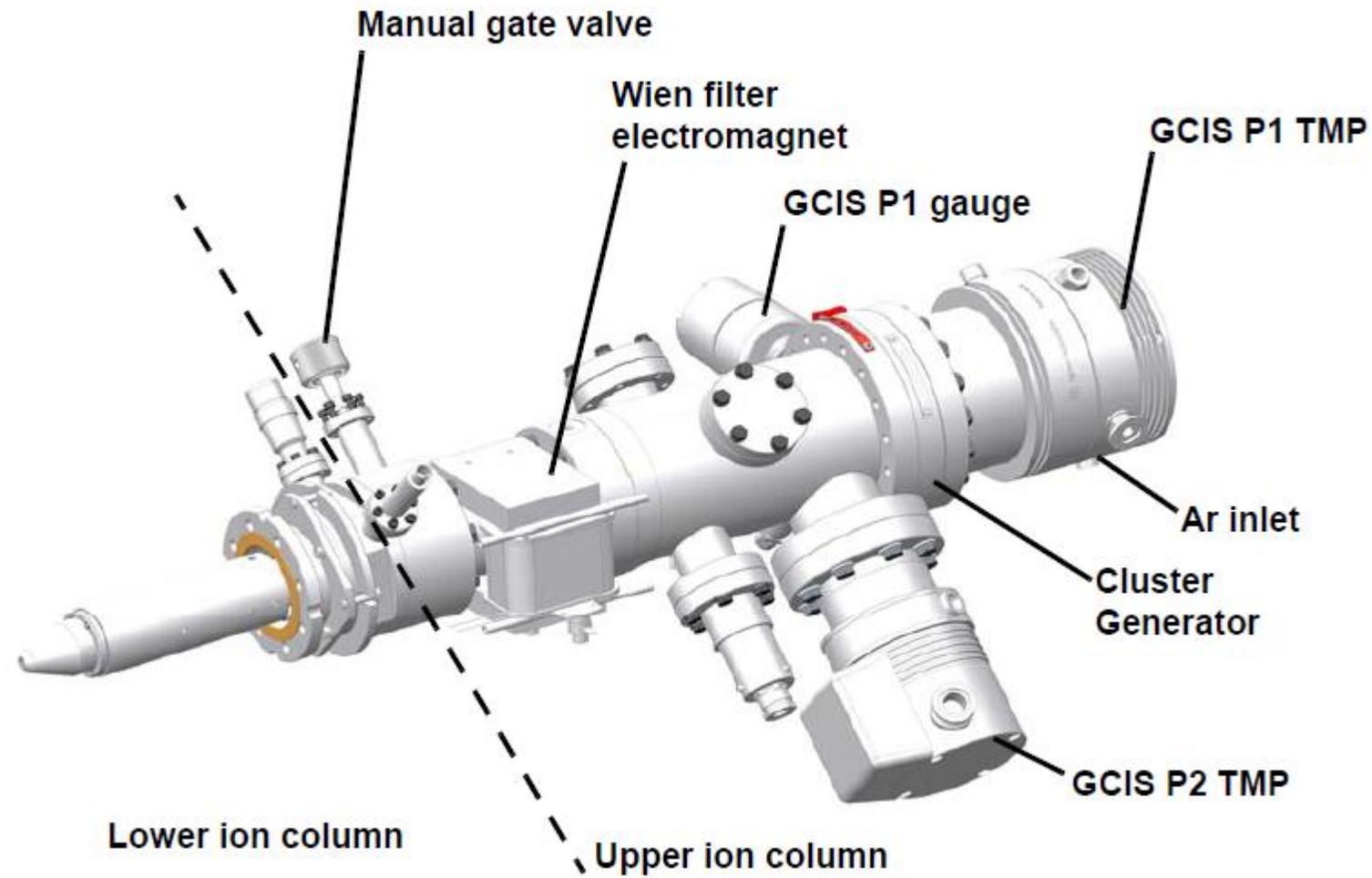


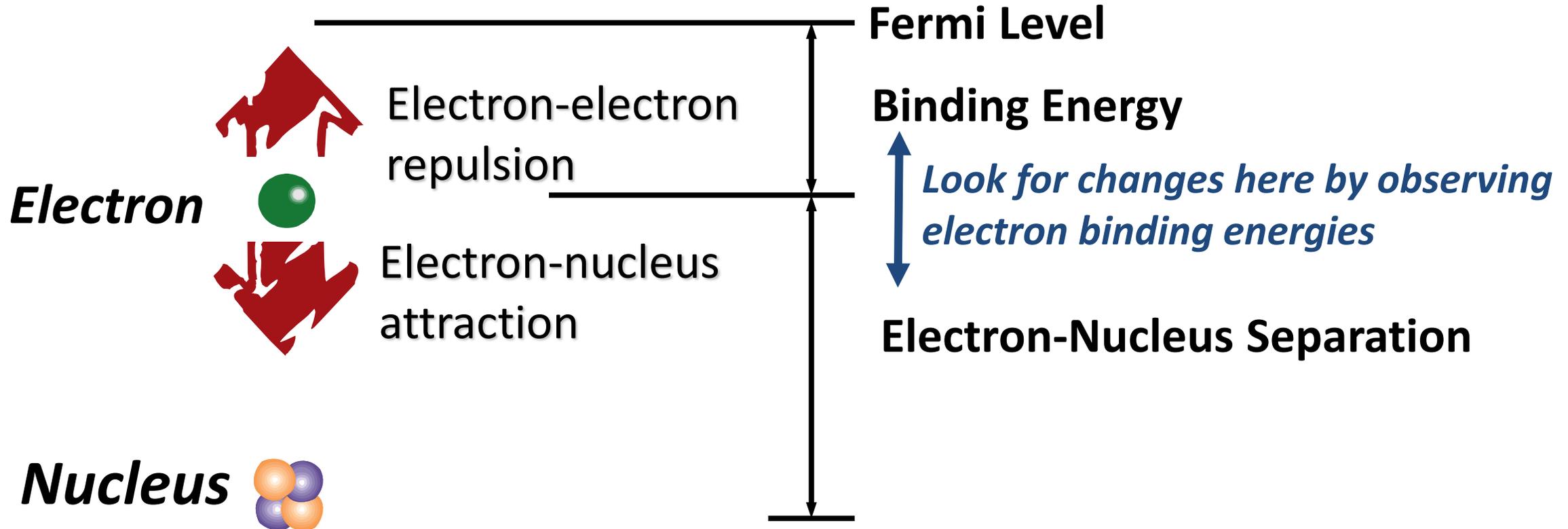
Image credit: <https://www.kratos.com/>

# Gas-cluster Ion Source (GCIS)

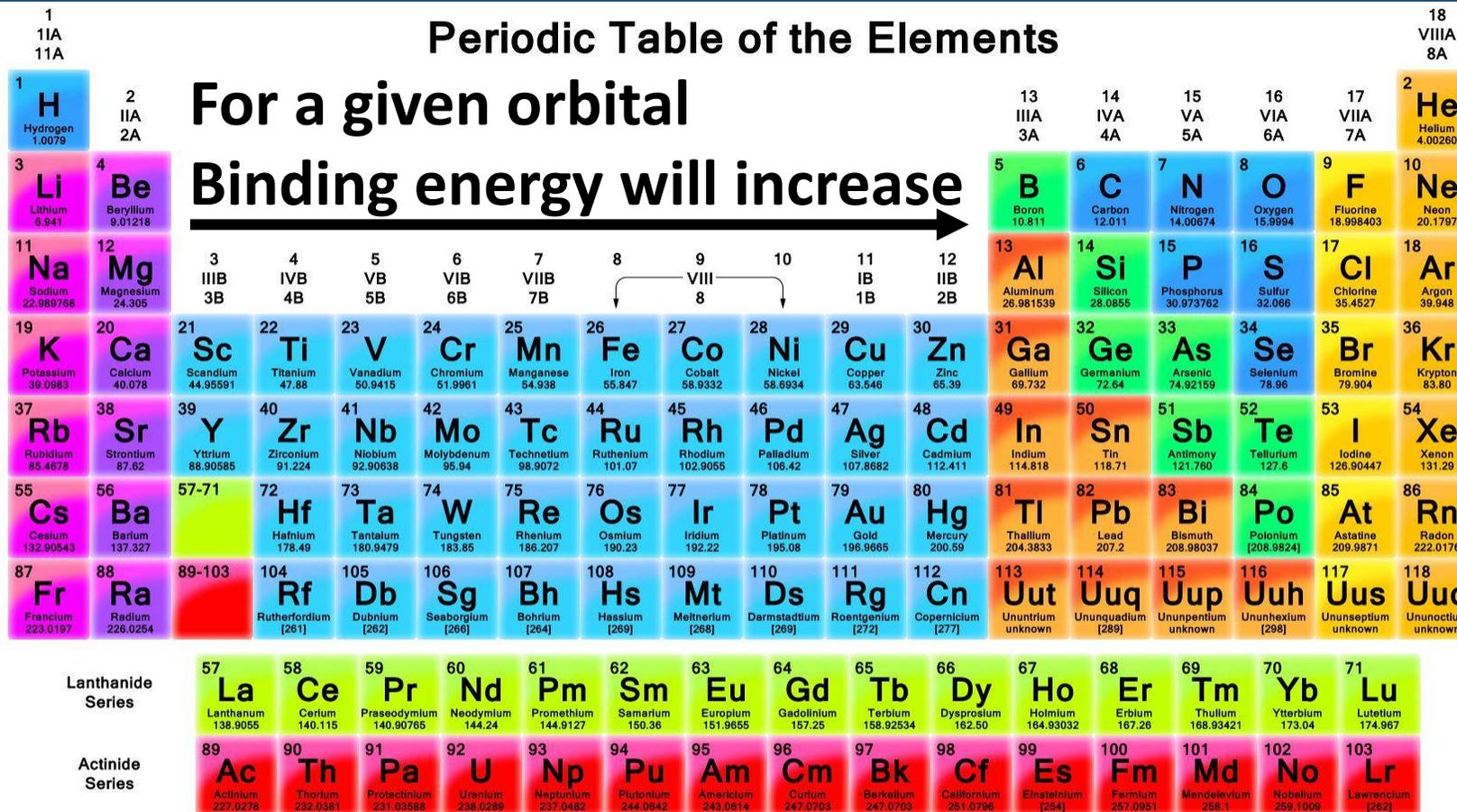


# Elemental Shifts

## Pure Element



# Elemental Shifts

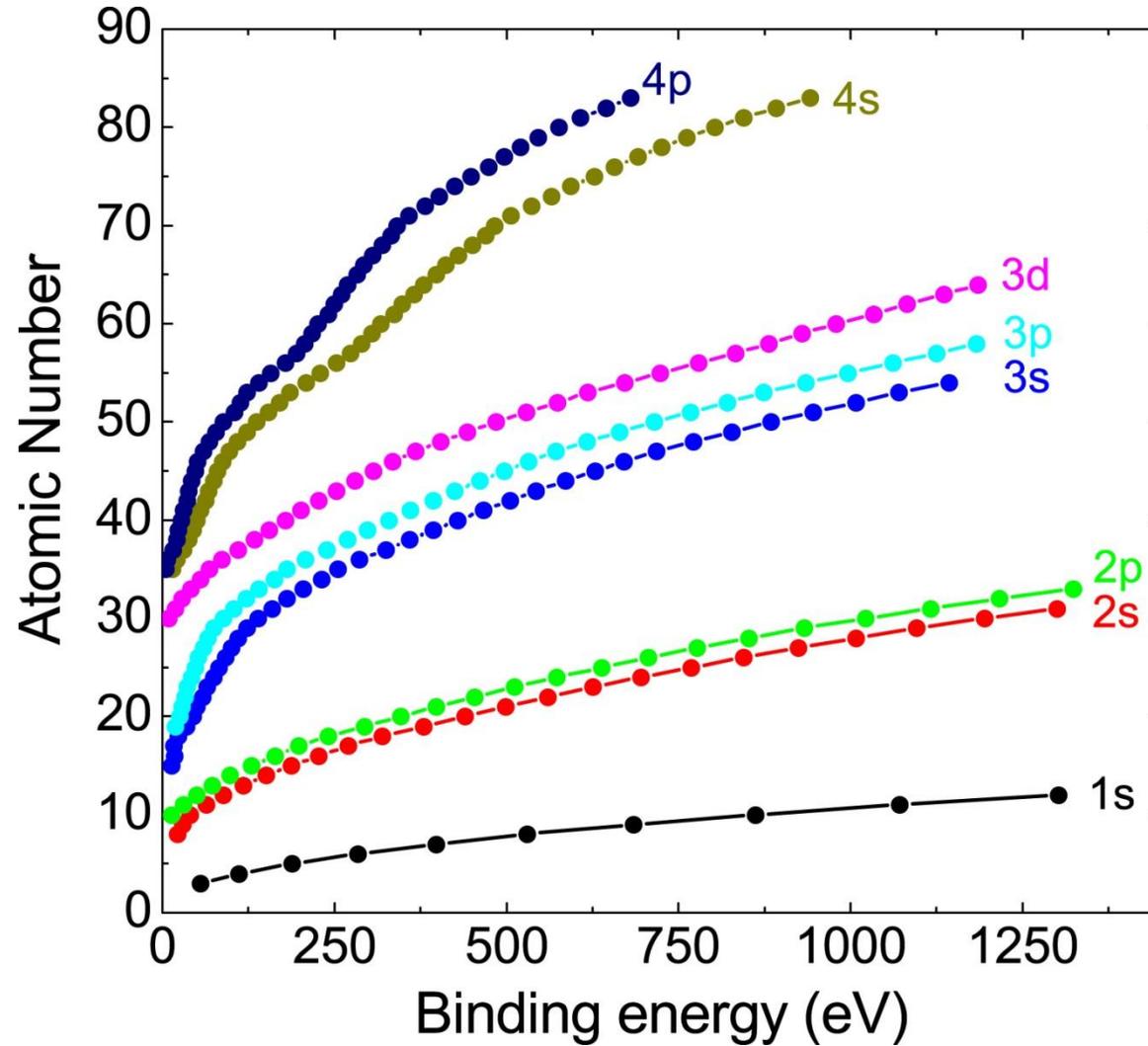


©okiraa.com

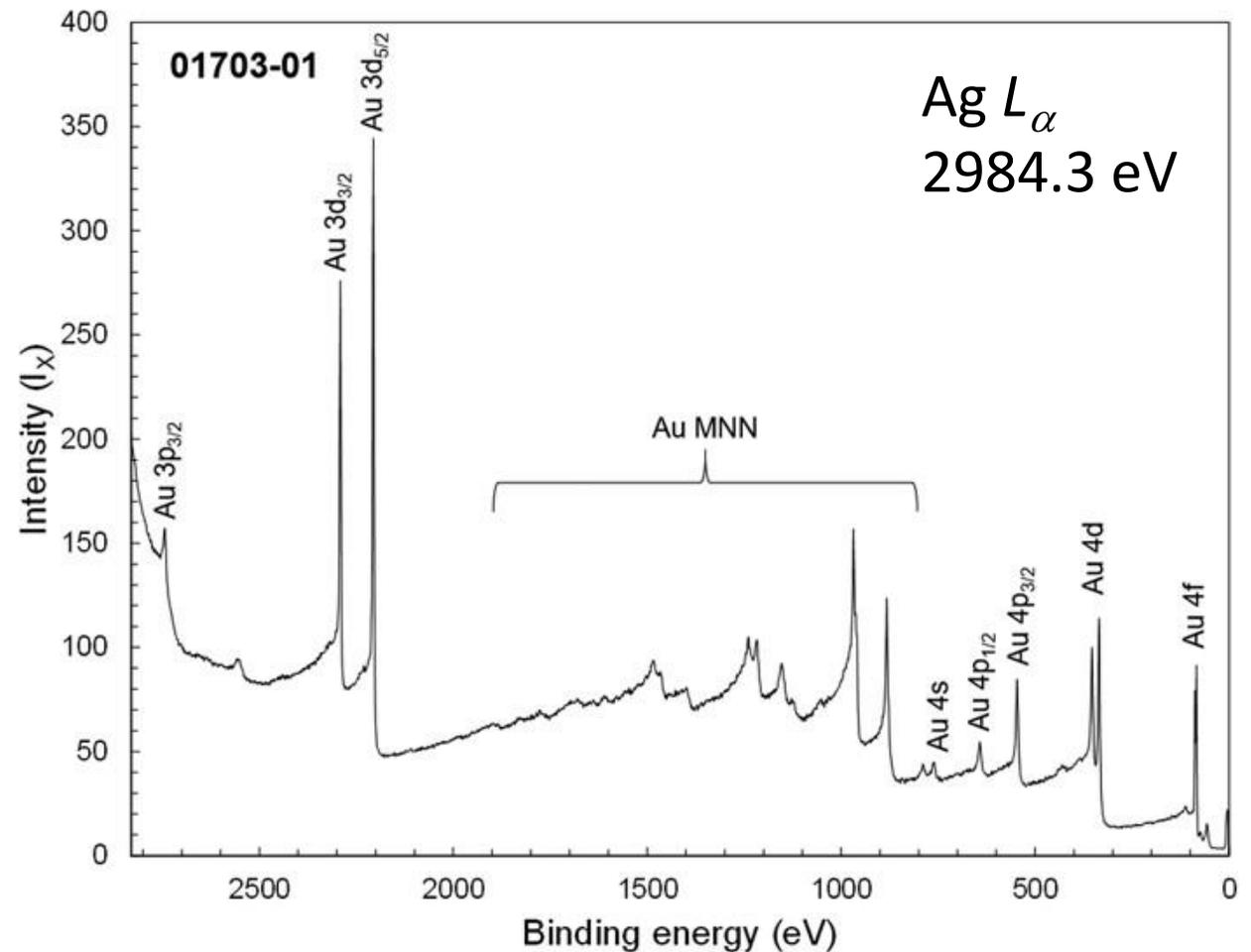
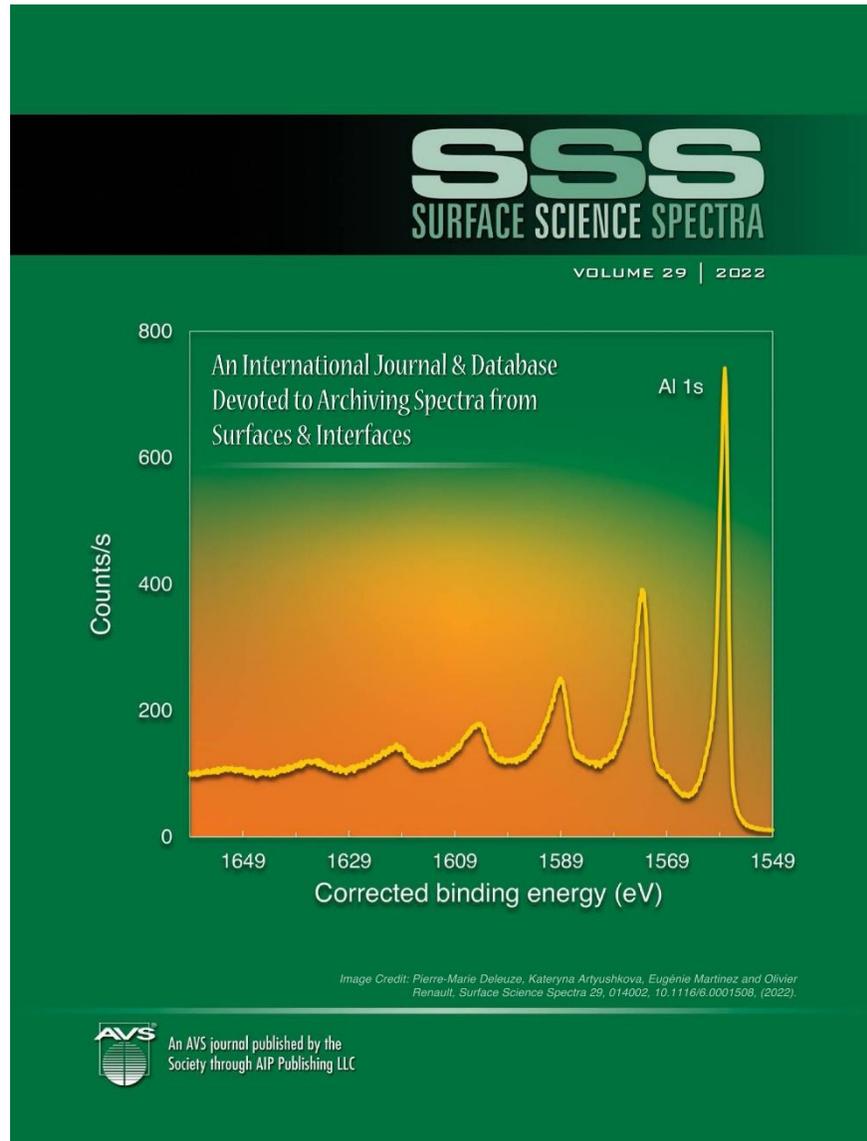


# Elemental Shifts

## Core Level Binding Energies



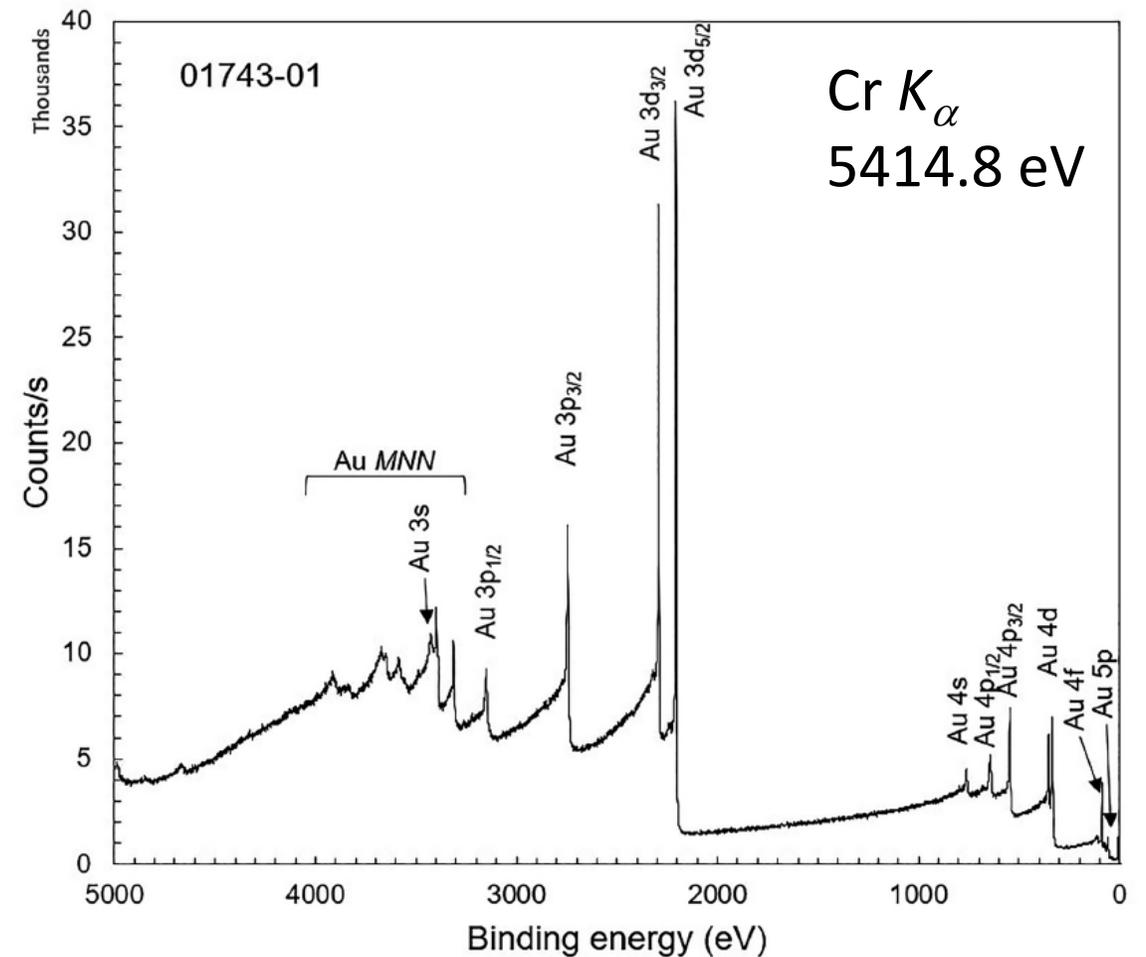
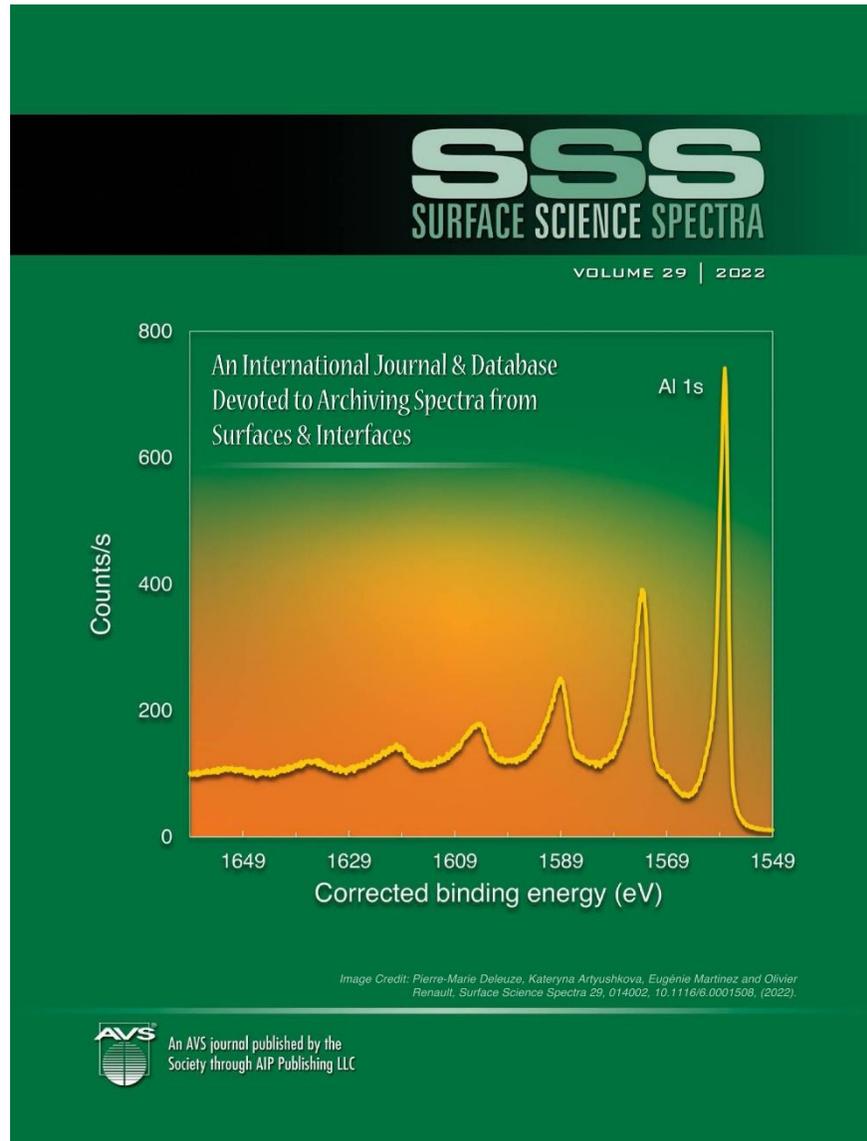
# Elemental Shifts – Higher Energy X-ray Sources



Jonathan D. P. Counsell; Alex G. Shard; David J. Cant; Christopher J. Blomfield; Parnia Navabpour; Xiaoling Zhang; *Surface Science Spectra* **28**, 024005 (2021). DOI: 10.1116/6.0001389  
Copyright © 2021 Author(s)



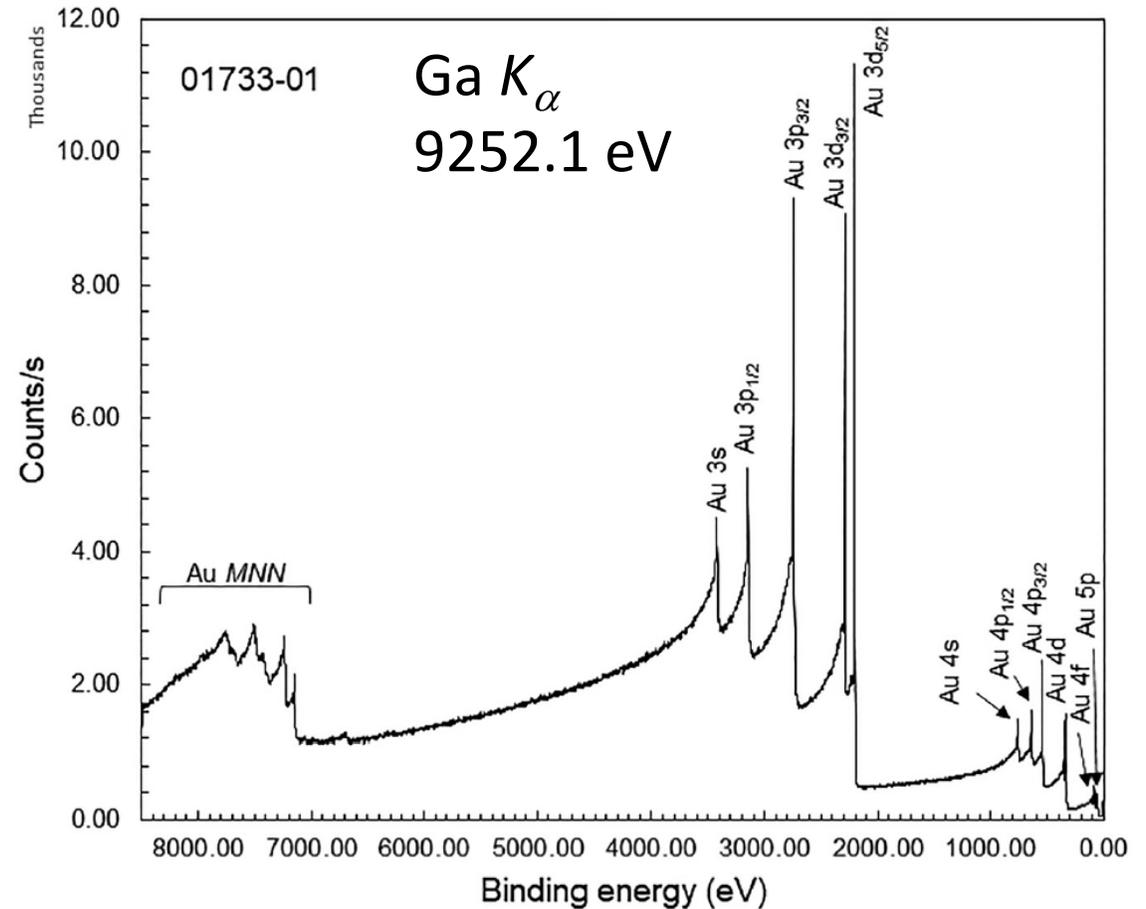
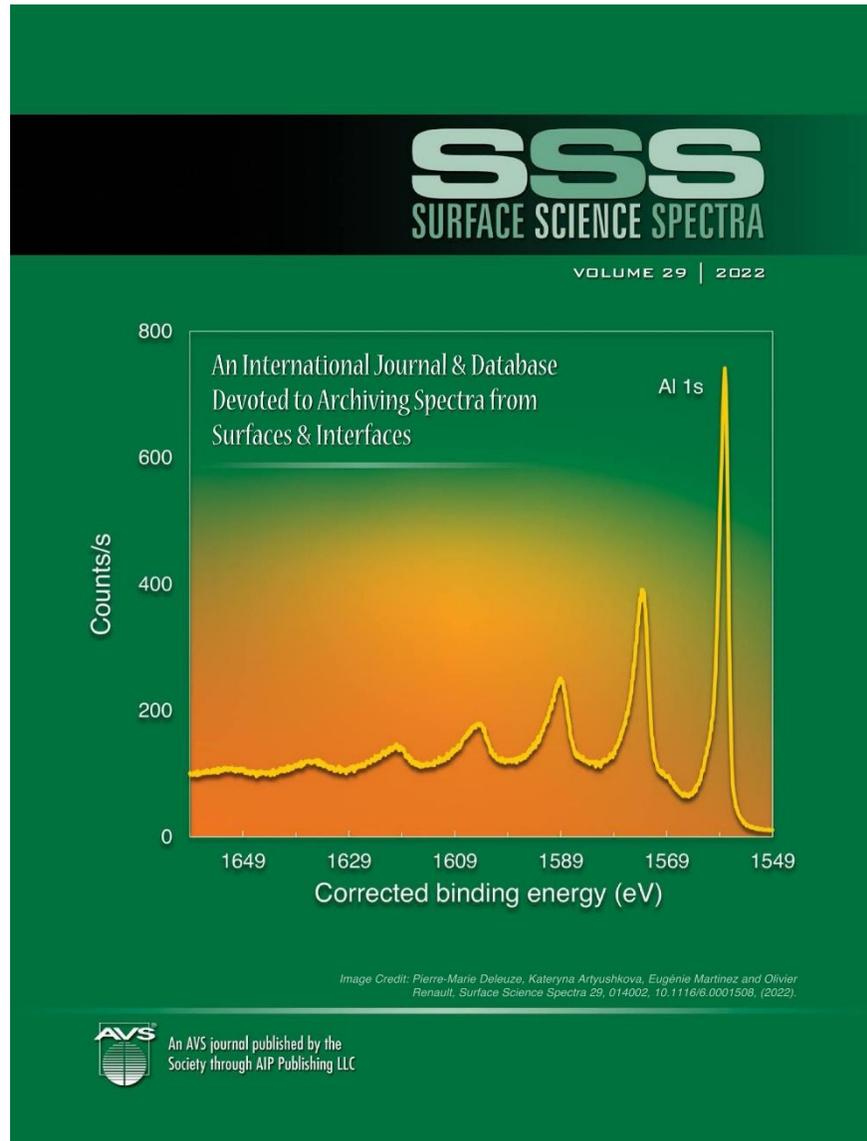
# Elemental Shifts – Higher Energy X-ray Sources



I. Hoflijk, A. Vanleenhove, I. Vaesen, C. Zborowski, K. Artyushkova, T. Conard; High energy x-ray photoelectron spectroscopy spectra of  $\text{Si}_3\text{N}_4$  measured by  $\text{Cr } K_{\alpha}$ . *Surface Science Spectra* 1 June 2022; 29 (1): 014013. <https://doi.org/10.1116/6.0001524>



# Elemental Shifts – Higher Energy X-ray Sources



Anja Vanleenhove, Fiona Crystal Mascarenhas, Ilse Hoflijck, Inge Vaesen, Charlotte Zborowski, Thierry Conard; HAXPES on SiO<sub>2</sub> with Ga K $\alpha$  photons. *Surface Science Spectra* 1 June 2022; 29 (1): 014012. <https://doi.org/10.1116/6.0001523>



# Elemental Shifts

## First-Row Transition Metals

3 IIIB 3B	4 IVB 4B	5 VB 5B	6 VIB 6B	7 VIIB 7B	8 VIII 8	9 VIII 8	10 VIII 8	11 IB 1B	12 IIB 2B
21 <b>Sc</b> Scandium 44.95591	22 <b>Ti</b> Titanium 47.88	23 <b>V</b> Vanadium 50.9415	24 <b>Cr</b> Chromium 51.9961	25 <b>Mn</b> Manganese 54.938	26 <b>Fe</b> Iron 55.847	27 <b>Co</b> Cobalt 58.9332	28 <b>Ni</b> Nickel 58.6934	29 <b>Cu</b> Copper 63.546	30 <b>Zn</b> Zinc 65.39

Binding Energy (eV)			
Element	2p <sub>3/2</sub>	3p	Δ
Sc	399	29	370
Ti	454	33	421
V	512	37	475
Cr	574	43	531
Mn	639	48	591
Fe	707	53	654
Co	778	60	718
Ni	853	67	786
Cu	933	75	858
Zn	1022	89	933

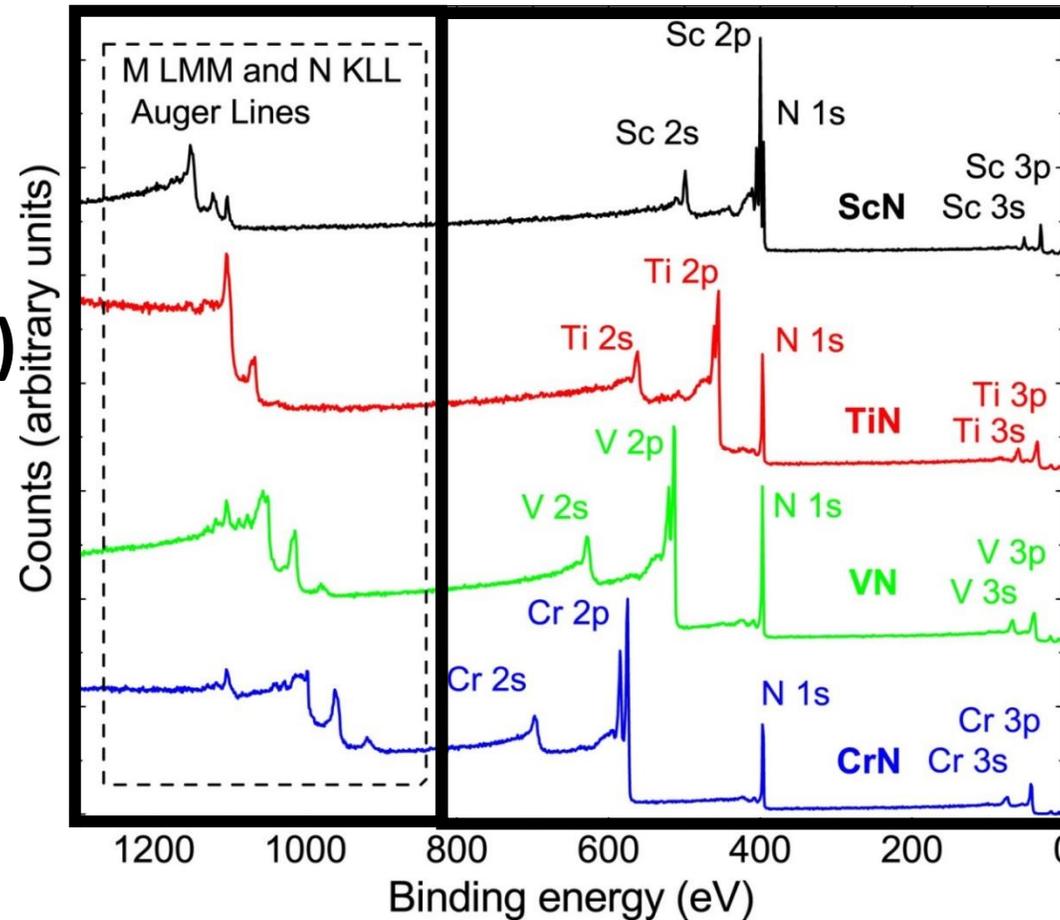


# Elemental Shifts: Transition Metal Nitrides

21 Sc Scandium 44.95591	22 Ti Titanium 47.88	23 V Vanadium 50.9415	24 Cr Chromium 51.9961
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## First-Row Transition Metal Nitrides: ScN, TiN, VN, and CrN

Auger transition kinetic energies increase (binding energies decrease)

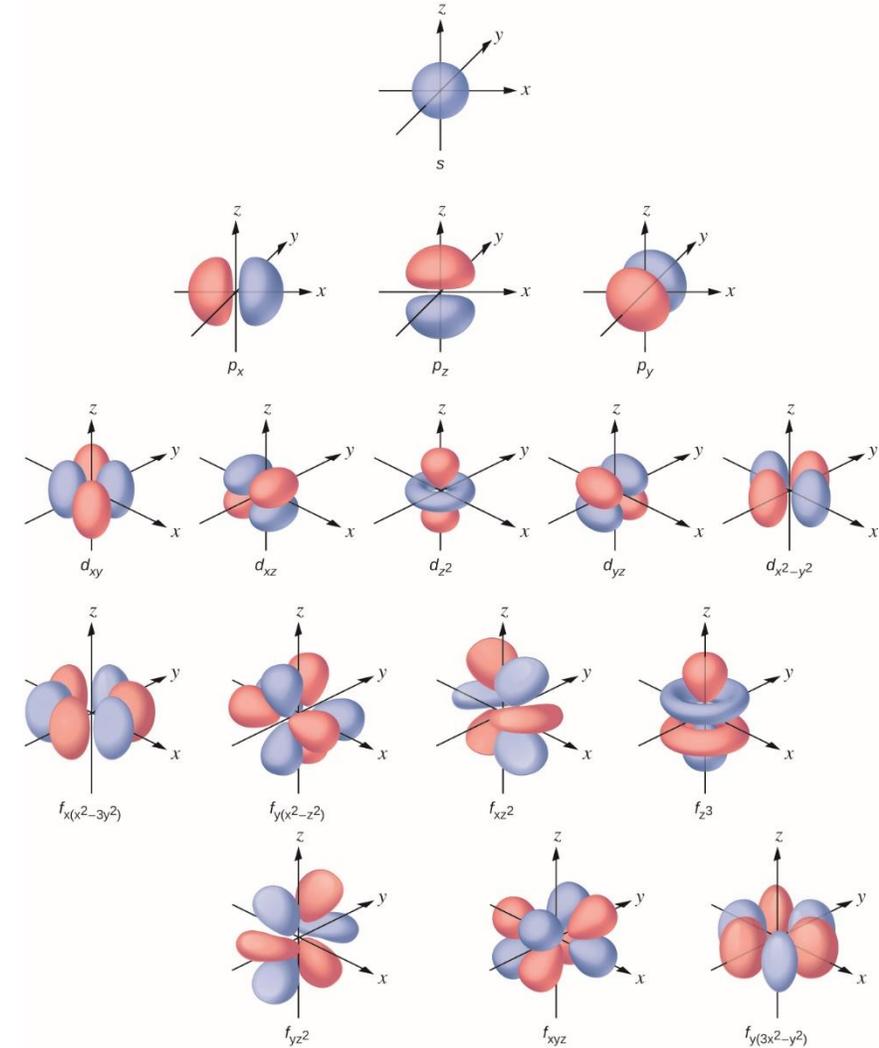
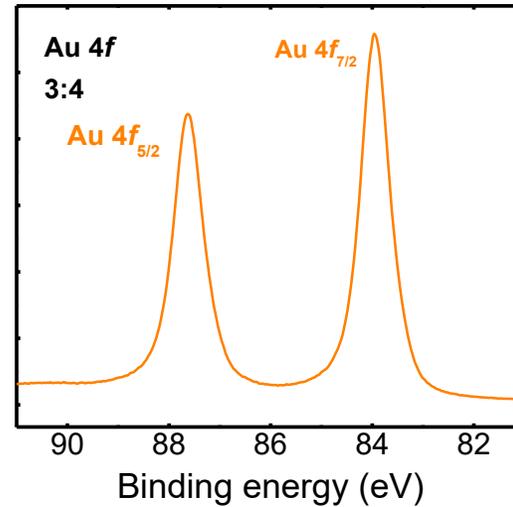
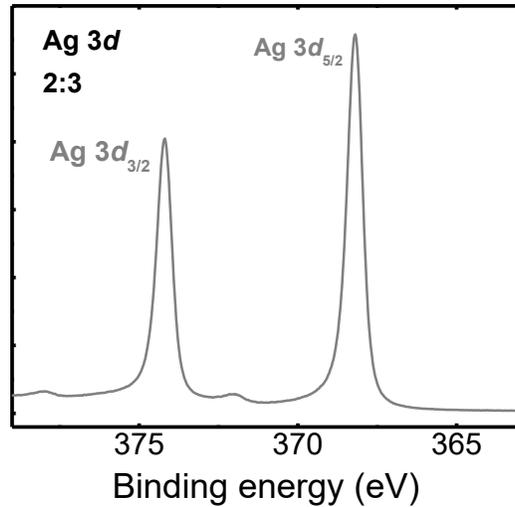
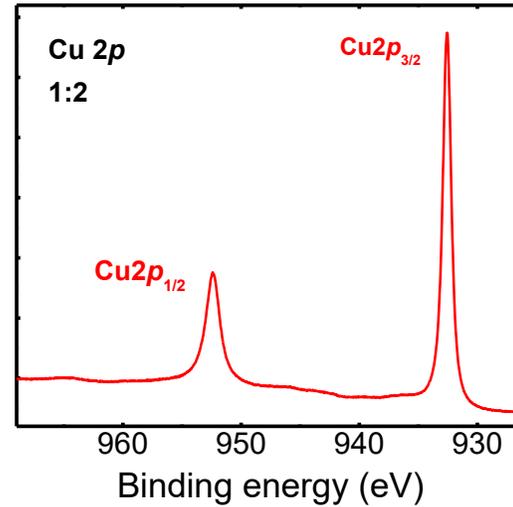
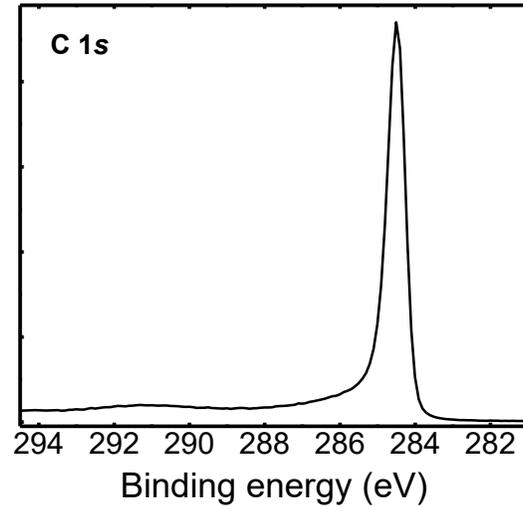


XPS Core-level binding energies increase



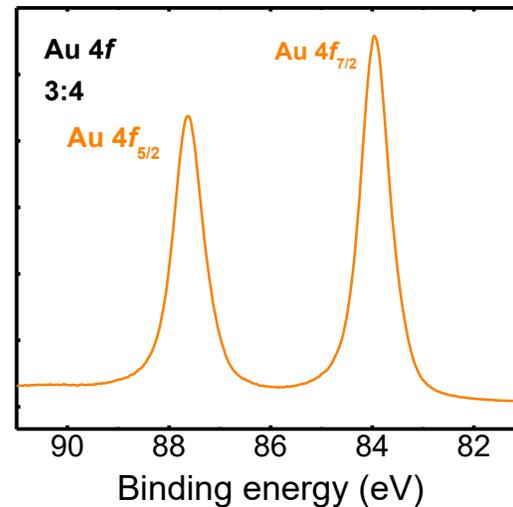
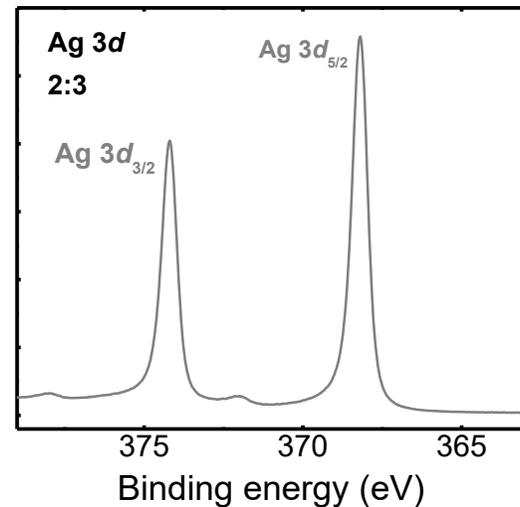
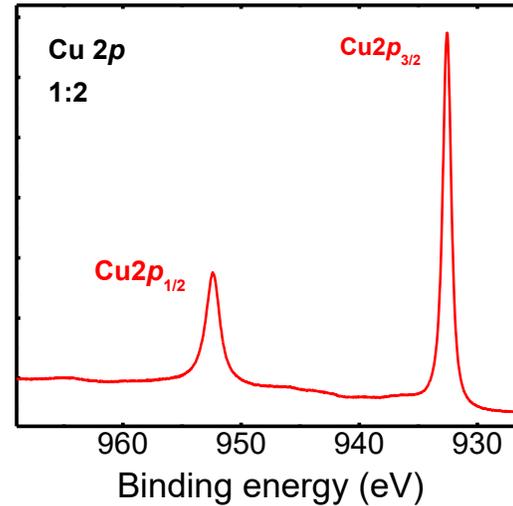
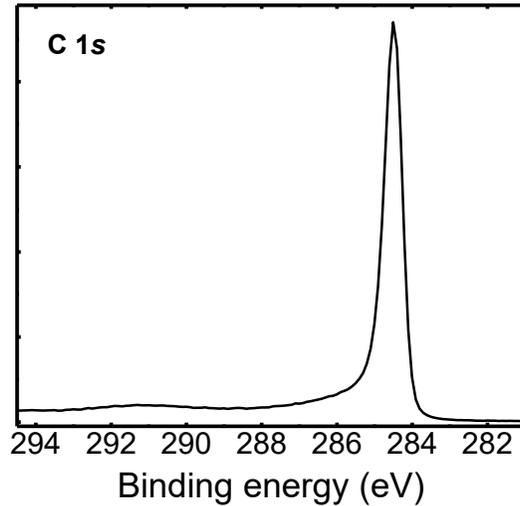
R. T. Haasch, T.-Y. Lee, D. Gall, C.-S. Shin, J. E. Greene, I. Petrov, *Surf. Sci. Spectra*, **7**, 169 (2000), *Surf. Sci. Spectra*, **7**, 193 (2000), *Surf. Sci. Spectra*, **7**, 221 (2000), *Surf. Sci. Spectra*, **7**, 250 (2000).

# Spin-orbit Splitting



R. T. Haasch, "X-ray Photoelectron Spectroscopy (XPS) and Auger Electron Spectroscopy (AES)," in *Practical Materials Characterization*, M. Sardela, ed., (Springer Science + Business Media, New York, 2014). ISBN 978-1-4614-9280-1. doi: 10.1007/978-1-4614-9281-8\_3. Atomic Orbitals and Quantum Numbers. (2019, June 5). <https://chem.libretexts.org/@go/page/122444>

# Spin-orbit Splitting



Electron spin:  $s = \pm \frac{1}{2}$

Orbital angular momentum:  
 $l = 0, 1, 2, 3 \dots$  for  $s, p, d, f$  orbitals

$$j = |l \pm s|$$

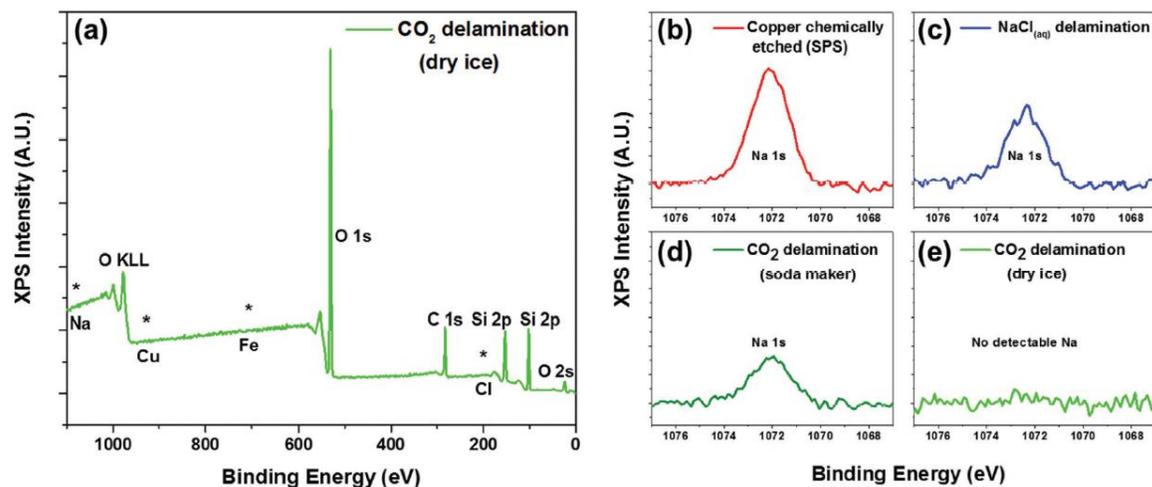
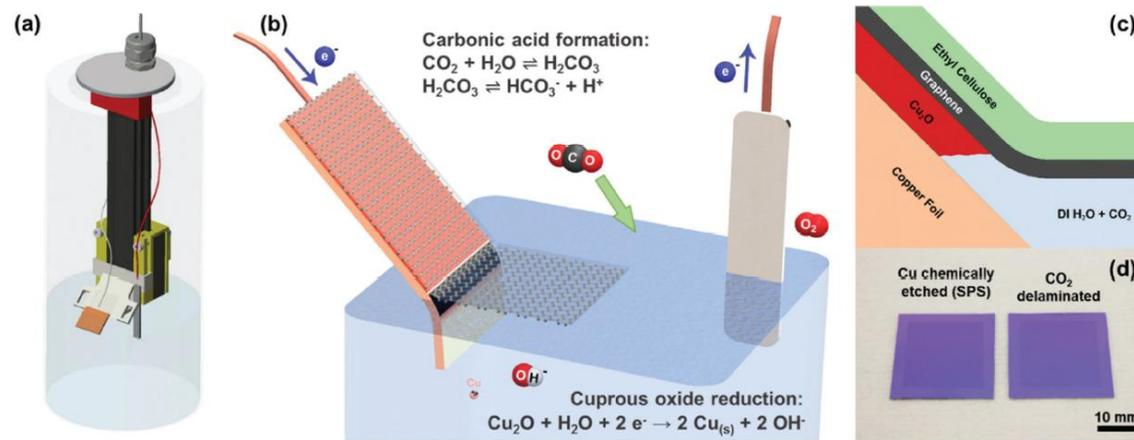
Momentum quantum number:  
 $m_j, -j$  to  $j$  ( $2j + 1$  states)



R. T. Haasch, "X-ray Photoelectron Spectroscopy (XPS) and Auger Electron Spectroscopy (AES)," in *Practical Materials Characterization*, M. Sardela, ed., (Springer Science + Business Media, New York, 2014). ISBN 978-1-4614-9280-1. doi: 10.1007/978-1-4614-9281-8\_3.  
Atomic Orbitals and Quantum Numbers. (2019, June 5). <https://chem.libretexts.org/@go/page/122444>

# Graphene Transfer

## A sustainable approach to large area transfer of graphene



- a) XPS survey of  $\text{CO}_2$  delamination (from dry ice)
- b) Chemically etched (sodium persulphate)
- c) NaCl electrolyte delaminated
- d)  $\text{CO}_2$  delamination using compressed  $\text{CO}_2$  from soda maker
- e) Delamination using carbonic acid generated from dry ice pellets

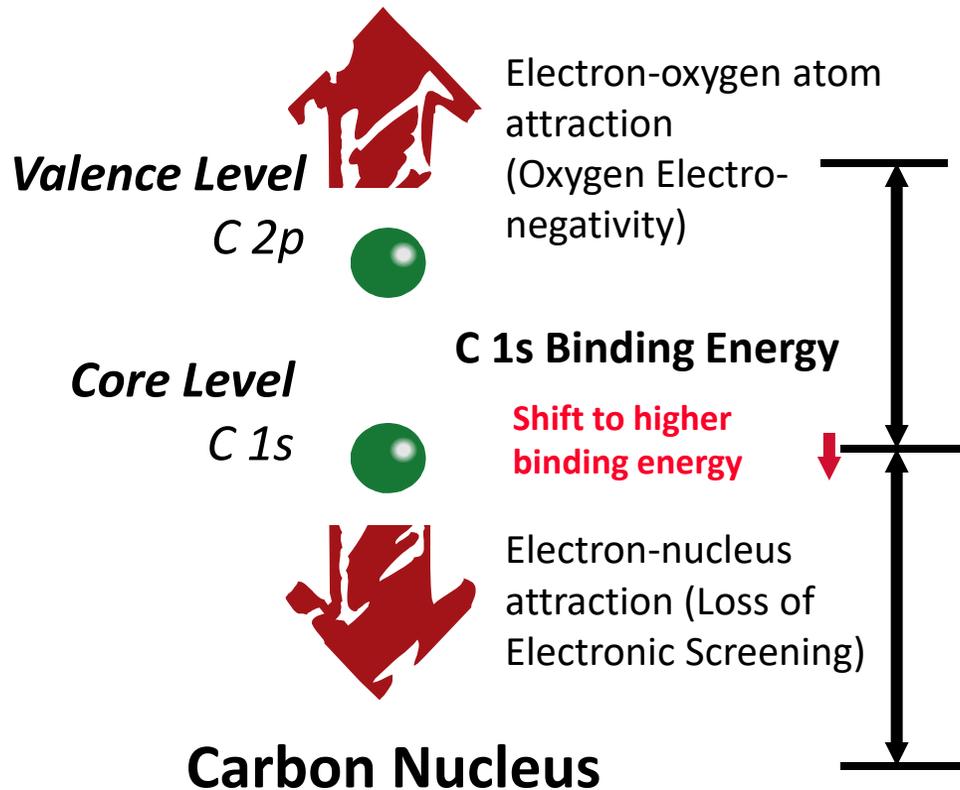


M. C. Wang, W. Moestopo, S. Takekuma, S. Farabi, R. T. Haasch, S.-W. Nam, "Sustainable approach for large area transfer of graphene and recycle of the catalyst substrate," *J. Mater. Chem. C*, **5**, 11226 (2017). [doi:10.1039/c7tc02487h](https://doi.org/10.1039/c7tc02487h).

## Electronegativity Effects

### Carbon-Oxygen Bond

#### Oxygen Atom



### Electronegativity

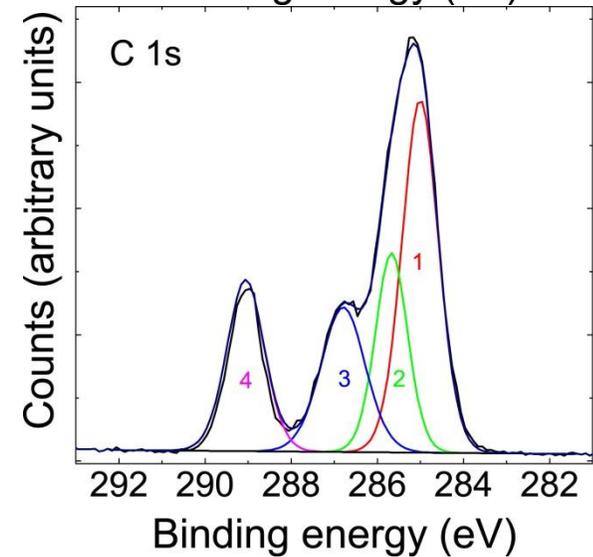
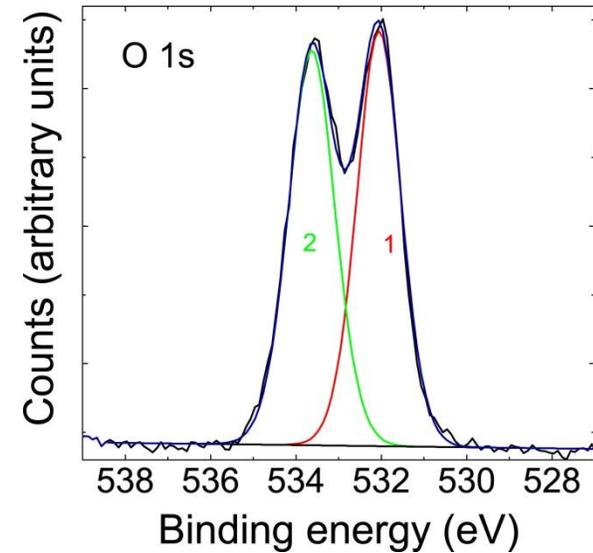
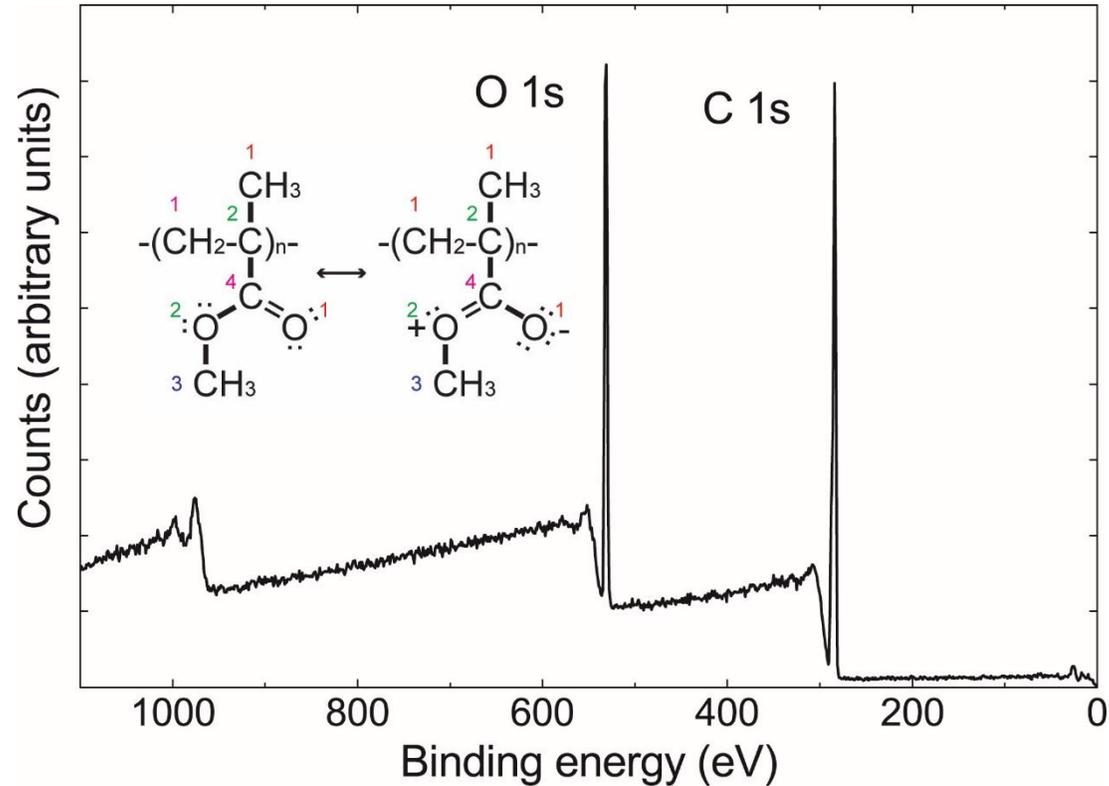
13 IIIA 3A	14 IVA 4A	15 VA 5A	16 VIA 6A	17 VIIA 7A
5 B Boron 10.811	6 C Carbon 12.011	7 N Nitrogen 14.00674	8 O Oxygen 15.9994	9 F Fluorine 18.998403

Functional Group	C 1s Binding Energy
hydrocarbon	$\underline{\text{C}}\text{-H}, \underline{\text{C}}\text{-C}$ 285.0
amine	$\underline{\text{C}}\text{-N}$ 286.0
alcohol, ether	$\underline{\text{C}}\text{-O-H}, \underline{\text{C}}\text{-O-C}$ 286.5
Cl bound to C	$\underline{\text{C}}\text{-Cl}$ 286.5
F bound to C	$\underline{\text{C}}\text{-F}$ 287.8
carbonyl	$\underline{\text{C}}\text{=O}$ 288.0



# Chemical Shifts

## XPS of polymethylmethacrylate

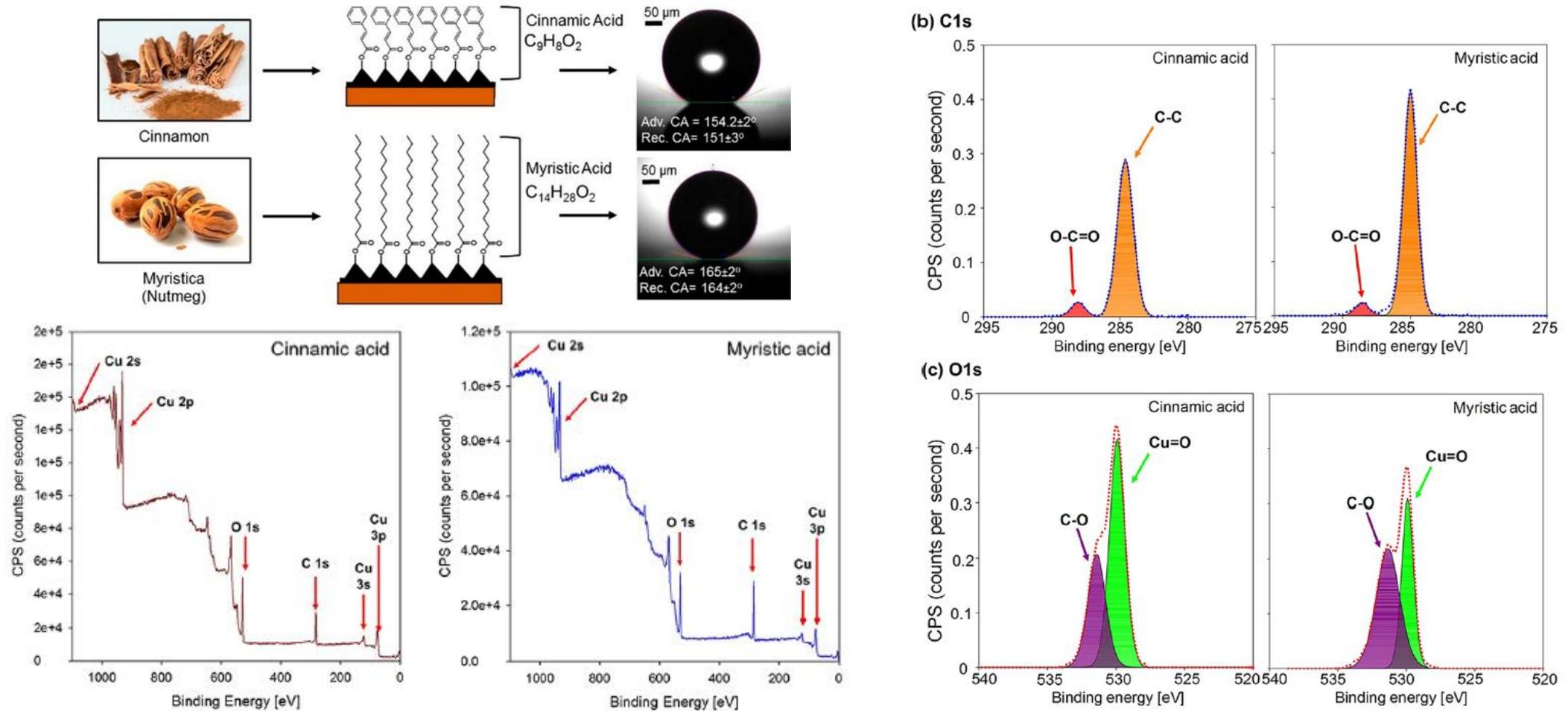


R. T. Haasch, "X-ray Photoelectron Spectroscopy (XPS) and Auger Electron Spectroscopy (AES)," in *Practical Materials Characterization*, M. Sardela, ed., (Springer Science + Business Media, New York, 2014). ISBN 978-1-4614-9280-1. doi: 10.1007/978-1-4614-9281-8\_3.

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# Superhydrophobic Materials

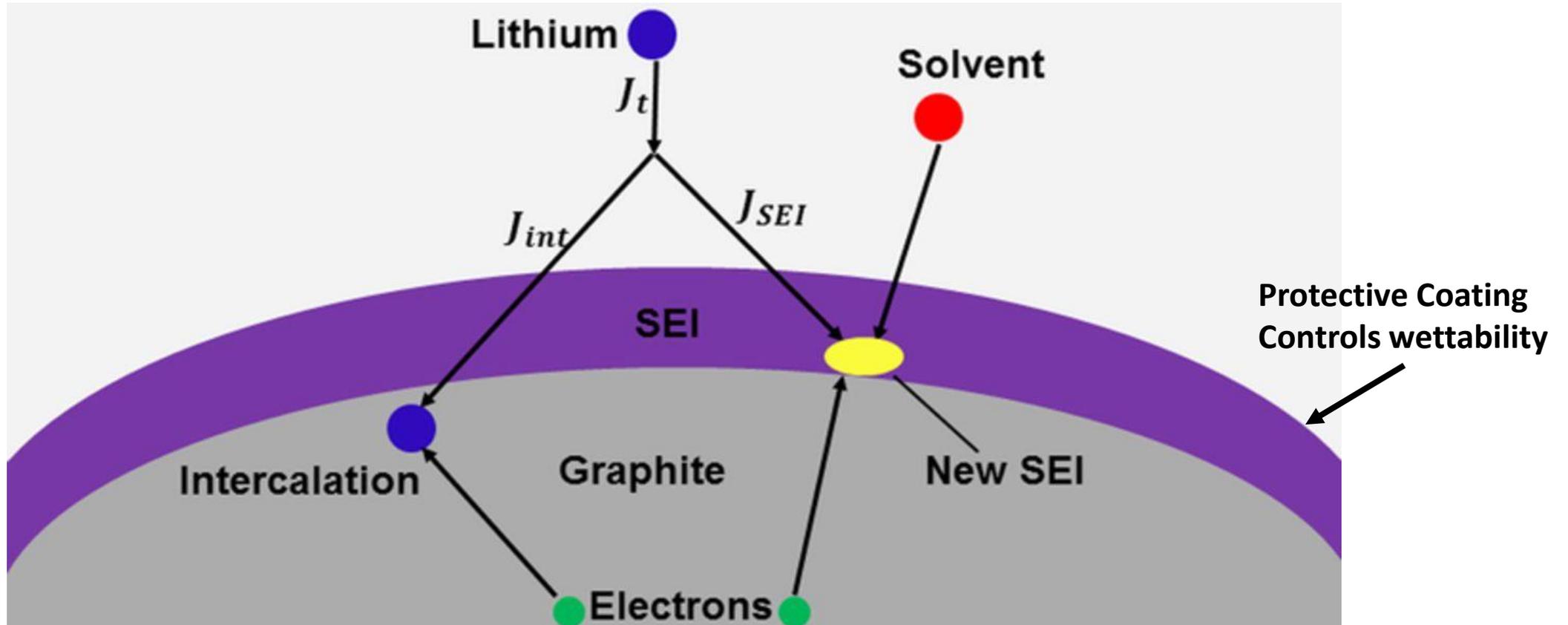
## Superhydrophobic Surfaces from Naturally Derived Hydrophobic Materials



S. M. R. Razavi, J. Oh, S. Sett, L. Feng, X. Yan, M. J. Hoque, A. Liu, R. T. Haasch, M. Masoomi, R. Bagheri, N. Miljkovic, "Superhydrophobic Surfaces Made From Naturally Derived Hydrophobic Materials," *ACS Sustainable Chem. Eng.*, 5(12), 11362 (2017). [doi:10.1021/acssuschemeng.7b02424](https://doi.org/10.1021/acssuschemeng.7b02424).

# Solid Electrolyte Interphase (SEI)

Parallel pathways for the transport and intercalation of Li ions into an active particle and the growth of the SEI layer through degradation reactions of solvent molecules with Li ions.



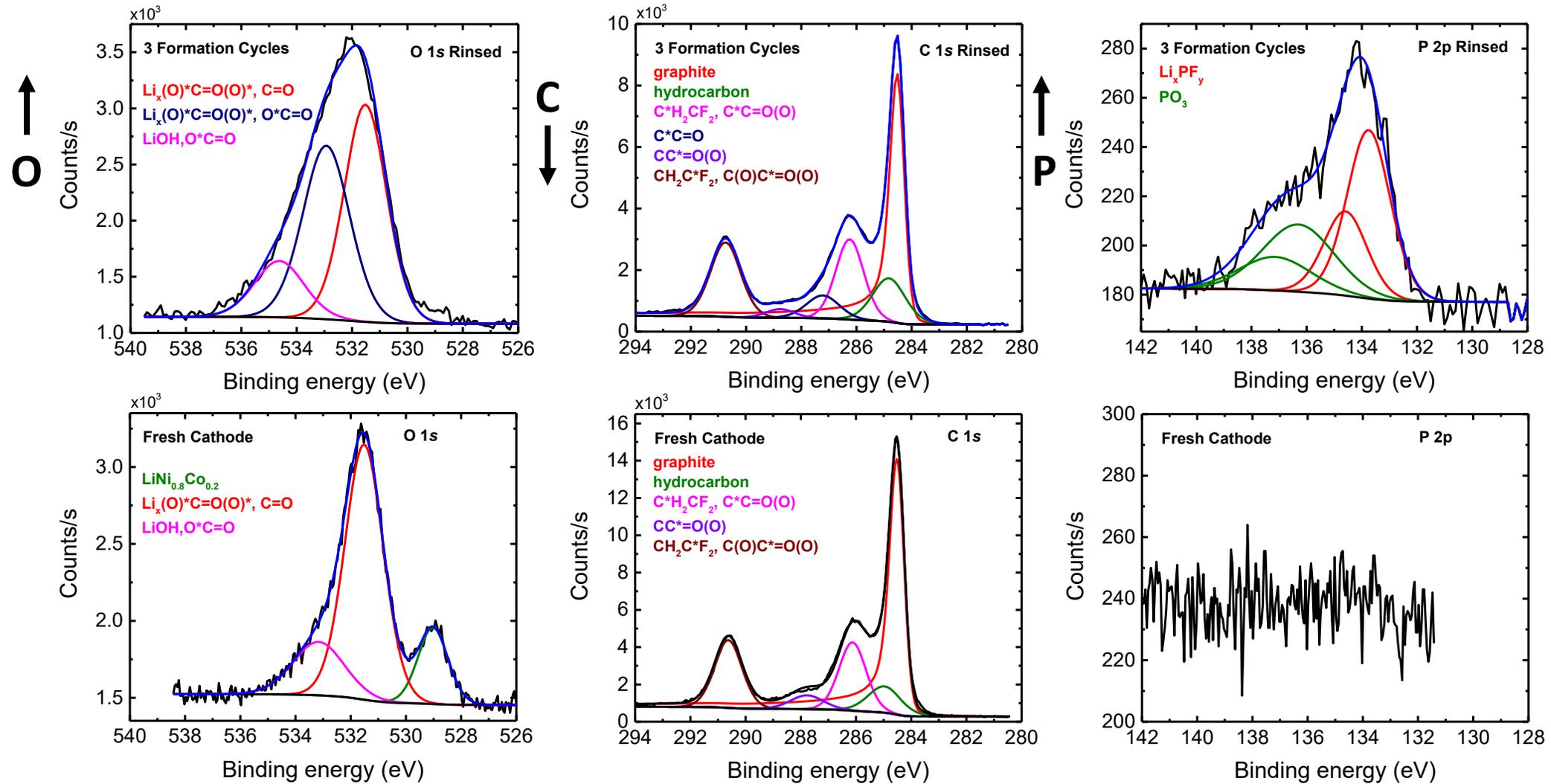
A. A. Tahmasbi et al. J. Electrochem. Soc. 2017;164:A1307-A1313

Journal of The Electrochemical Society

©2017 by The Electrochemical Society



# Cathode (positive electrode)- $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$



**3 Formation Cycles**

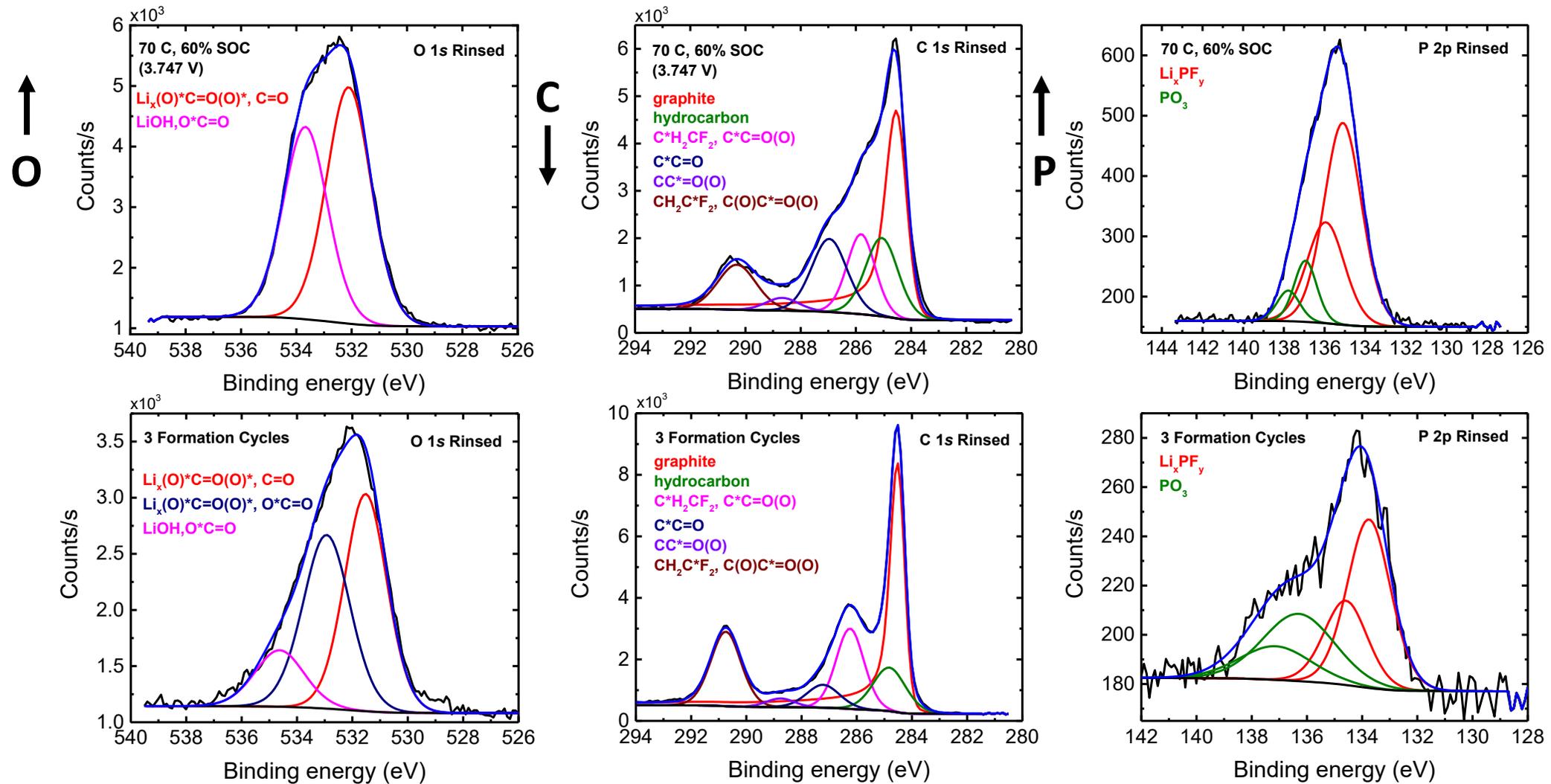
**Fresh**



D. P. Abraham, J. Liu, C. H. Chen, Y. E. Hyung, M. Stoll, N. Elsen, S. MacLaren, R. Twisten, R. Haasch, E. Sammann I. Petrov, K. Amine, G. Henriksen, "Diagnosis of power fade mechanisms in high-power lithium-ion cells," *J. Power Sources*, **119-121**, 511-516 (2003).

R. T. Haasch, D. P. Abraham, "LiNi<sub>0.8</sub>Co<sub>0.2</sub>O<sub>2</sub>-based high-power lithium-ion battery positive electrodes analyzed by X-ray photoelectron spectroscopy," *Surface Science Spectra*, **23**, 112-172 (2016).

# Cathode (positive electrode)- $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$



70 °C,  
60% SOC

3 Formation  
Cycles

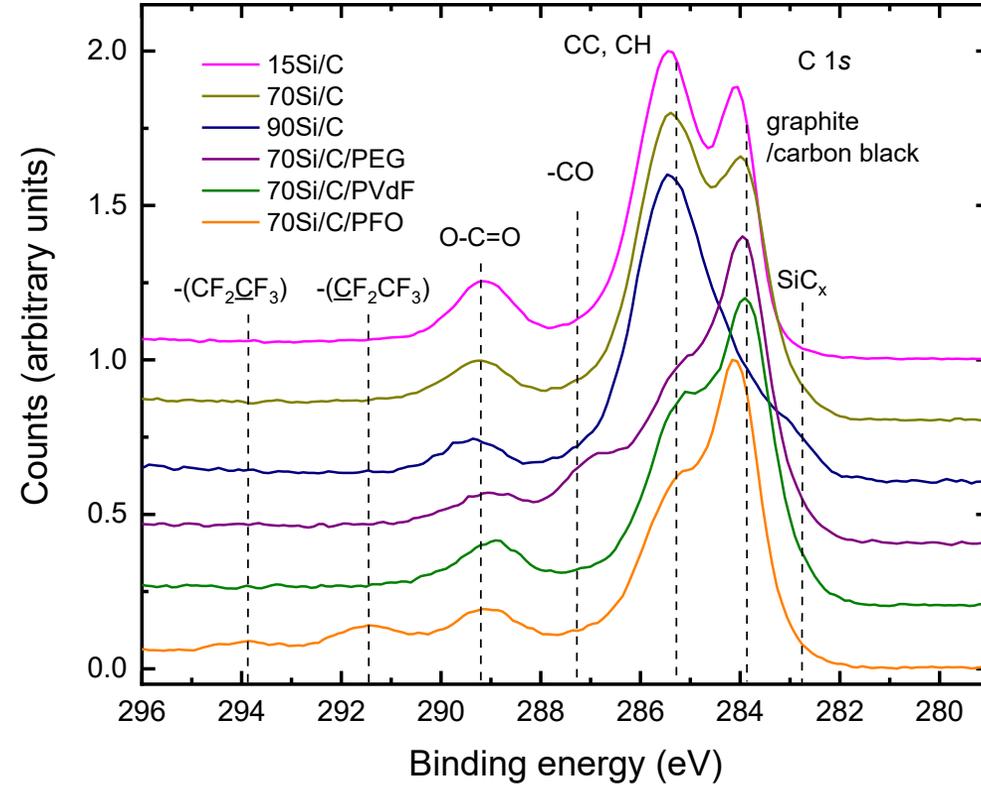
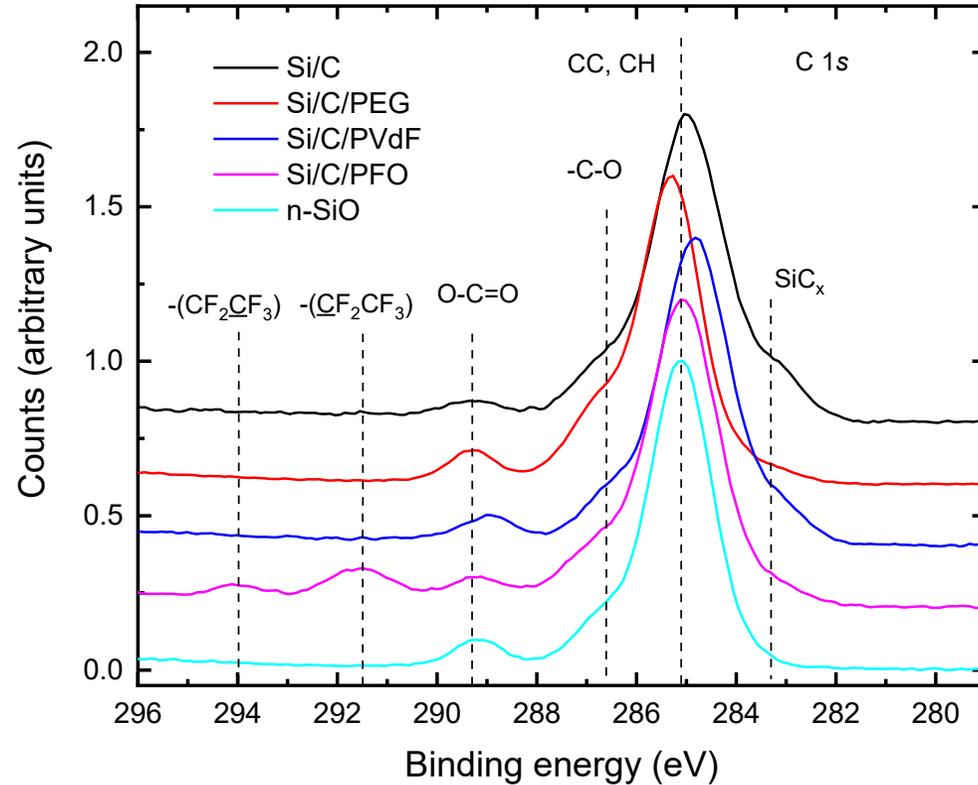


D. P. Abraham, J. Liu, C. H. Chen, Y. E. Hyung, M. Stoll, N. Elsen, S. Maclaren, R. Twisten, R. Haasch, E. Sammann I. Petrov, K. Amine, G. Henriksen, "Diagnosis of power fade mechanisms in high-power lithium-ion cells," *J. Power Sources*, **119-121**, 511-516 (2003).

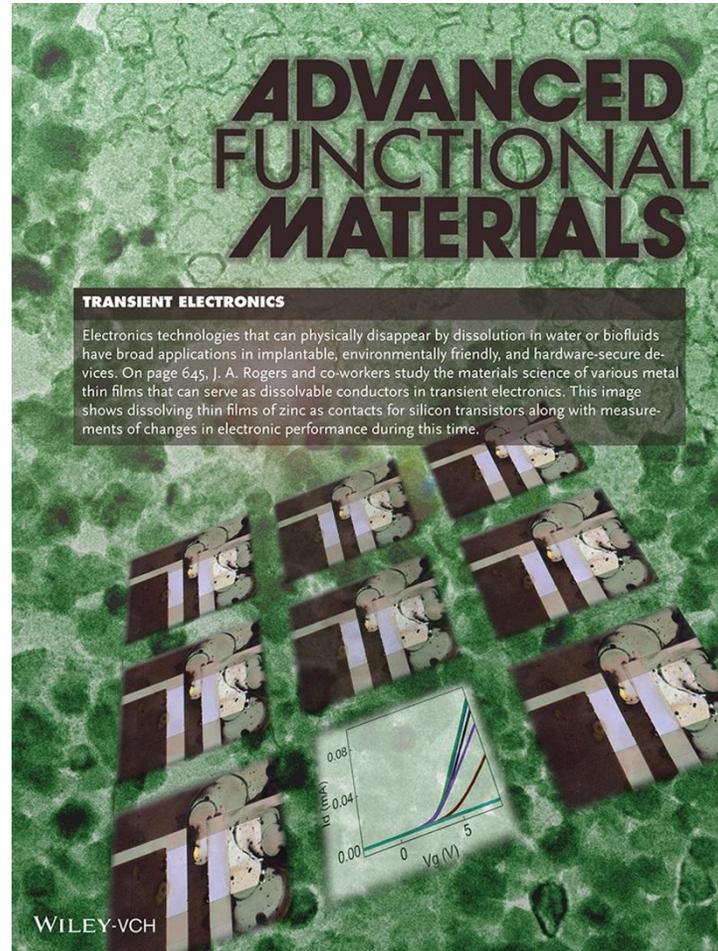
R. T. Haasch, D. P. Abraham, " $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$ -based high-power lithium-ion battery positive electrodes analyzed by X-ray photoelectron spectroscopy," *Surface Science Spectra*, **23**, 112-172 (2016).

# Anode (negative electrode)- Si Based Materials

## Si powders and electrodes for high-energy lithium-ion cells

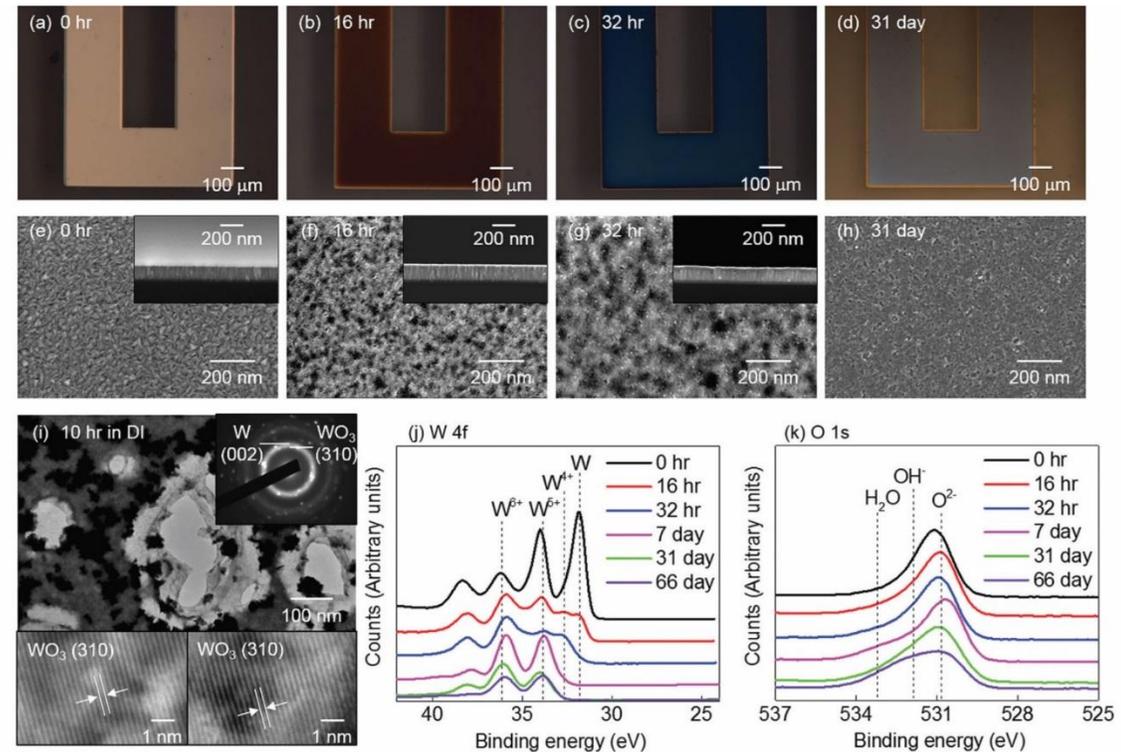


R. T. Haasch, D. P. Abraham, "Si powders and electrodes for high-energy lithium-ion cells," *Surf. Sci. Spectra*, **26**, 016801 (2020). [doi:10.1116/1.5130764](https://doi.org/10.1116/1.5130764).



## Dissolvable Metals for Transient Electronics

Lan Yin, Huanyu Cheng, Shimin Mao, Richard Haasch, Yuhao Liu, Xu Xie, Suk-Won Hwang, Harshvardhan Jain, Seung-Kyun Kang, Yewang Su, Rui Li, Yonggang Huang, and John A. Rogers\*



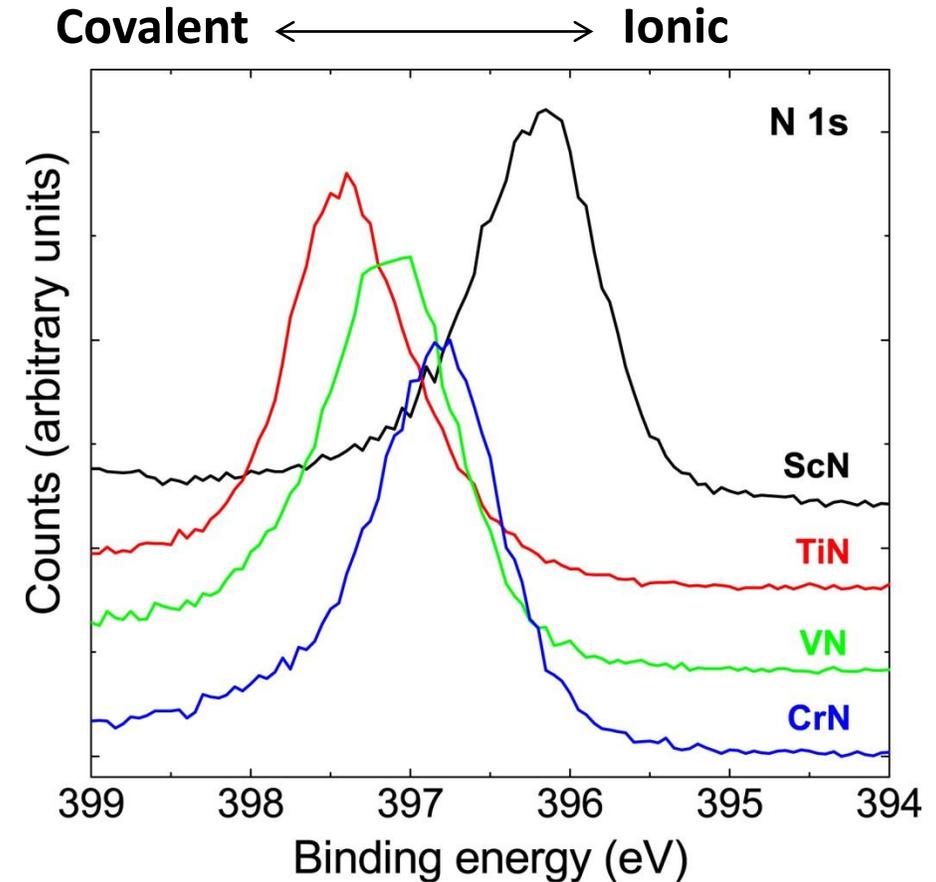
L. Yin, H. Cheng, S. Mao, R. Haasch, Y. Liu, X. Xie, S.-W. Hwang, H. Jain, S.-K. Kang, Y. Su, R. Li, Y. Huang, J. A. Rogers, "Dissolvable Metals for Transient Electronics," *Adv. Funct. Mater.*, **24**, 645 (2014).

# Transition Metal Nitrides

## N 1s spectra of First-Row Transition Metal Nitrides: ScN, TiN, VN, and CrN

p-d hybridization 8 MO's

	Anti-bonding e <sup>-</sup> /Formula Unit (nominal)	Binding Energy, eV
ScN	-0.17 (0)	396.1
TiN	1 (1)	397.3
VN	1.9 (2)	397.0
CrN	2.9 (3)	396.7

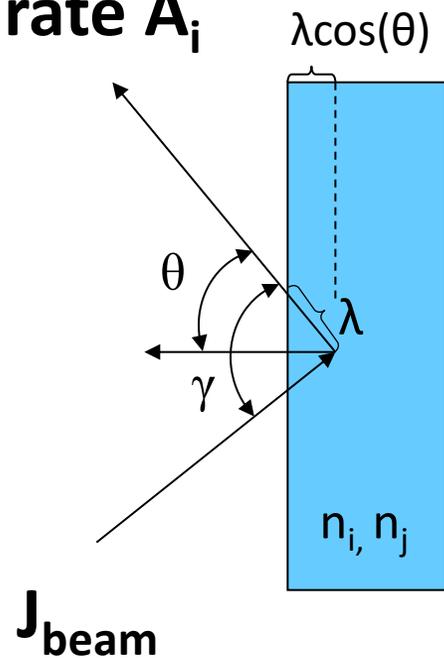


R. T. Haasch, T.-Y. Lee, D. Gall, C.-S. Shin, J. E. Greene, I. Petrov, *Surf. Sci. Spectra*, **7**, 169 (2000), *Surf. Sci. Spectra*, **7**, 193 (2000), *Surf. Sci. Spectra*, **7**, 221 (2000), *Surf. Sci. Spectra*, **7**, 250 (2000).

# Quantitative Surface Analysis: XPS

detector count

rate  $A_i$



Assuming a Homogeneous sample:

$A_i$  = detector count rate

$$A_i = ( \text{electrons/volume} ) ( \text{volume} )$$

$$A_i = ( N_i \sigma_i(\gamma) J T(E_i) ) ( a \lambda_i(E_i) \cos\theta )$$

Sample Dependent Terms

where:  $N$  = atoms/cm<sup>3</sup>

$\sigma(\gamma)$  = photoelectric (scattering) cross-section, cm<sup>2</sup>

$\lambda(E_i)$  = inelastic electron mean-free path, cm

Instrument Dependent Terms

$J$  = X-ray flux, photon/cm<sup>2</sup>-sec

$T(E_i)$  = analyzer transmission function

$a$  = analysis area, cm<sup>2</sup>

$\theta$  = photoelectron emission angle



# Quantitative Surface Analysis: XPS

**By assuming the concentration to be a relative ratio of atoms, we can neglect the terms that depend only on the instrument:**

$$N_i = A_i / \sigma_i T(E_i) \lambda_i(E_i)$$

It is difficult to accurately determine  $\lambda_i$  so it is usually neglected. Modern acquisition and analysis software can account for the transmission function.

$$N_i = A_i / S_i$$

$$C_i = A_i / S_i / \sum A_{i,j} / S_{i,j}$$

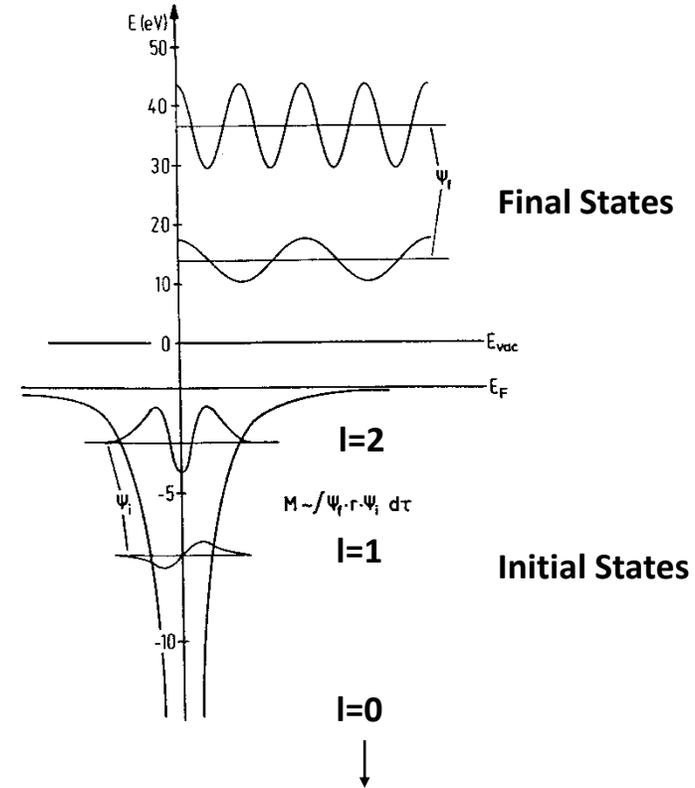
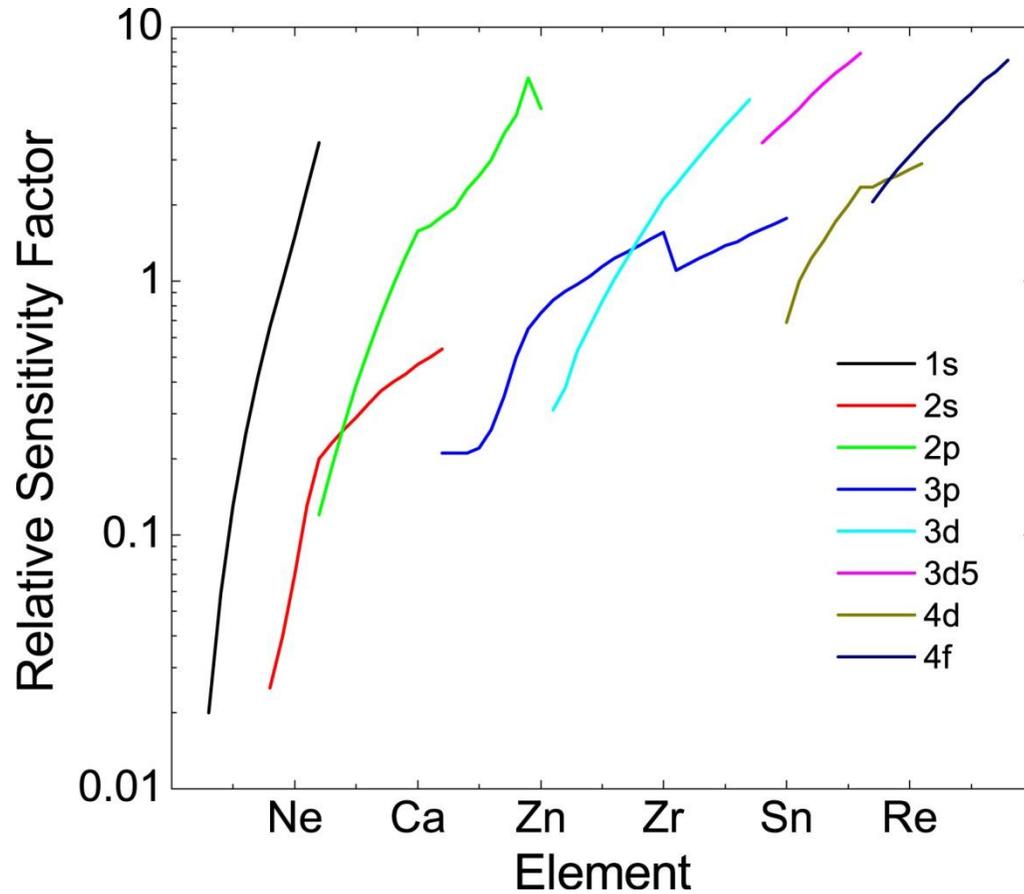
The values of S are determined theoretically or empirically with standards.

**XPS is considered to be a *semi-quantitative* technique.**



# Quantitative Surface Analysis: XPS

## XPS Relative Elemental Sensitivities

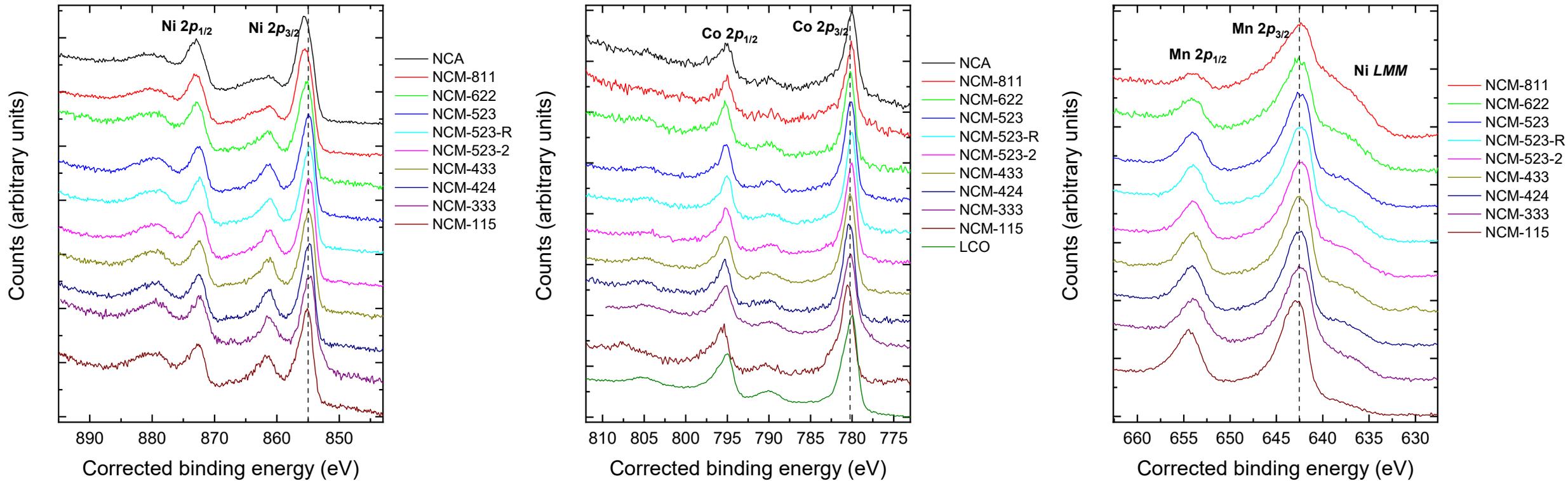


S. Hüfner, *Photoelectron Spectroscopy Principles and Applications*, Second Edition, (Springer, Berlin Heidelberg, 1996). ISBN 3-540-60875-3.



# NCM Family of Oxide Materials - Raw Powder

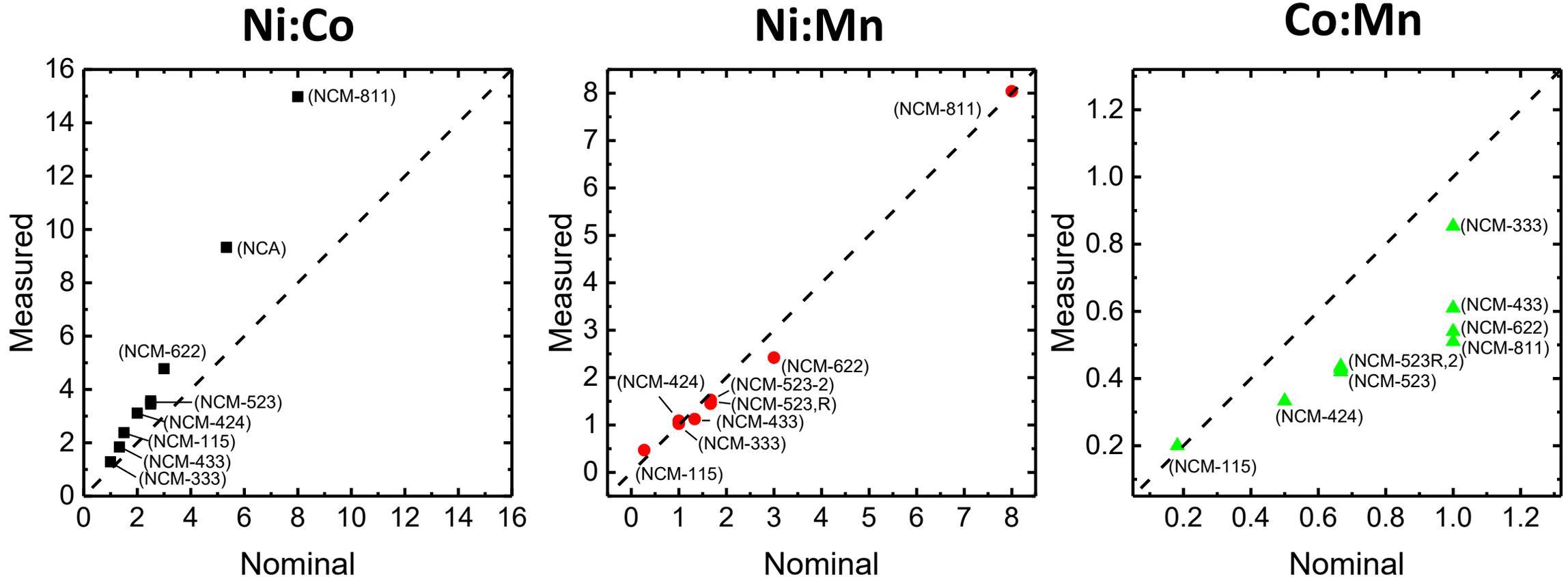
## Lithium-bearing Oxides for Rechargeable Li-ion Batteries:



R. T. Haasch, S. E. Trask, D. P. Abraham, "Lithium-bearing oxides for rechargeable Li-ion batteries," *Surf. Sci. Spectra*, **26**, 014002 (2019). [doi:10.1116/1.5080232](https://doi.org/10.1116/1.5080232).

# NCM Family of Oxide Materials - Raw Powder

## Lithium-bearing Oxides for Rechargeable Li-ion Batteries:



# Transition Metal Nitrides

## First-Row Transition Metal Nitrides: ScN, TiN, VN, and CrN

<i>XPS Analysis</i>		ScN	TiN	VN	CrN	
Binding energy (eV)	Metal 2p <sub>3/2</sub>	Major peak	400.4	455.1	513.2	574.4
		Satellite <sup>a</sup>		457.9	515.5	575.5
	Metal 2p <sub>1/2</sub>	Major peak	404.9	461.0	520.7	584.0
		Satellite <sup>a</sup>		463.8	523.0	585.1
	N 1s		396.1	397.3	397.0	396.7
Composition (N/metal)	As Deposited	1.13	1.00	1.02	0.73 <sup>b</sup>	
	After ion bombardment	0.99	0.73	0.46	0.55 <sup>b</sup>	
	Bulk value from RBS	1.11±0.03	1.02±0.02	1.06±0.02	1.04±0.02	

- The satellite is due to a transition into a relaxed final state
- The composition determination of the CrN layers by peak fitting is less reliable because the commonly used Shirley method for background subtraction does not accurately describe the experimental data.

### Nitrogen/Metal peak ratio decreases after sputtering



R. T. Haasch, T.-Y. Lee, D. Gall, C.-S. Shin, J. E. Greene, I. Petrov, *Surf. Sci. Spectra*, **7**, 169 (2000), *Surf. Sci. Spectra*, **7**, 193 (2000), *Surf. Sci. Spectra*, **7**, 221 (2000), *Surf. Sci. Spectra*, **7**, 250 (2000).

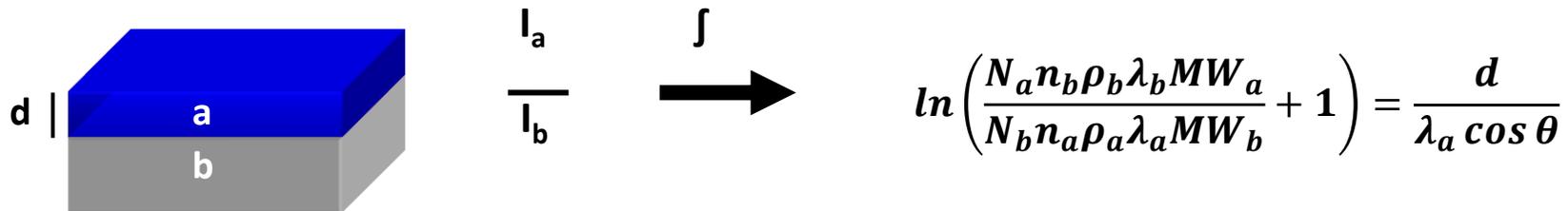
# Layer Thickness Measurement

## Layer thickness calculation: Two-Layer Model

Assuming only inelastic scattering

Beer-Lambert relationship:

$$I = I_0 \exp(-d/\lambda \cos \theta)$$

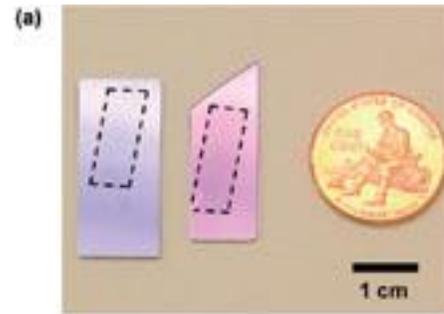
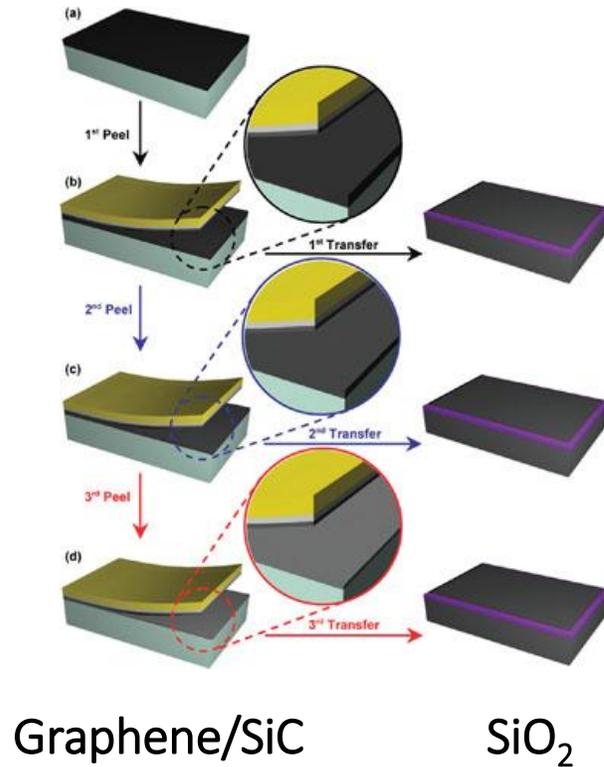


Where:  $\eta$  = number of atoms per molecule unit,  
 $\rho$  = molecular density,  
 $\lambda$  = inelastic mean-free path,  
MW = molecular weight,  
N = atomic concentration.

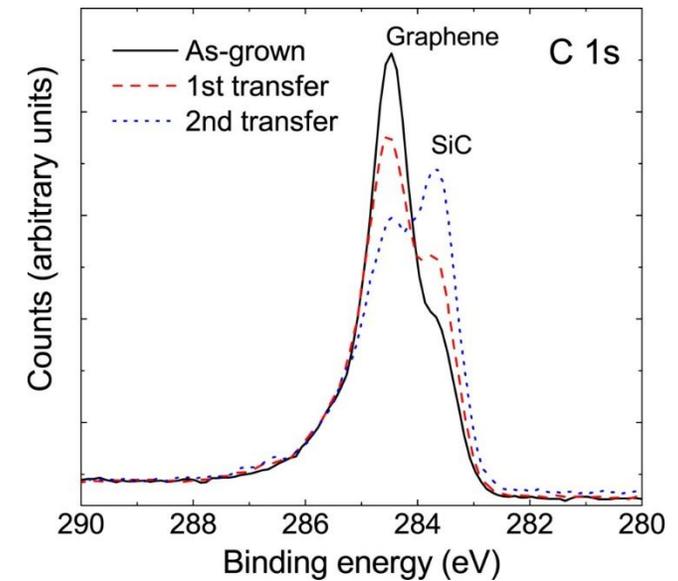


# Graphene Transfer

## Layer-by-Layer Transfer of Multiple, Large Area Sheets of Graphene Grown in Multilayer Stacks on a Single SiC Wafer



	Thickness, nm
As-grown	2.0
1 <sup>st</sup> Transfer	1.5
2 <sup>nd</sup> Transfer	0.8

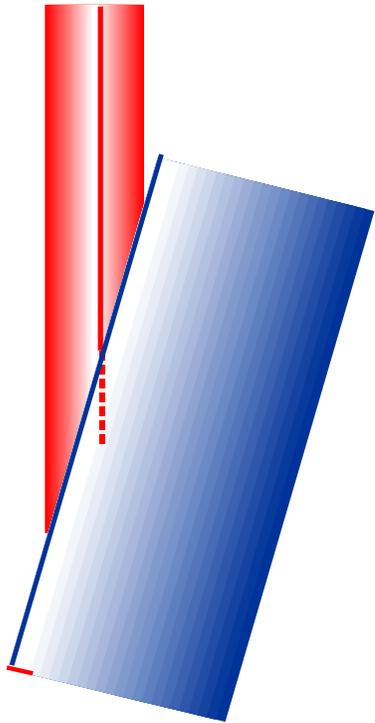


S. Unarunotai, J. Koepke, C.-L. Tsai, F. Du, C. Chialvo, Y. Murata, R. Haasch, I. Petrov, N. Mason, M. Shim, J. Lyding, J. A. Rogers, *ACS Nano*, **4(10)**, 5591-5598, (2010).

# Angle-resolved XPS

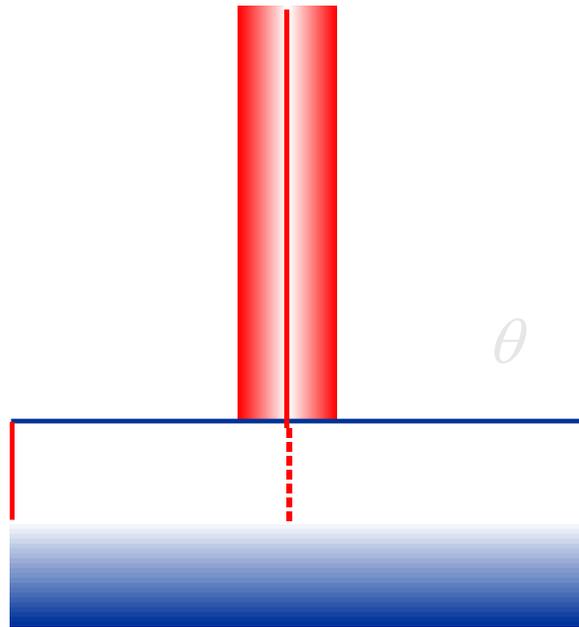
More Surface Sensitive

$$\theta = 75^\circ$$



Less Surface Sensitive

$$\theta = 0^\circ$$

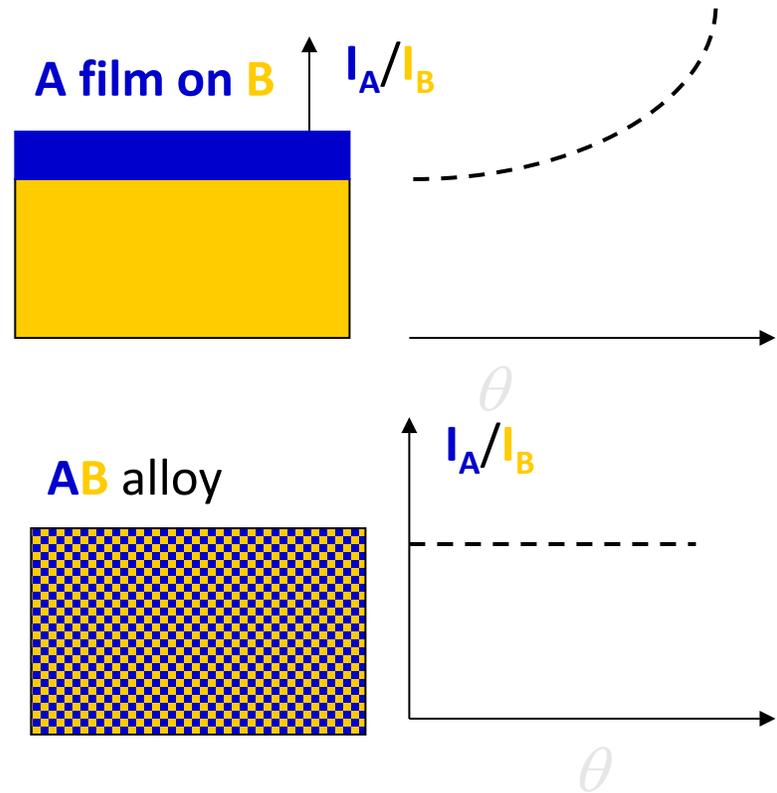


Information depth =  $d \cos \theta$

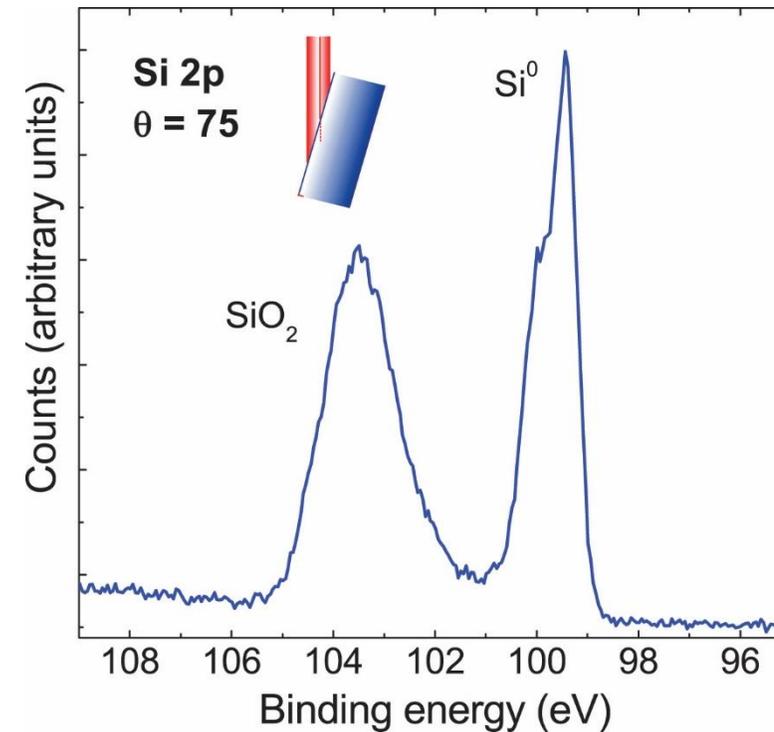
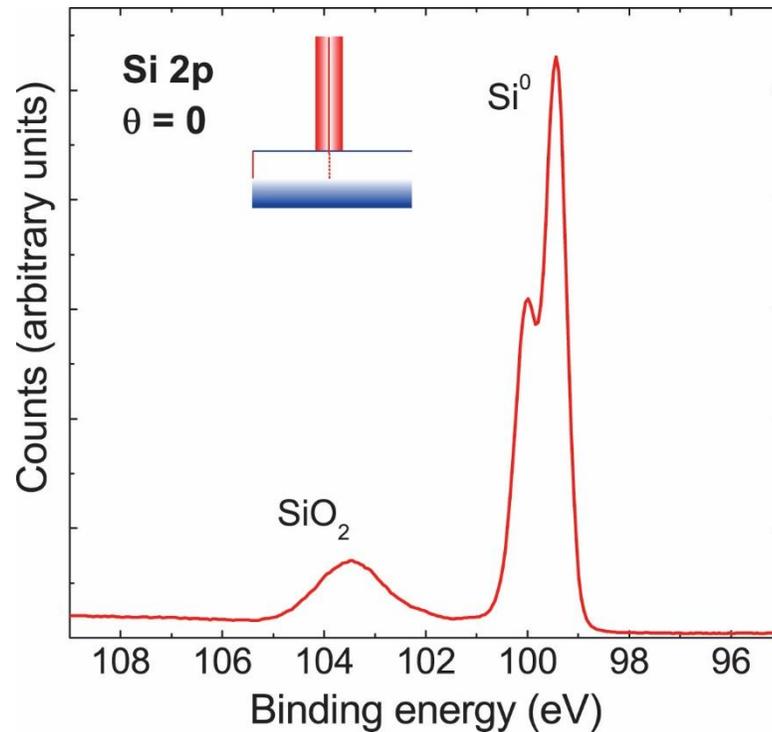
$d$  = Escape depth  $\sim 3 \lambda$

$\theta$  = Emission angle (relative to surface normal)

$\lambda$  = Inelastic Mean Free Path



# Angle-resolved XPS - SiO<sub>2</sub>/Si

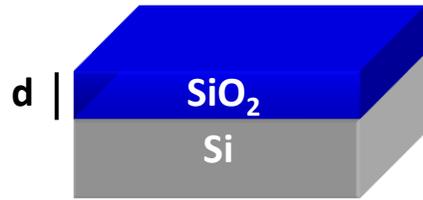


R. T. Haasch, "X-ray Photoelectron Spectroscopy (XPS) and Auger Electron Spectroscopy (AES)," in *Practical Materials Characterization*, M. Sardela, ed., (Springer Science + Business Media, New York, 2014). ISBN 978-1-4614-9280-1. doi: 10.1007/978-1-4614-9281-8\_3.

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# Angle-resolved XPS - SiO<sub>2</sub>/Si

## Layer thickness calculation: Angle-resolved XPS



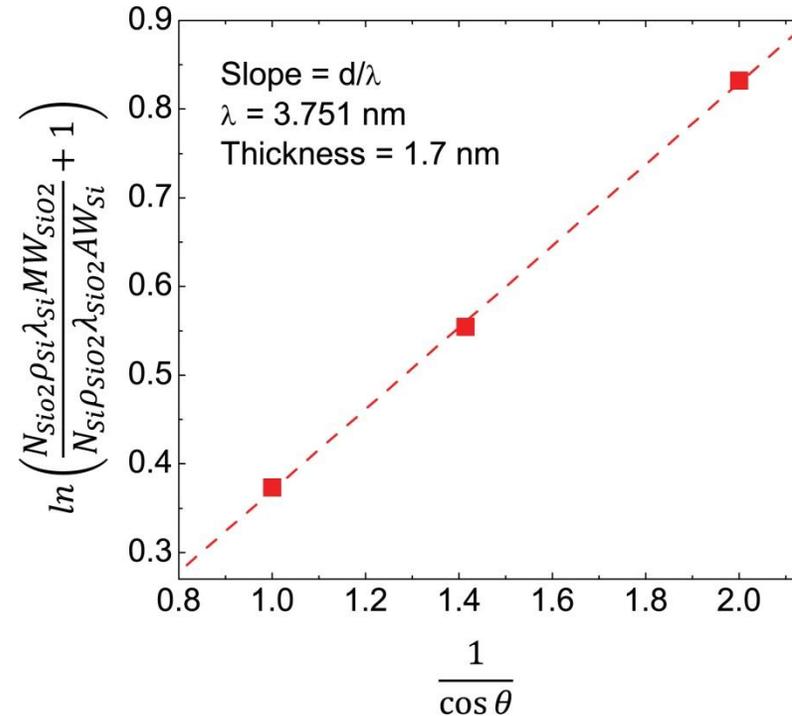
Beer-Lambert relationship:

$$I = I_0 \exp(-d/\lambda \cos \theta)$$

$$\frac{I_{\text{SiO}_2}}{I_{\text{Si}}} \xrightarrow{\int} \ln \left( \frac{N_{\text{SiO}_2} n_{\text{Si}} \rho_{\text{Si}} \lambda_{\text{Si}} MW_{\text{SiO}_2}}{N_{\text{Si}} n_{\text{SiO}_2} \rho_{\text{SiO}_2} \lambda_{\text{SiO}_2} MW_{\text{Si}}} + 1 \right) = \frac{d}{\lambda_{\text{SiO}_2} \cos \theta}$$

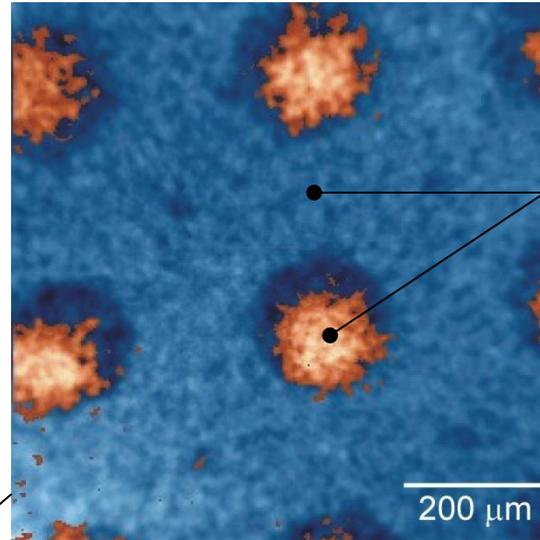
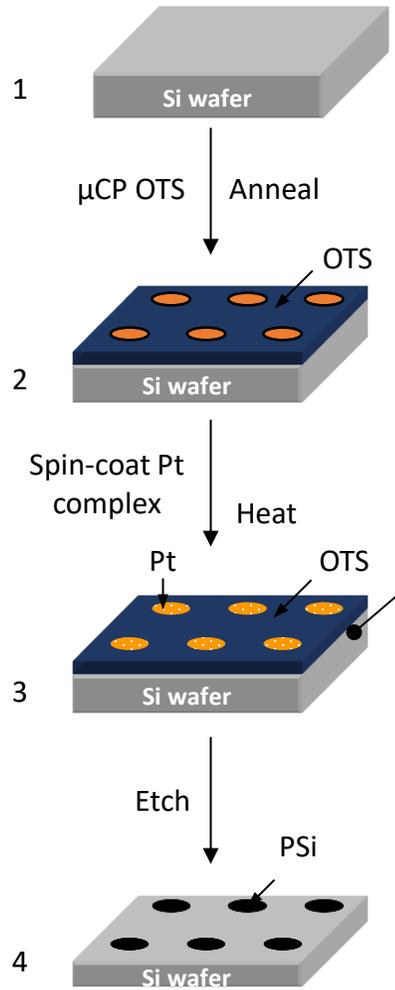
Plot:

$$\ln \left( \frac{N_{\text{SiO}_2} n_{\text{Si}} \rho_{\text{Si}} \lambda_{\text{Si}} MW_{\text{SiO}_2}}{N_{\text{Si}} n_{\text{SiO}_2} \rho_{\text{SiO}_2} \lambda_{\text{SiO}_2} MW_{\text{Si}}} + 1 \right) = \frac{d}{\lambda_{\text{SiO}_2} \cos \theta}$$

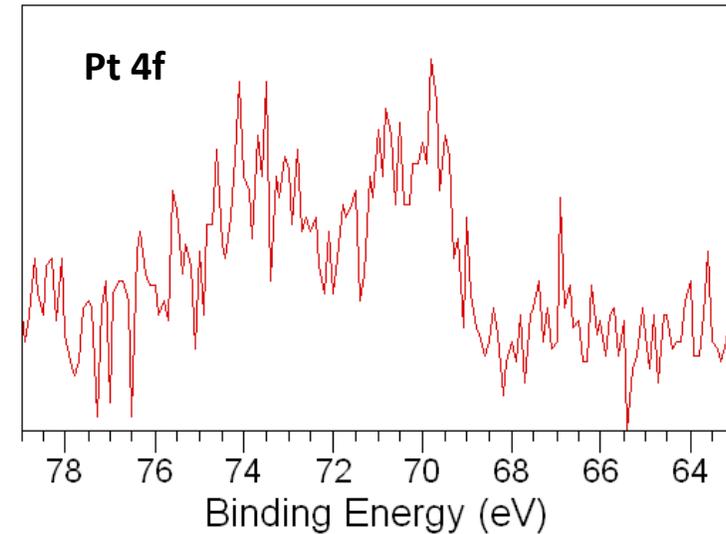
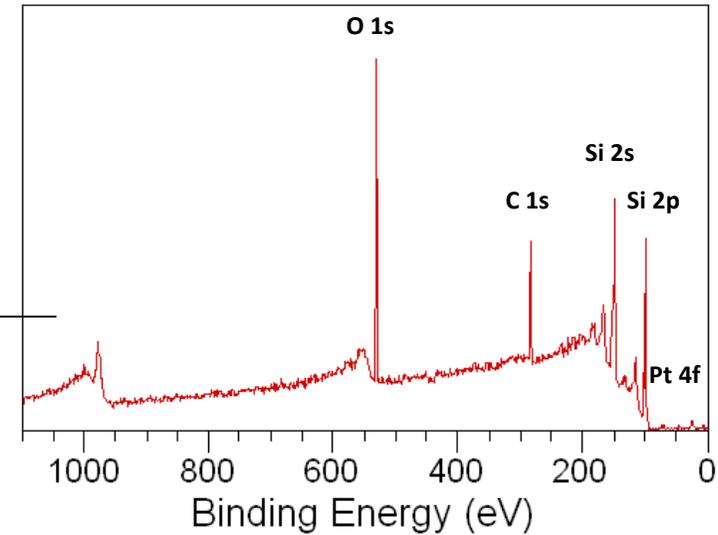


# XPS Imaging: Porous Silicon Pixel Array

## Pt catalyzed etching of patterned porous silicon



Cross-correlated, low-magnification XPS image after step 3 for the Pt 4f<sub>7/2</sub> (shown in orange) and C 1s (shown in blue) core levels measured at 74 and 285 eV, respectively. The image confirms the selective deposition of the Pt-complex in the OTS-free areas of the substrate.



Y. Harada, X. Li, P. W. Bohn, R. G. Nuzzo, *JACS*, **123**, 8709-8717 (2001).



# XPS Depth Profiling : LIB Solid-state Electrolyte

## Monoatomic ion

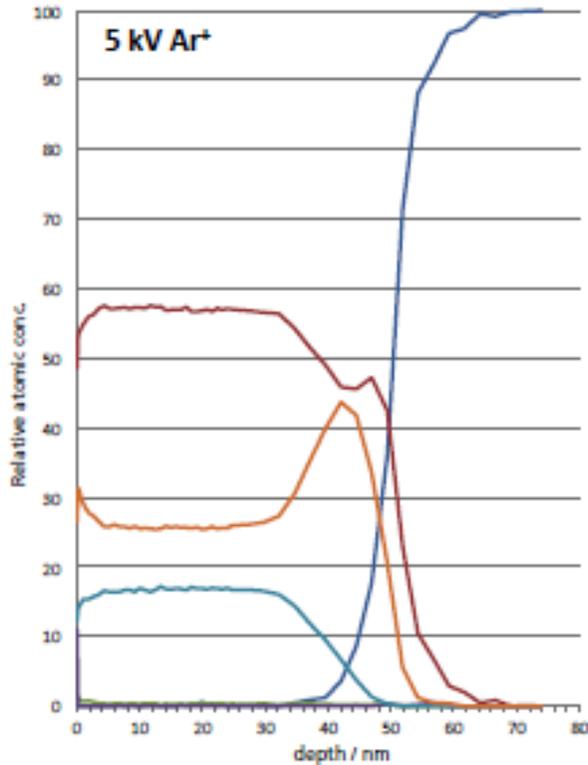


Figure 1(a) Sputter depth profile through ALD LiPON thin film using 5 kV Ar<sup>+</sup>

## Cluster ion

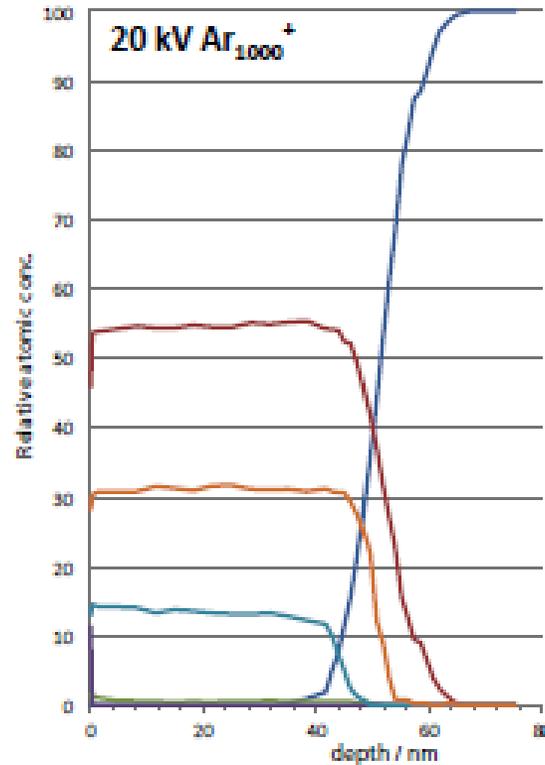


Figure 1(b) Sputter depth profile through ALD LiPON thin film using 20 kV Ar<sub>1000</sub><sup>+</sup>

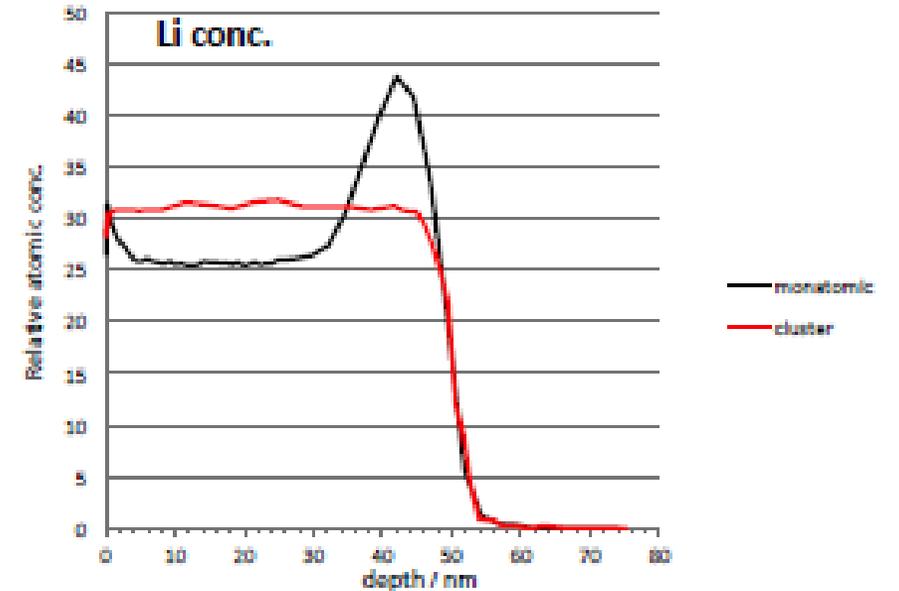


Figure 1(c) comparison of the Li concentration through the same sample generated using monoatomic and cluster ion projectiles.



Image credit: <https://www.kratos.com/>

# Technique Comparison: Resolution vs. Detection Limit

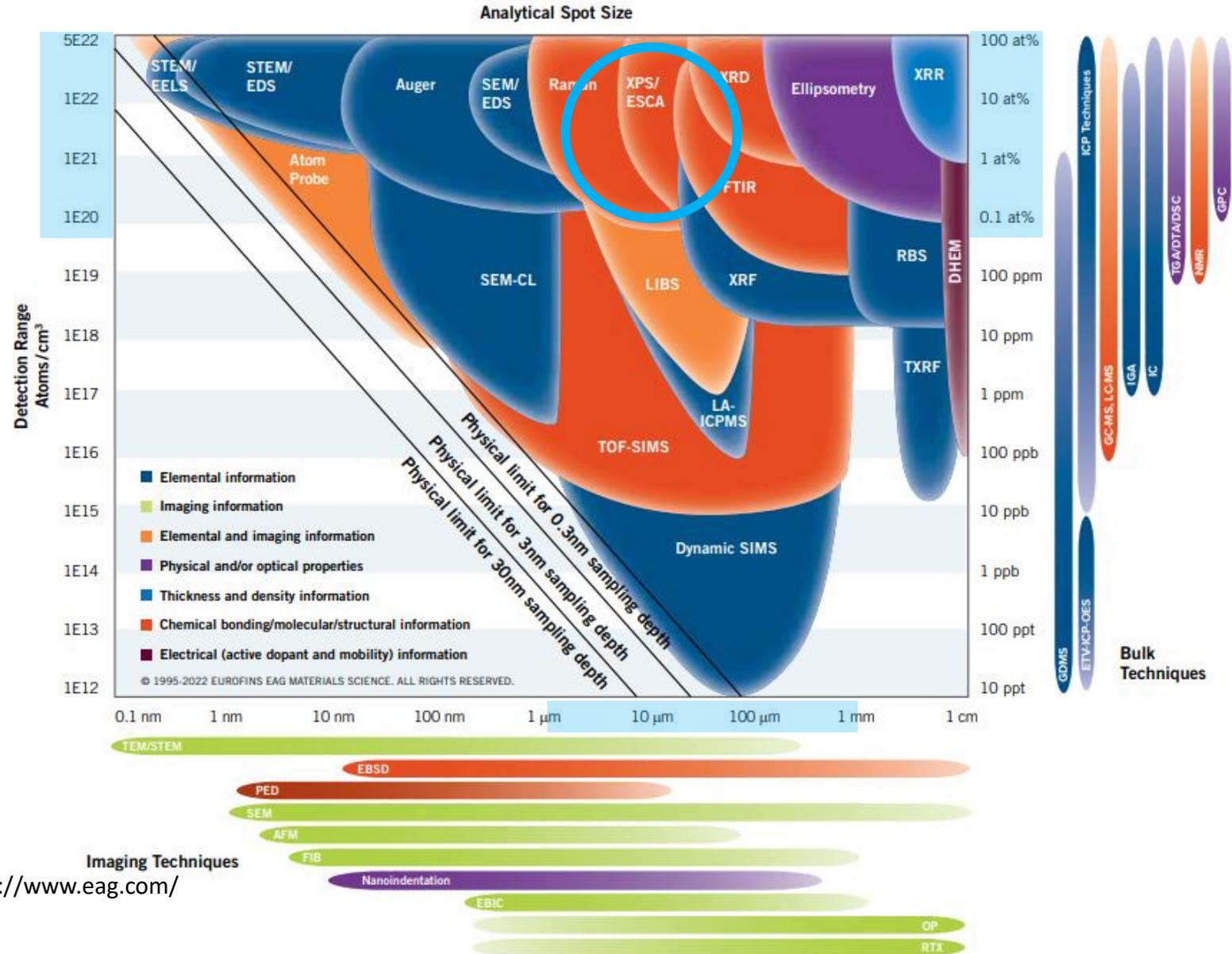


Image credit: <https://www.eag.com/>

# Technique Comparison: Typical Analysis Depth

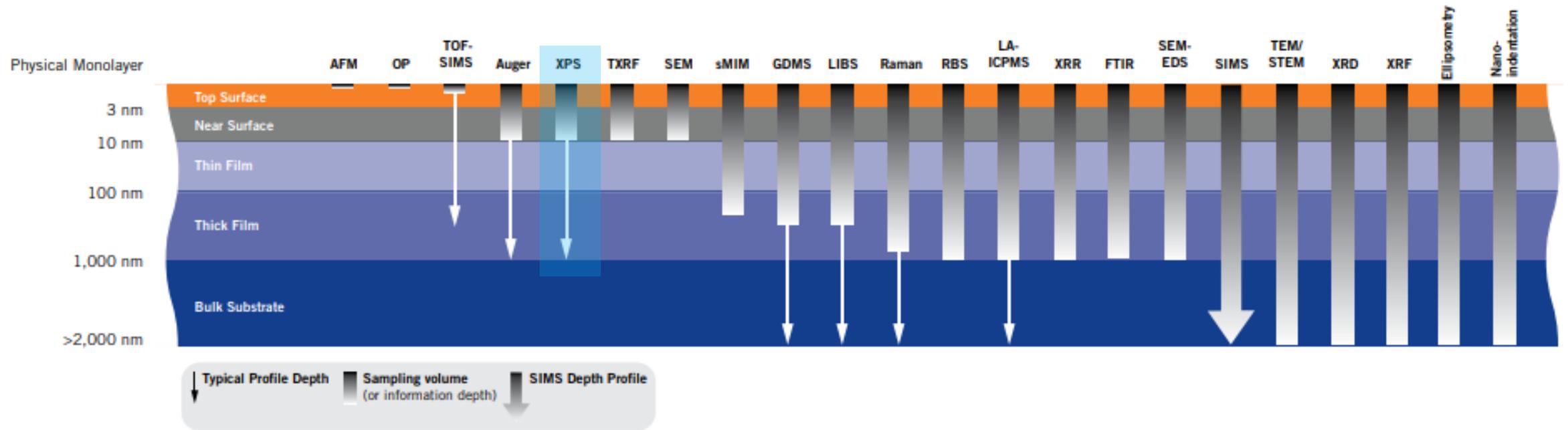
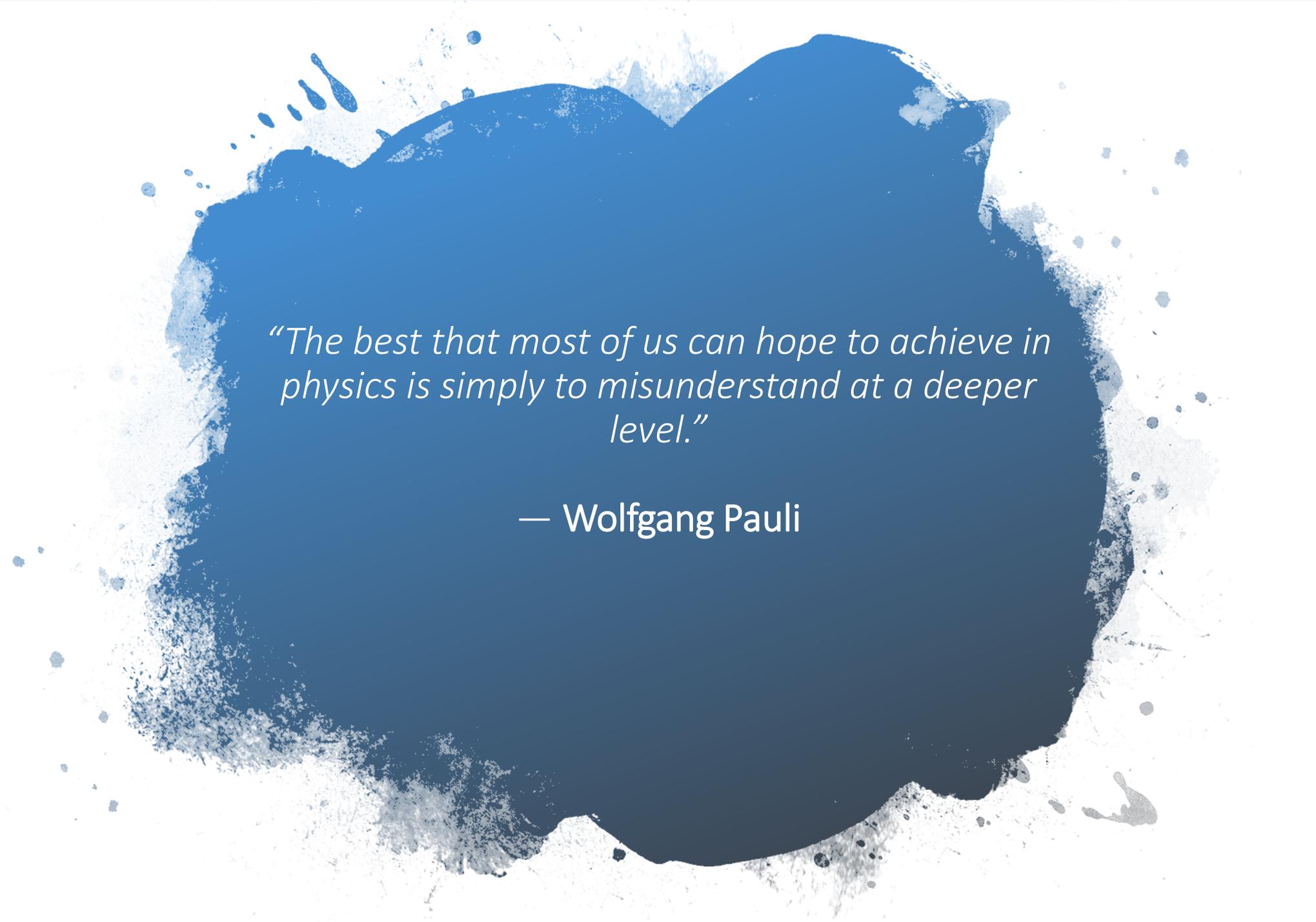


Image credit: <https://www.eag.com/>



*“The best that most of us can hope to achieve in physics is simply to misunderstand at a deeper level.”*

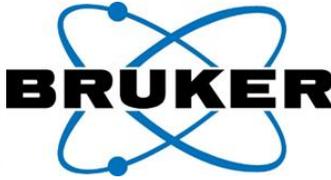
— Wolfgang Pauli

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