

X-ray Photoelectron Spectroscopy (XPS)

Rick Haasch, Ph.D.

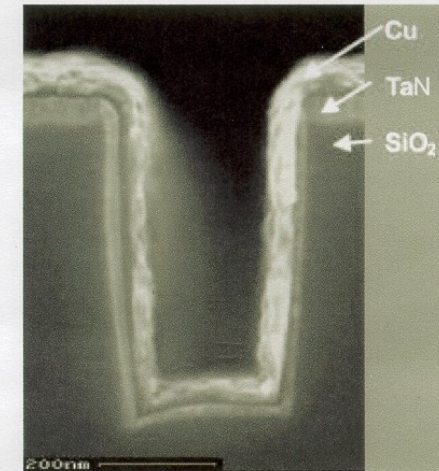
University of Illinois at Urbana-Champaign

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Materials Research Laboratory

GRAINGER COLLEGE OF ENGINEERING

Surfaces and Interfaces



High-power Lithium-ion Battery



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HOME / SUSTAINABILITY SCIENCE / BATTERIES / DAHN UNVEILS MILLION MILE BATTERY IN GROUND-BREAKING ARTICLE

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EMAIL SIGN UP



Dahn Unveils Million Mile Battery in Ground-breaking Article

Posted on September 25, 2019 by Frances Chaves




Elon Musk promised—and Jeff Dahn delivered! With the publishing of a [ground-breaking paper](#) in the *Journal of The Electrochemical Society* (JES), Dahn announced to the world that Tesla may soon have a battery that makes their robot taxis and long-haul electric trucks viable. Dahn and his research group is Tesla's battery research partner. [Dahn says](#) "... that cells of this type should be able to power an electric vehicle for over one million miles and last at least two decades in grid energy storage."



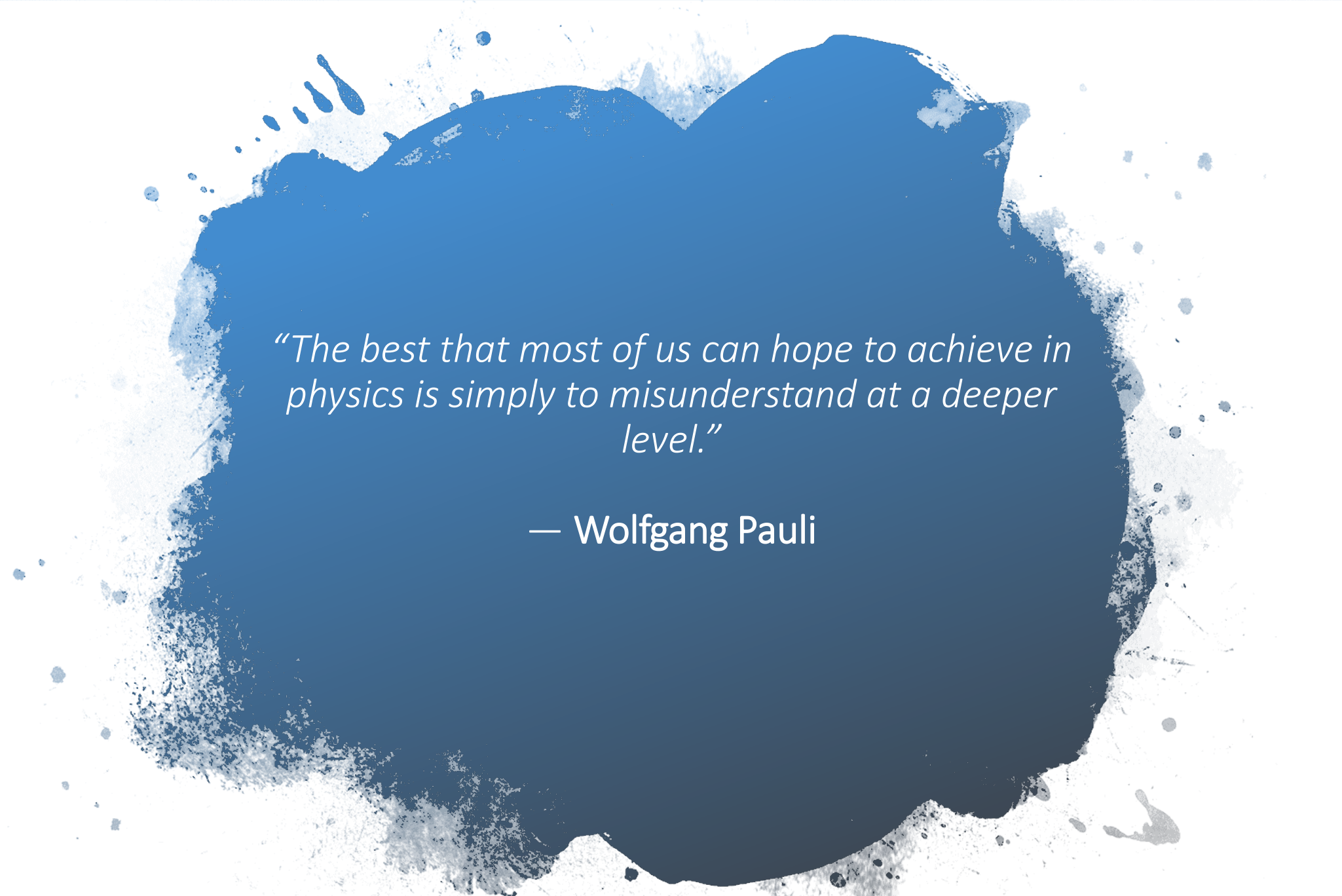
According to [Doron Aurbach](#), JES batteries and energy storage technical editor, "This comprehensive article is expected to be impactful in the field of batteries and energy storage. It is a very systematic study by one of the most renowned and prestigious electrochemistry groups in the world. It was a pleasure for me as a technical editor to handle this paper. It substantiates all the statements about the truly high quality and importance of JES, one of the leading and most prestigious journals in electrochemistry."





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

— Wolfgang Pauli



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

— Wolfgang Pauli

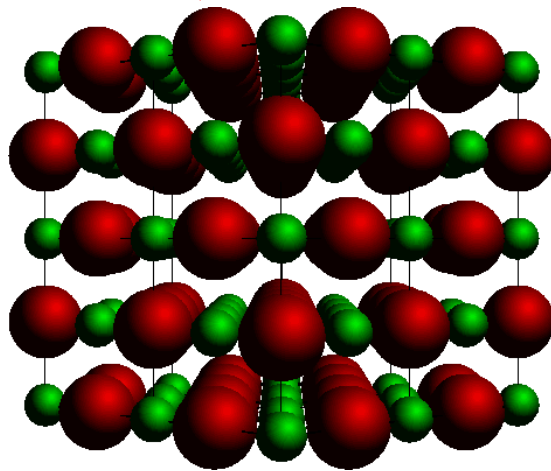
Particle Surface Interactions

Primary beam
(source)

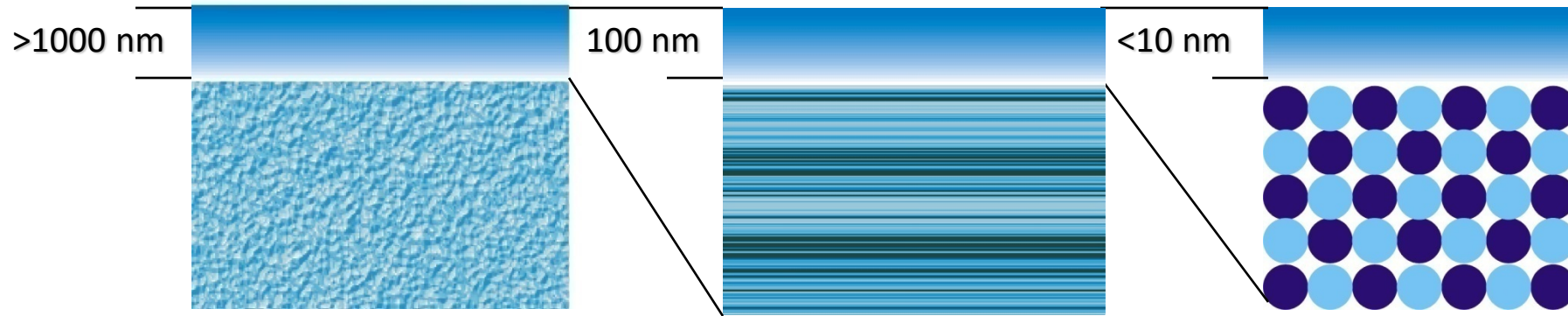
Ions
Electrons
Photons

Secondary beam
(spectrometers, detectors)

Ions
Electrons
Photons



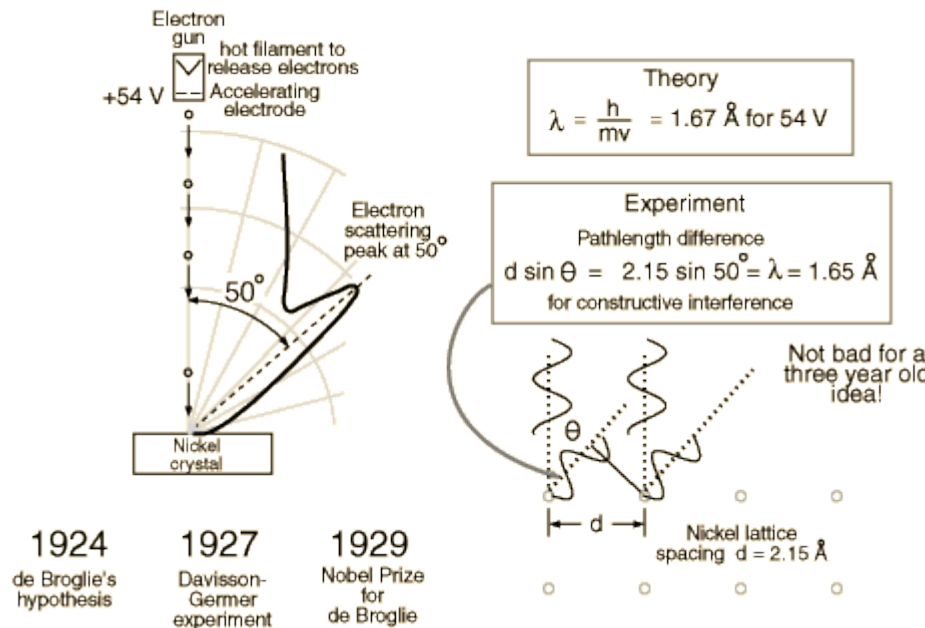
What is the Surface?



Bulk Analysis

Thin-film Analysis

Surface Analysis



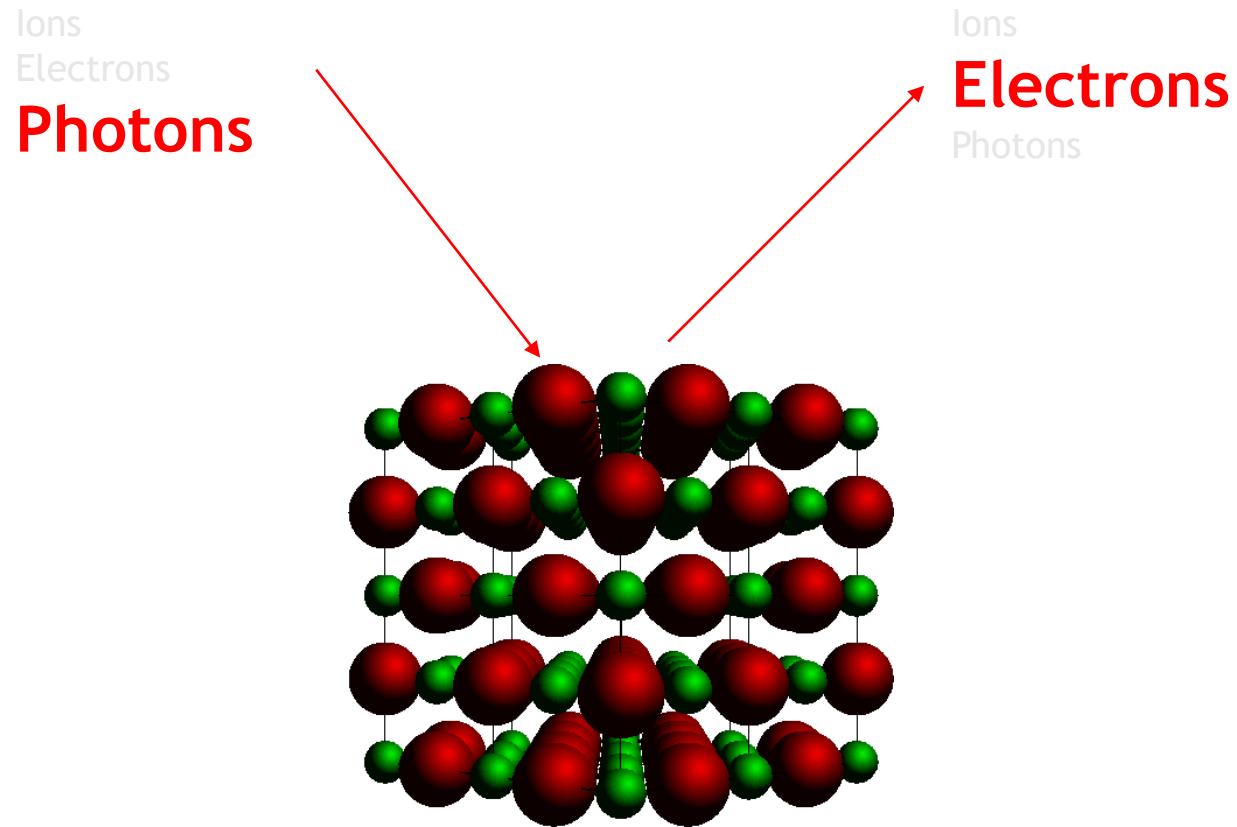
For an electron with KE = 1 eV and rest mass energy of 0.511 MeV, the de Broglie wavelength is **1.23 nm** (~1000X less than a 1 eV photon).

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



Particle Surface Interactions

Photoelectron Spectroscopy



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.

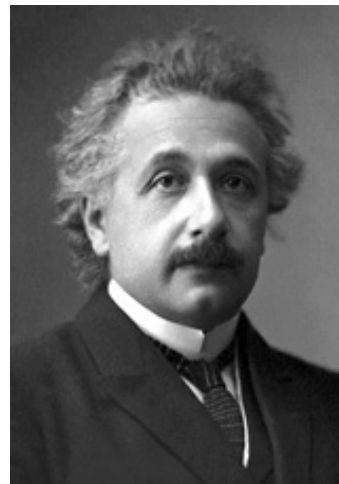
X-ray¹ Photoelectron spectroscopy, based on the photoelectric effect,^{2,3} was developed in the mid-1960's as a practical technique by **Kai Siegbahn** and his research group at the University of Uppsala, Sweden.⁴



Wilhelm Conrad Röntgen



Heinrich Rudolf Hertz



Albert Einstein



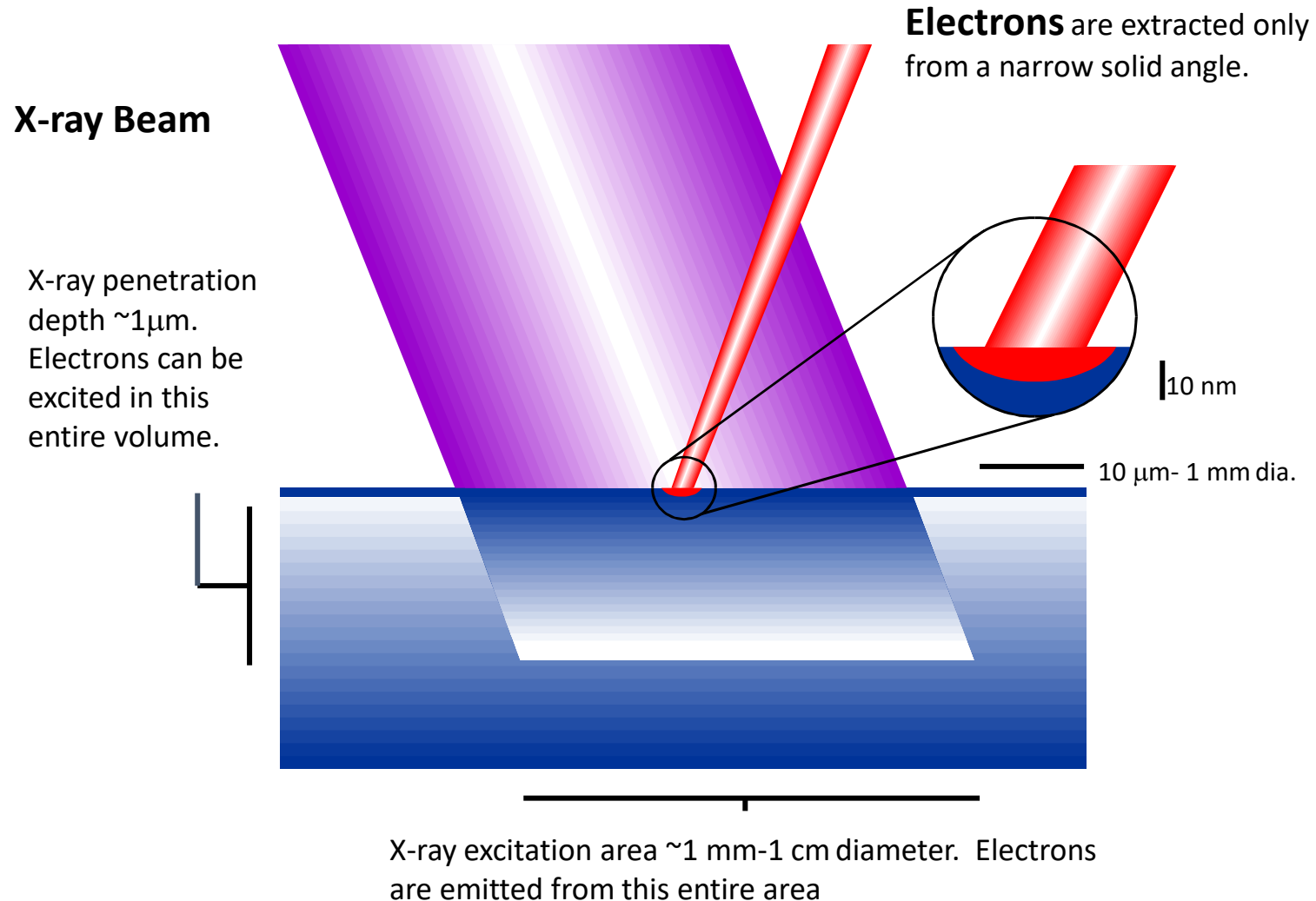
Kai M. Siegbahn



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."

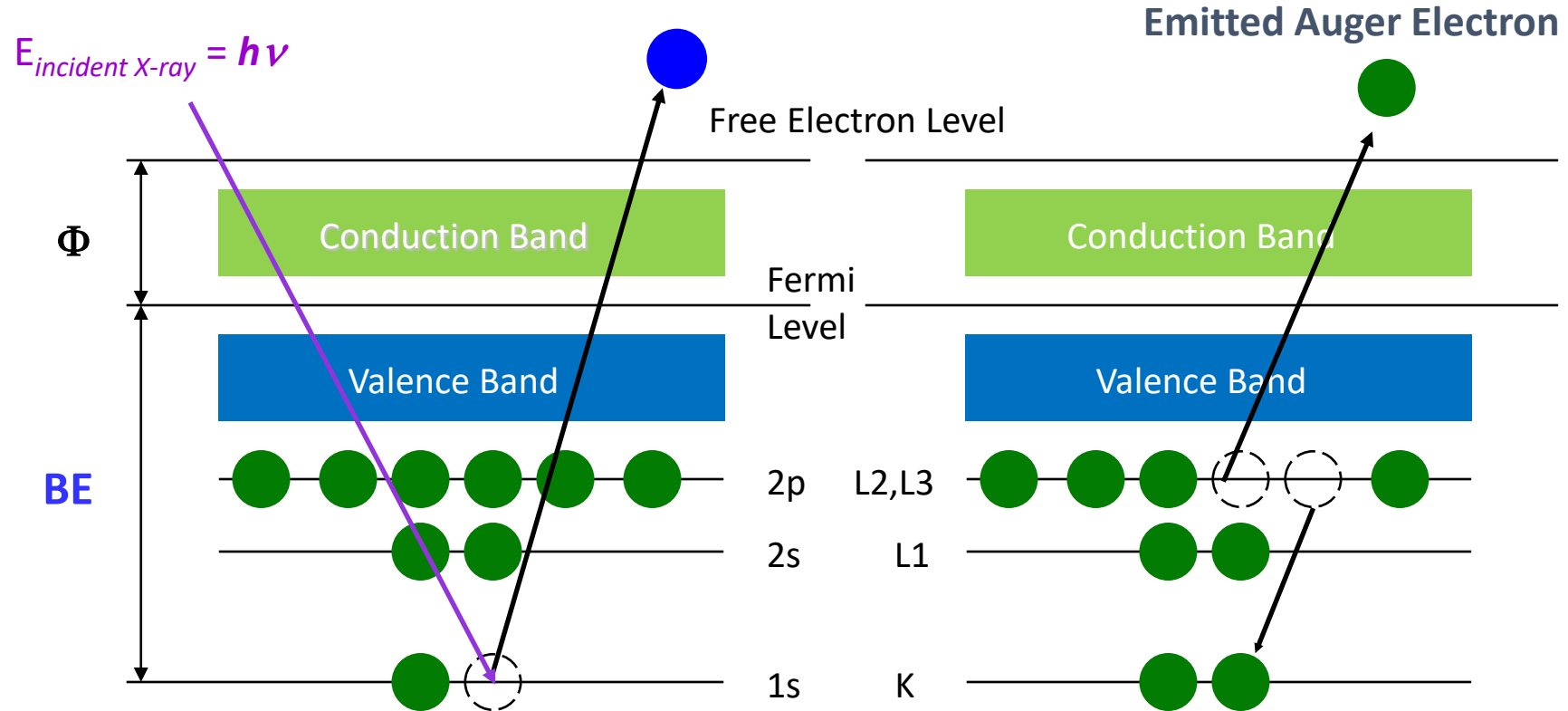


X-ray Photoelectron Spectroscopy Small Area Detection



Photoelectron and Auger Electron Emission

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



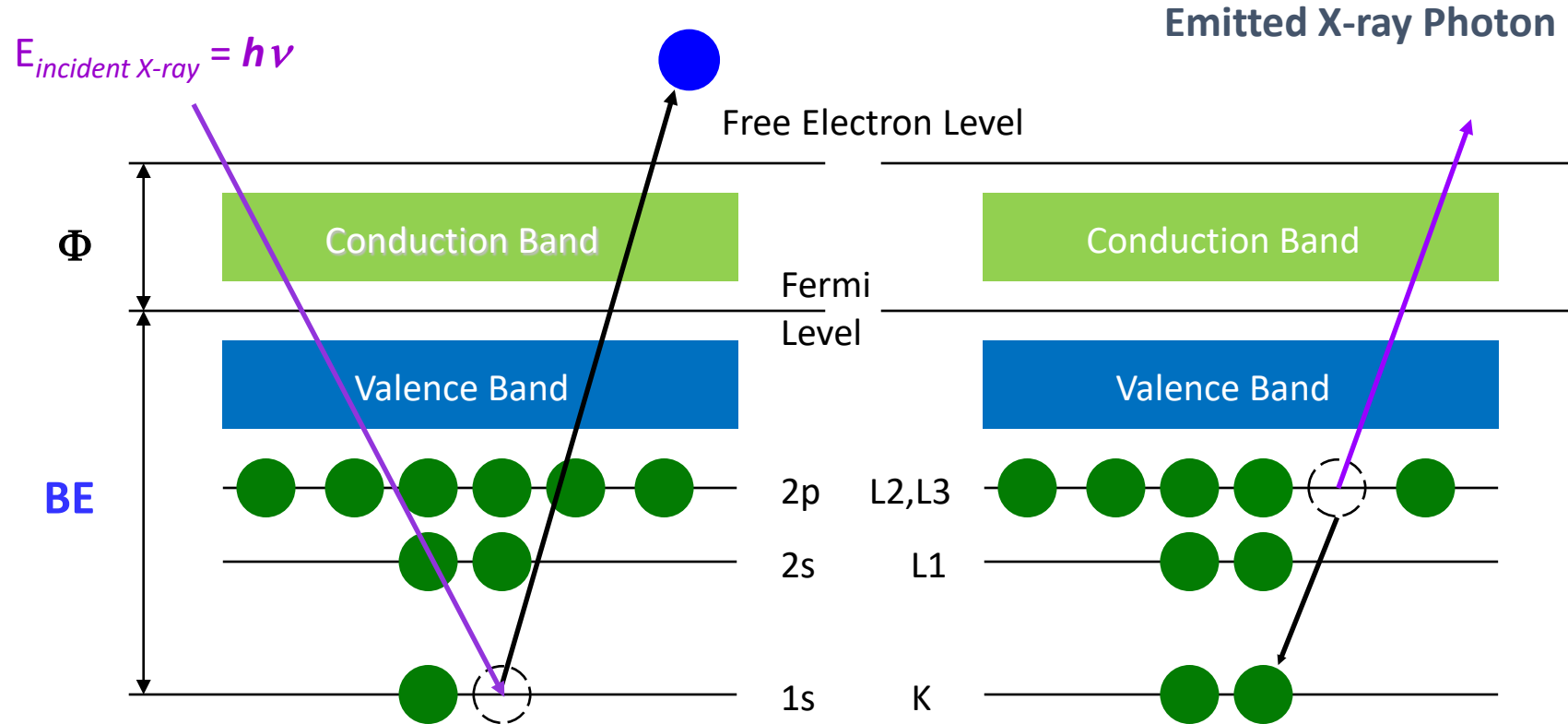
$$\text{Calculate: } BE = h\nu - KE - \Phi_{\text{spec}}$$

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



Photoelectron and Auger Electron Emission

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



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

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



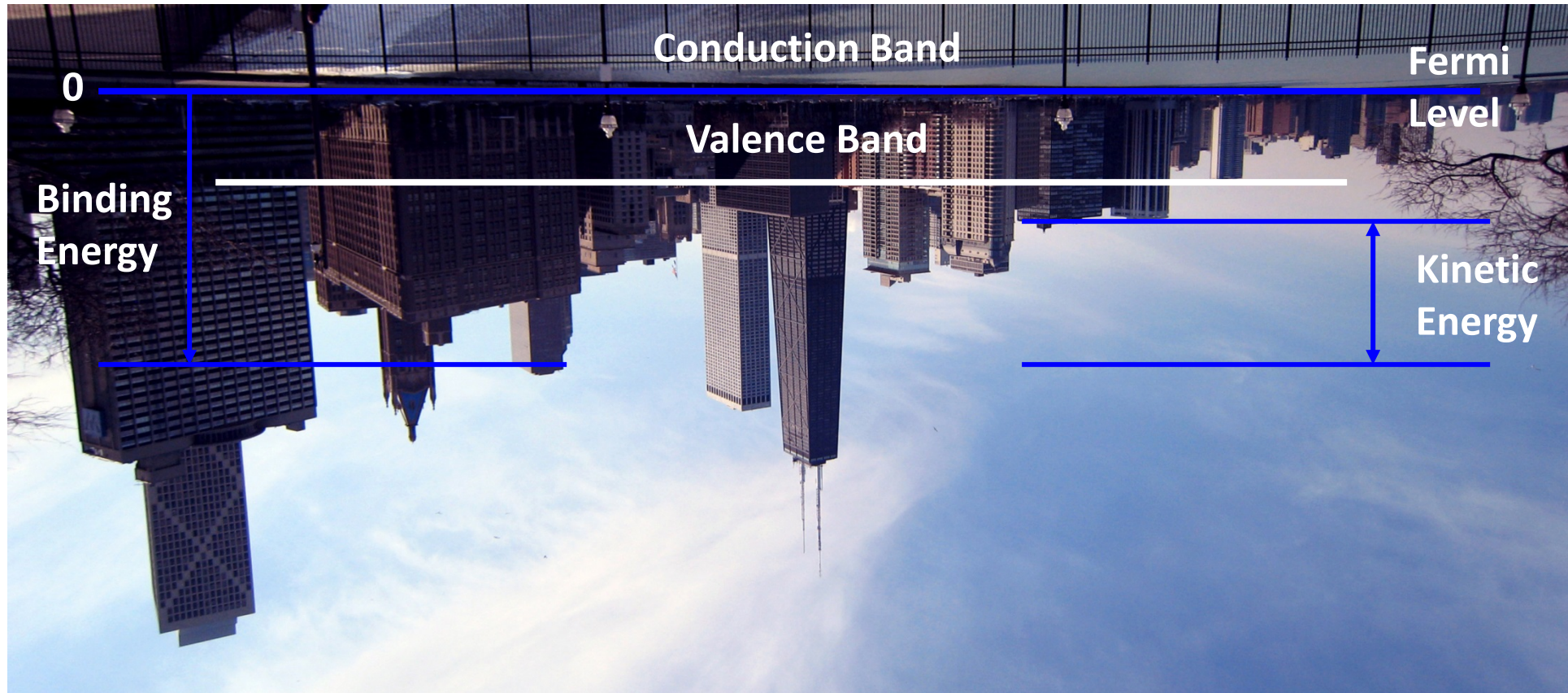
Photoelectron and Auger Electron Emission



Photoelectron and Auger Electron Emission



Photoelectron and Auger Electron Emission



Photoelectron Lines

Auger Electron Lines



Photoelectron and Auger Electron Emission

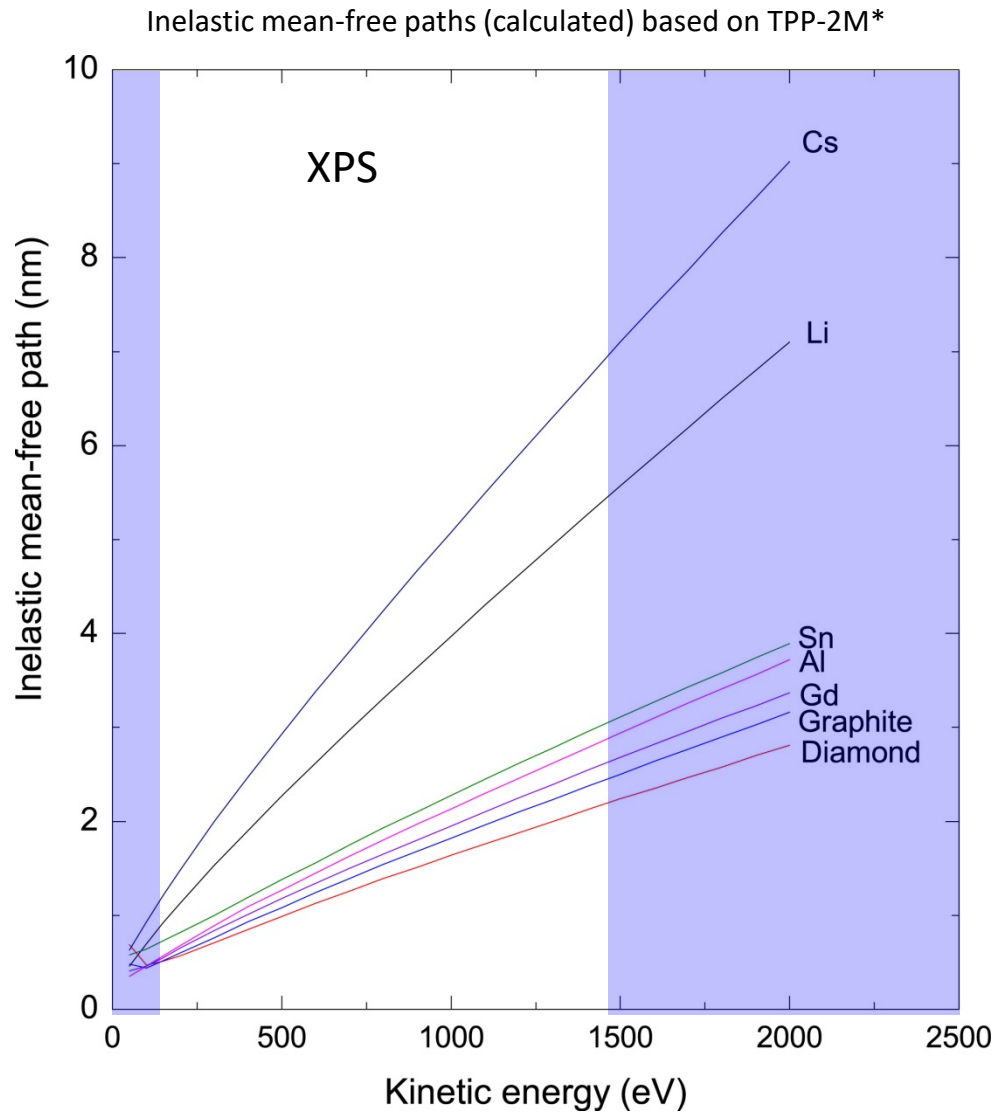


XPS can probe all of the orbitals in only the light elements.
e.g. BE C 1s = 285 eV, Mg 1s = 1304 eV, Au 1s \approx 81000 eV



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:

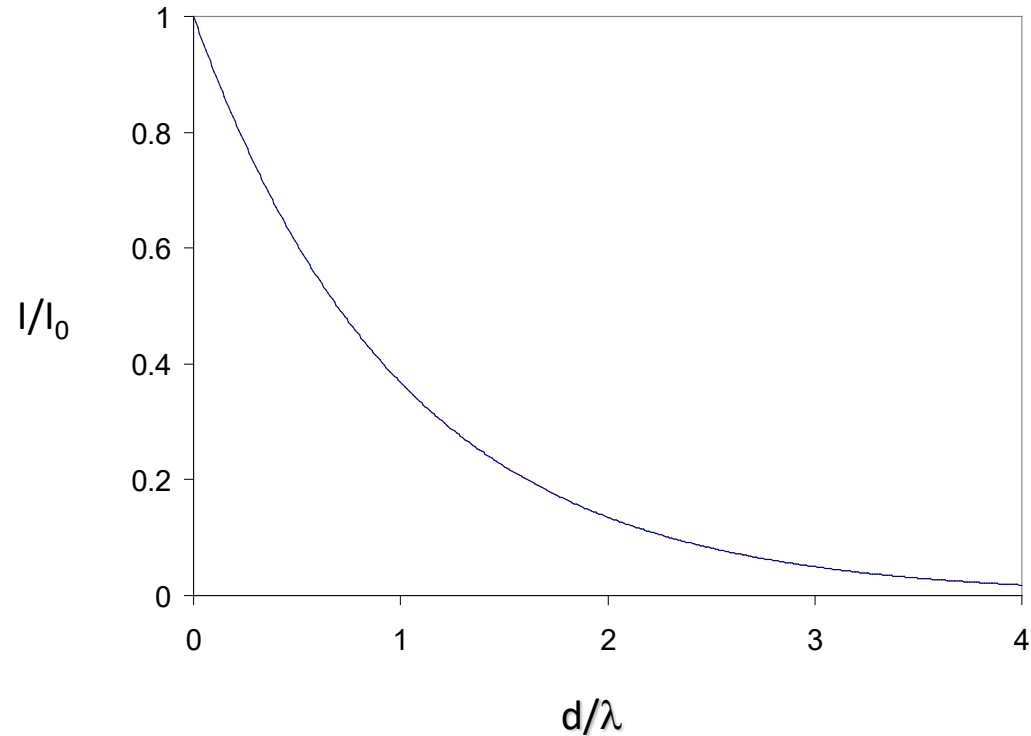
$$I = I_0 \exp(-d/\lambda \cos\theta)$$

where d = depth

λ = 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

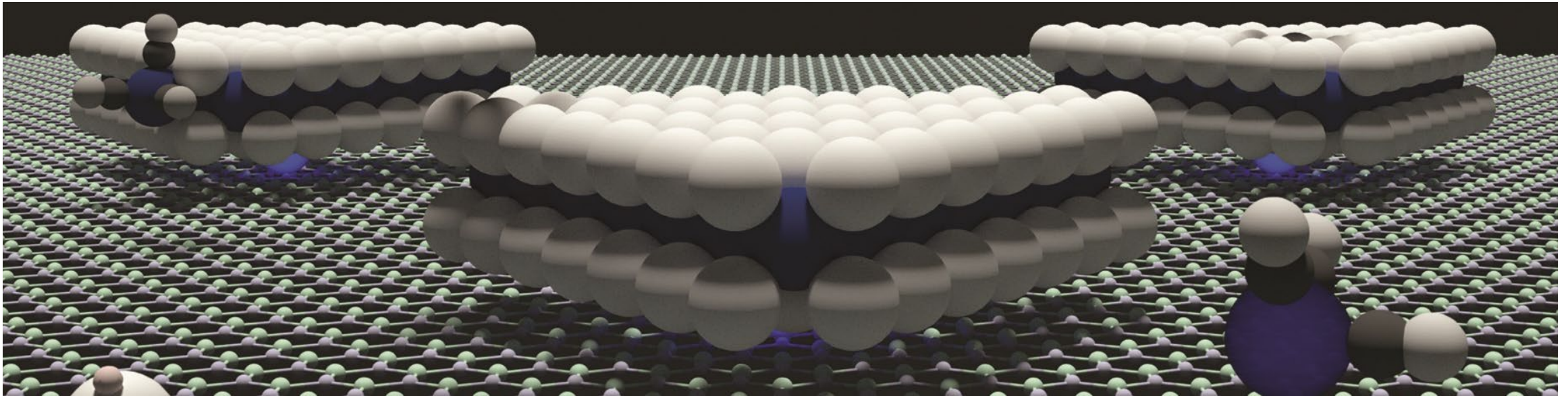
X-ray Photoelectron Spectroscopy

Advantage

Extremely surface sensitive!

Disadvantage

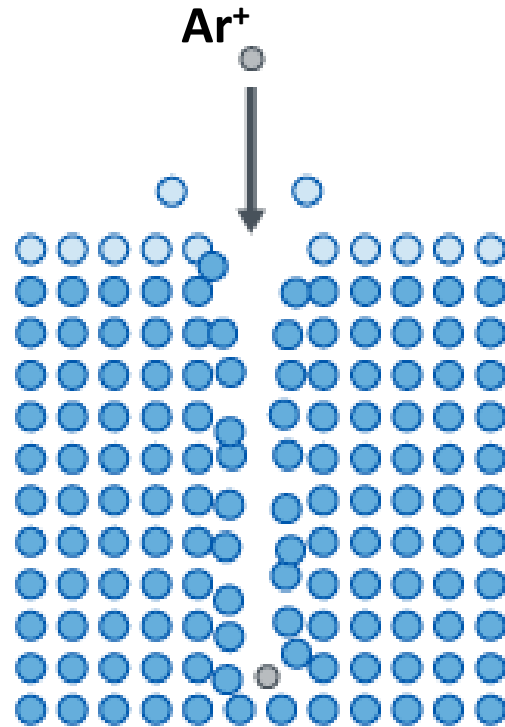
Extremely surface sensitive!



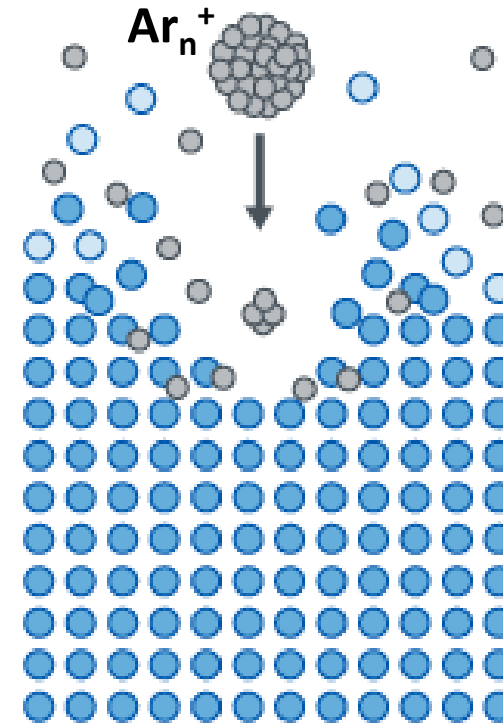
<https://phys.org/news/2019-05-substrate-defects-key-growth-d.html>

Ion Sputtering

Single atomic ion beam



Cluster ion beam

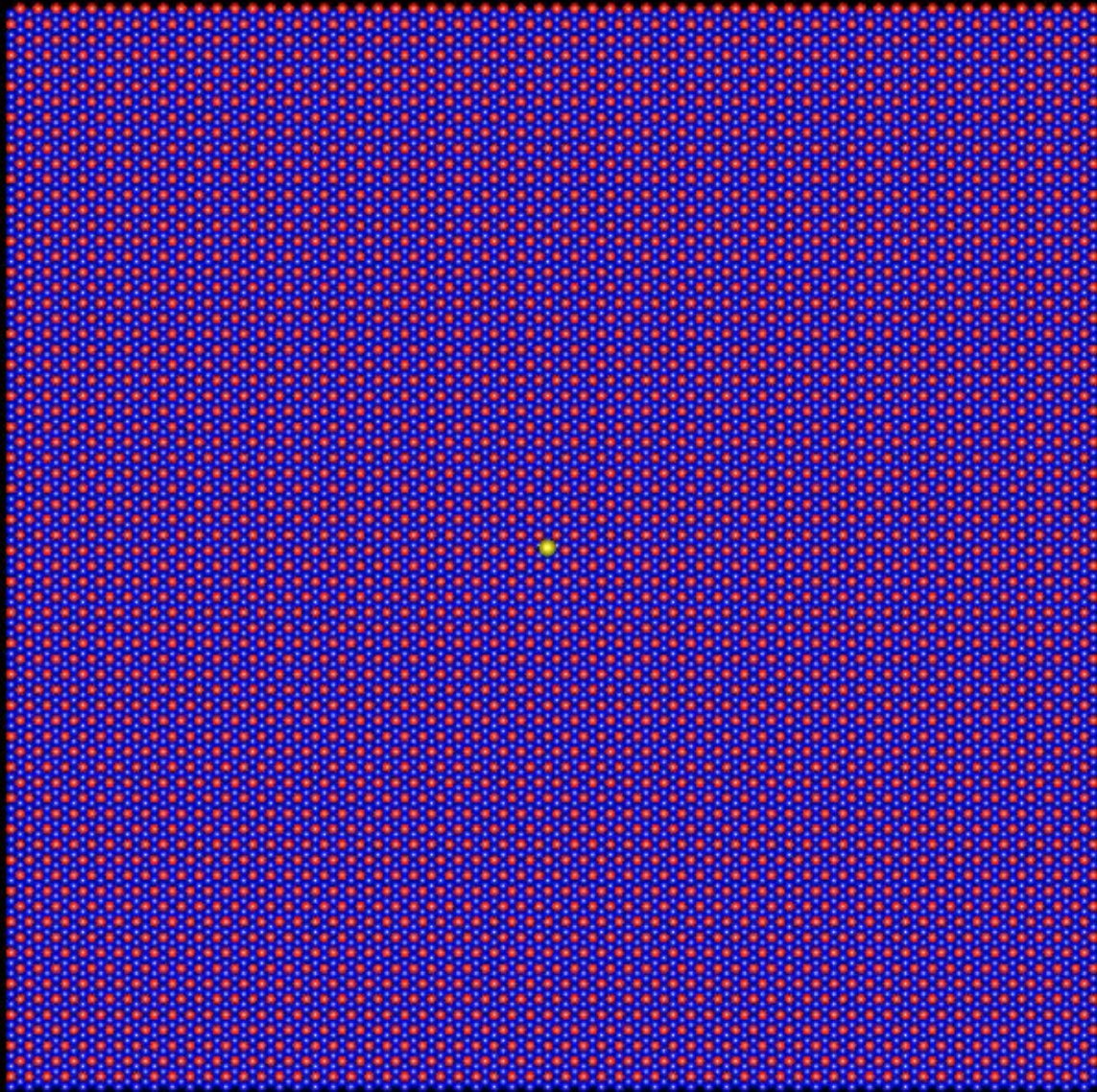


- Ions striking a surface interact with atoms in a series collisions.
- recoiled target atoms in turn collide with atom at rest generating a collision cascade.
- The initial ion energy and momentum are distributed among the target recoil atoms.
- When $E_i > 1$ keV, the cascade is “linear,” *i.e.* approximated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

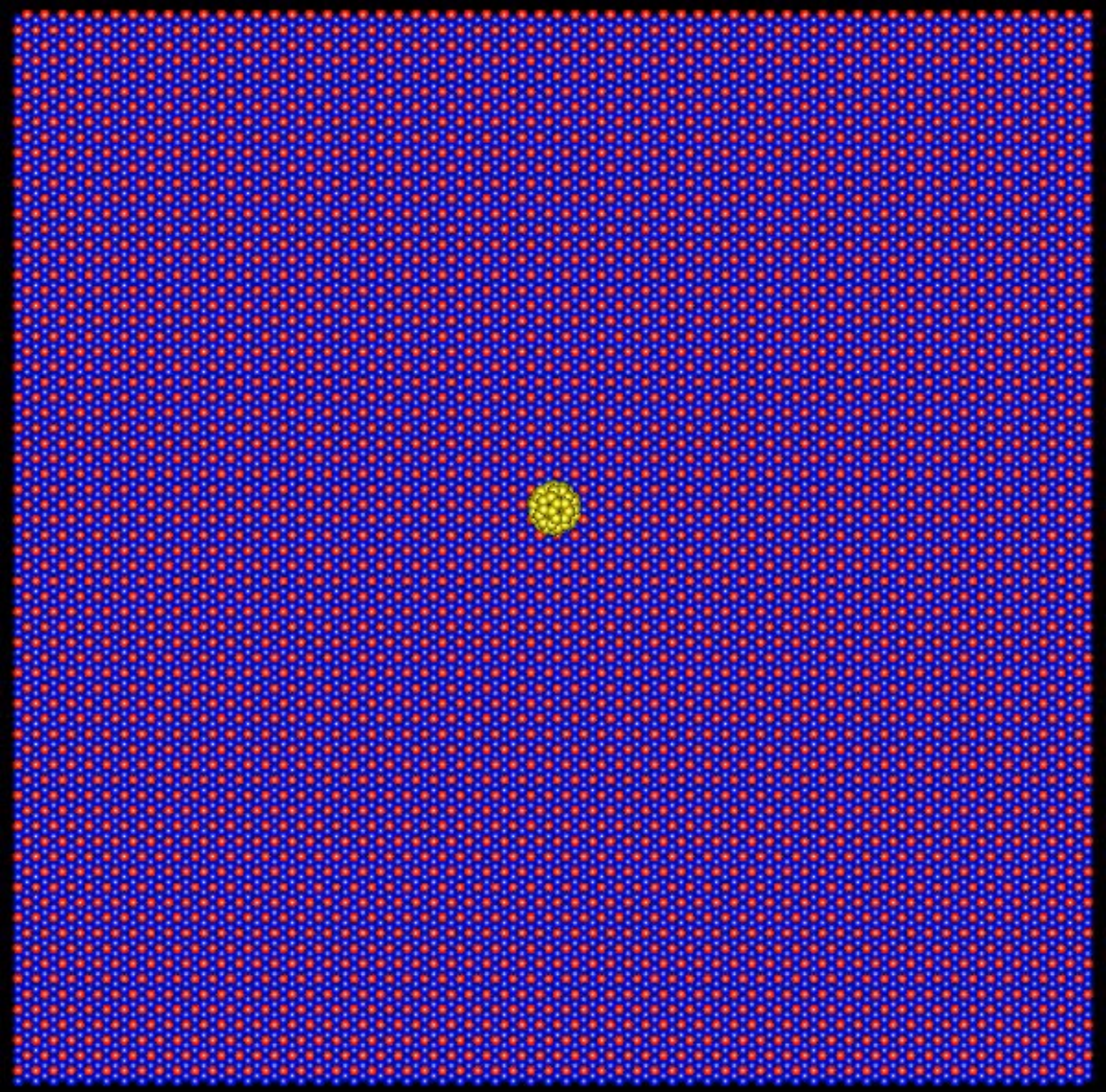


P. Sigmund, “Sputtering by ion bombardment: theoretical concepts,” in *Sputtering by particle bombardment I*, edited by R. Behrish, Springer-Verlag, 1981.
Image credit: <https://ulvac-phi.com/>

15 KeV Ga⁺



15 KeV C₆₀⁺



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

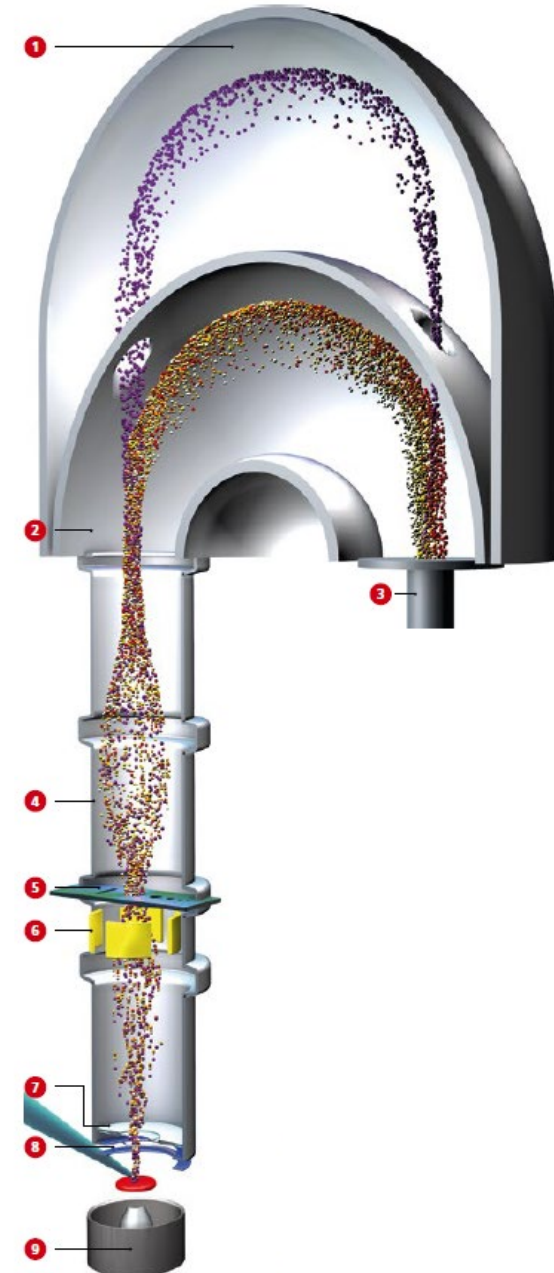
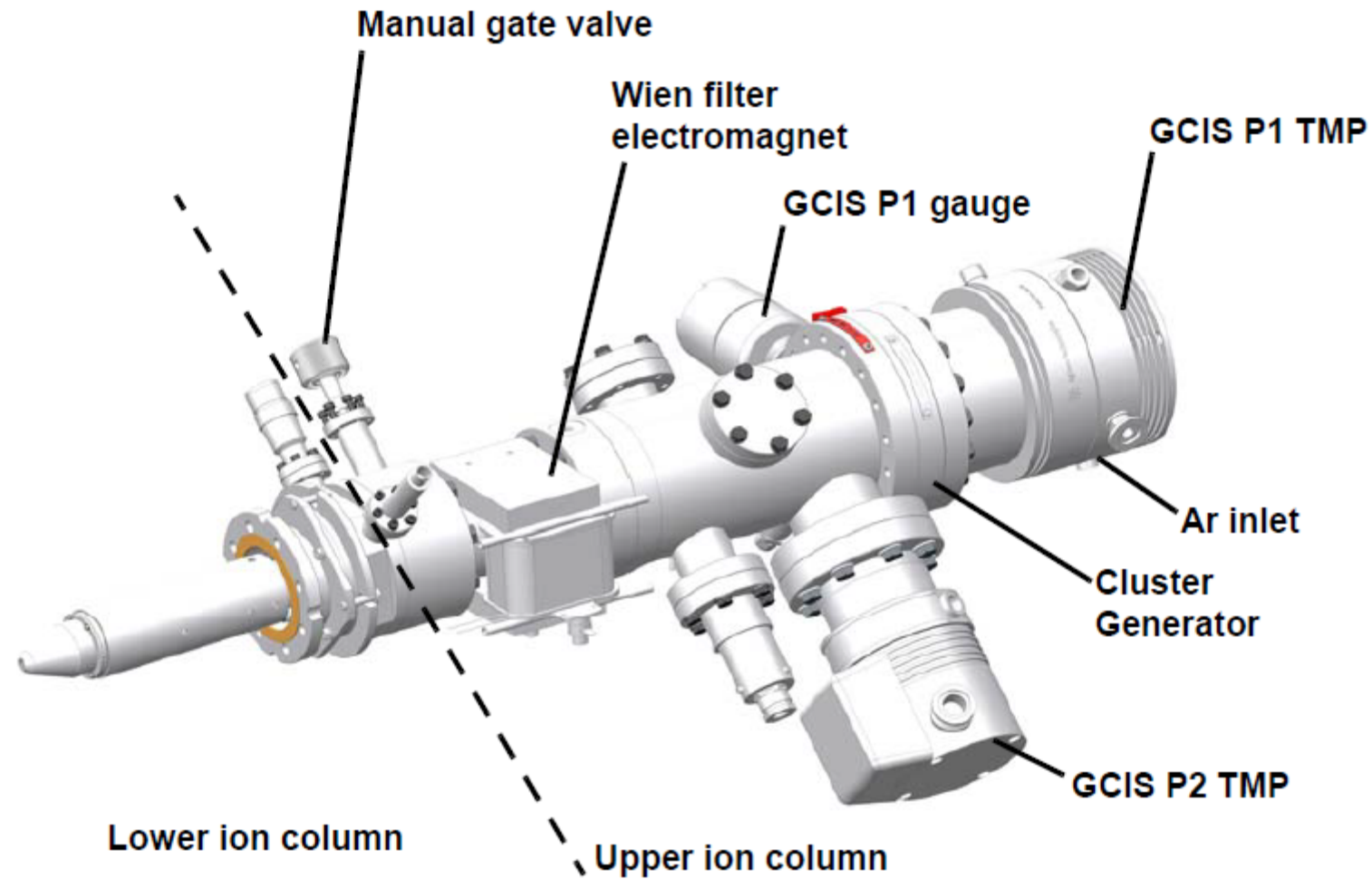
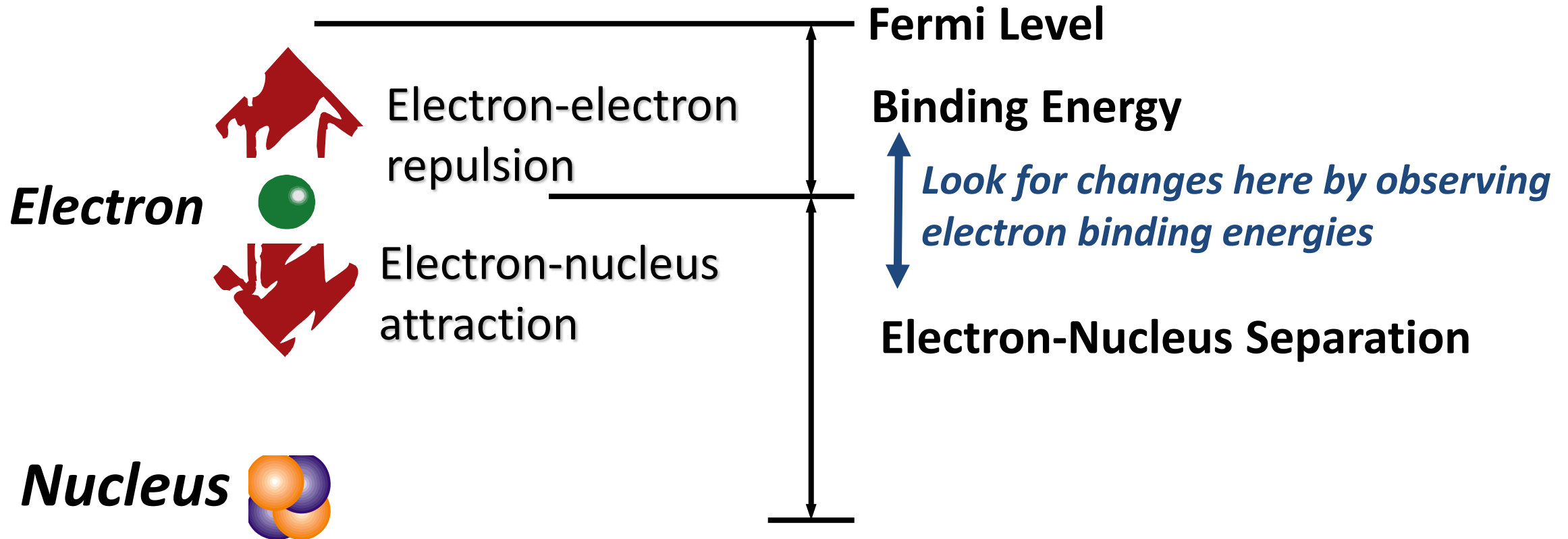


Image credit: <https://www.kratos.com/>

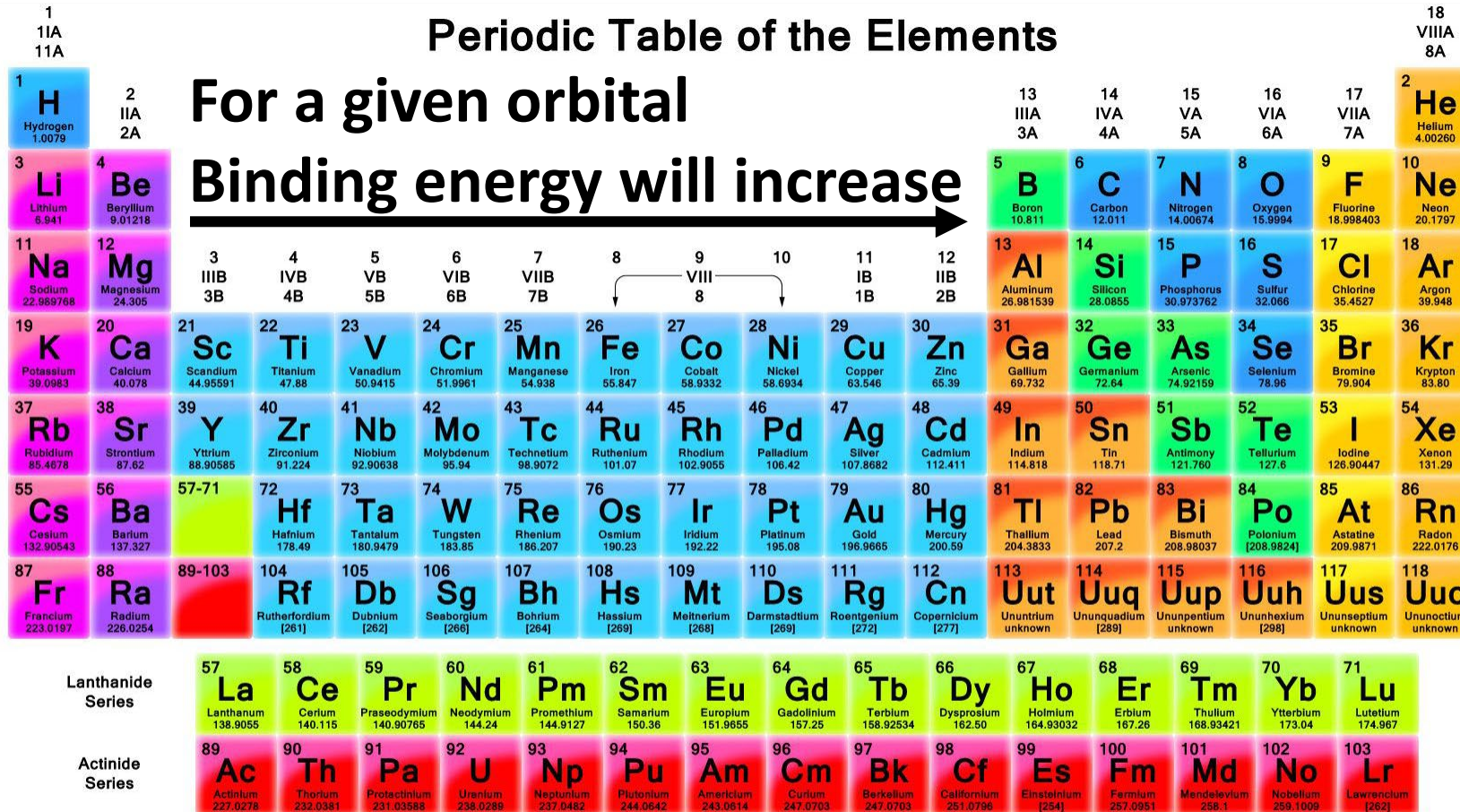
Gas-cluster Ion Source (GCIS)



Pure Element



Elemental Shifts



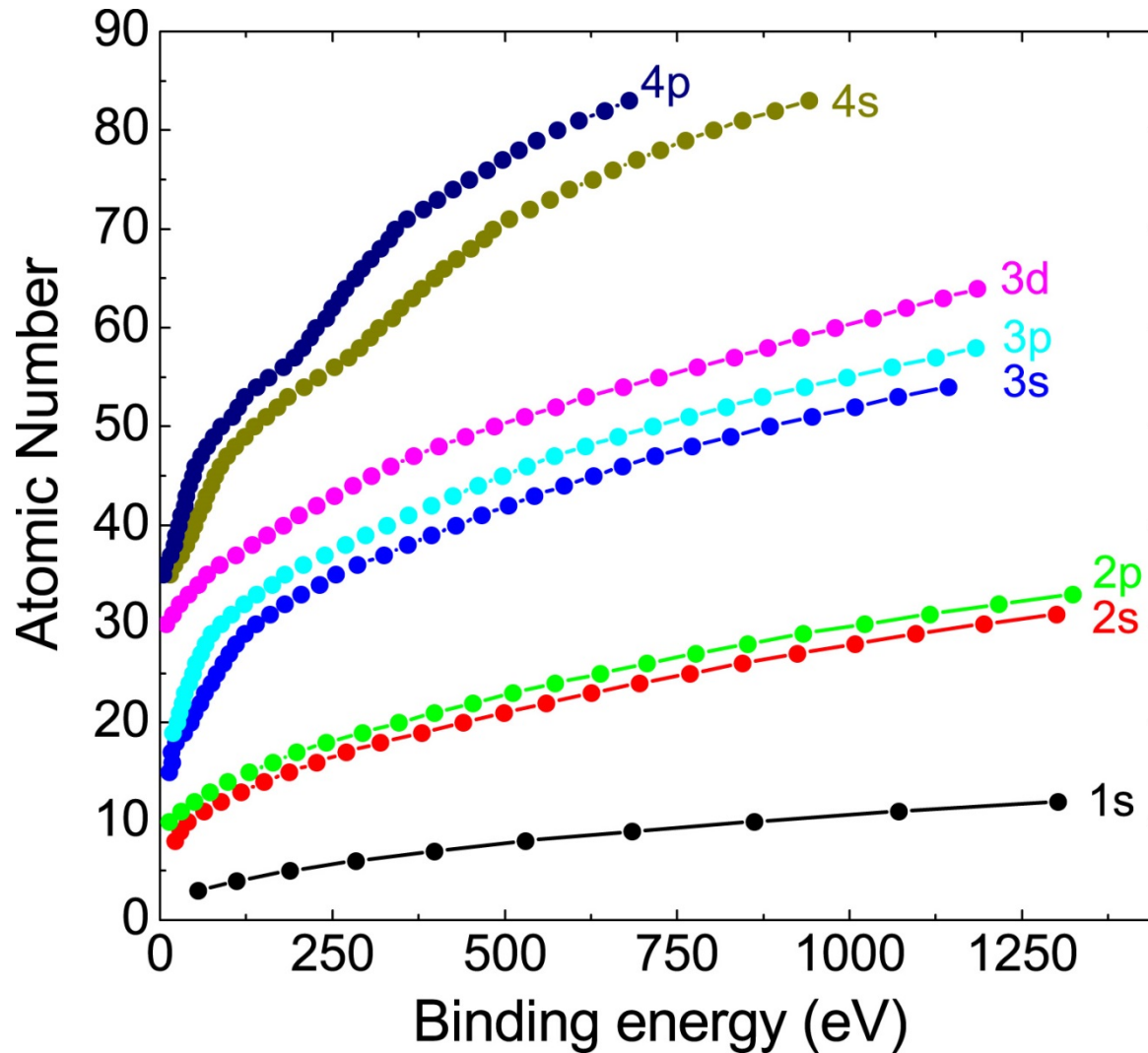
- Alkali Metal
- Alkaline Earth
- Transition Metal
- Basic Metal
- Semimetals
- Nonmetals
- Halogens
- Noble Gas
- Lanthanides
- Actinides

©okiraa.com

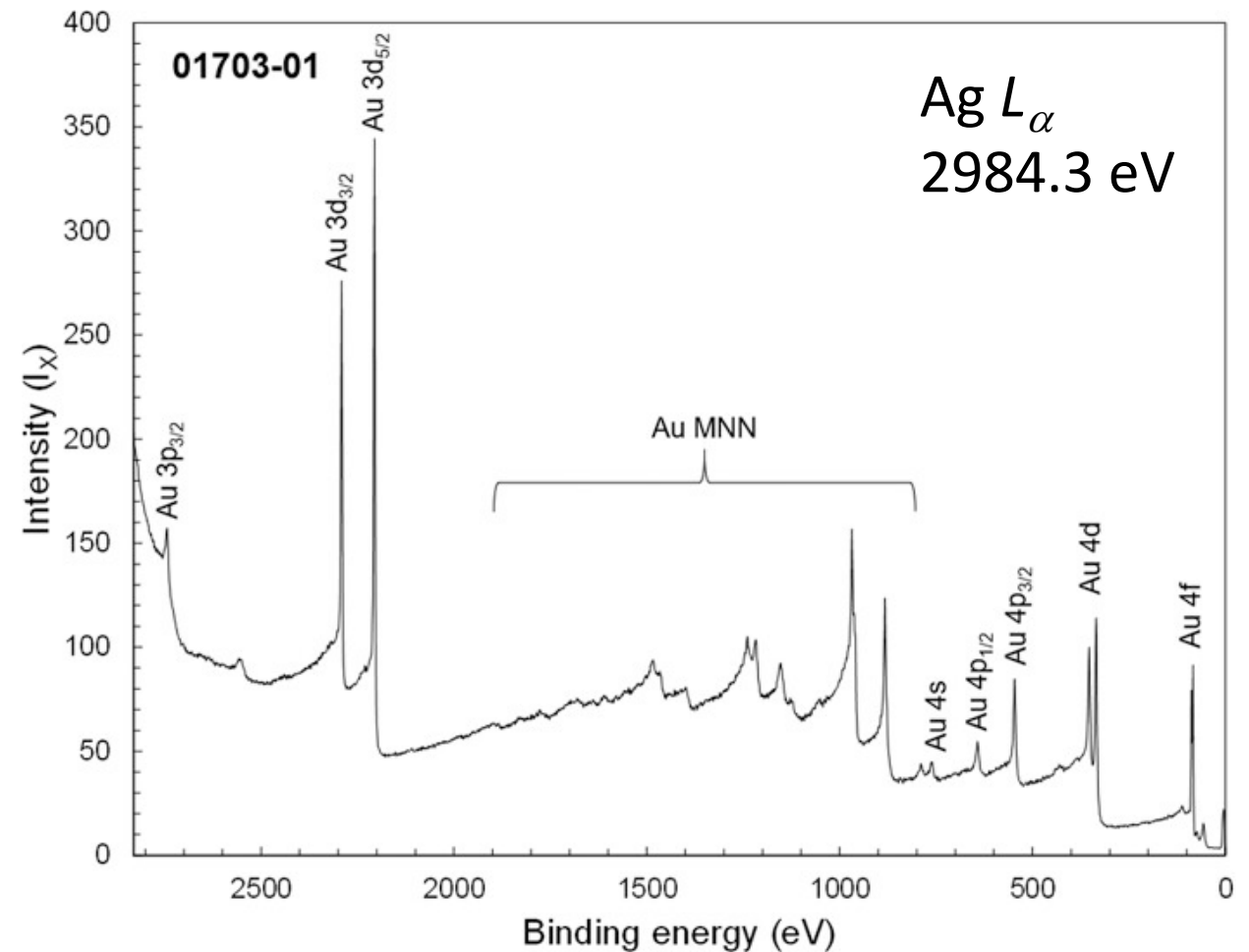
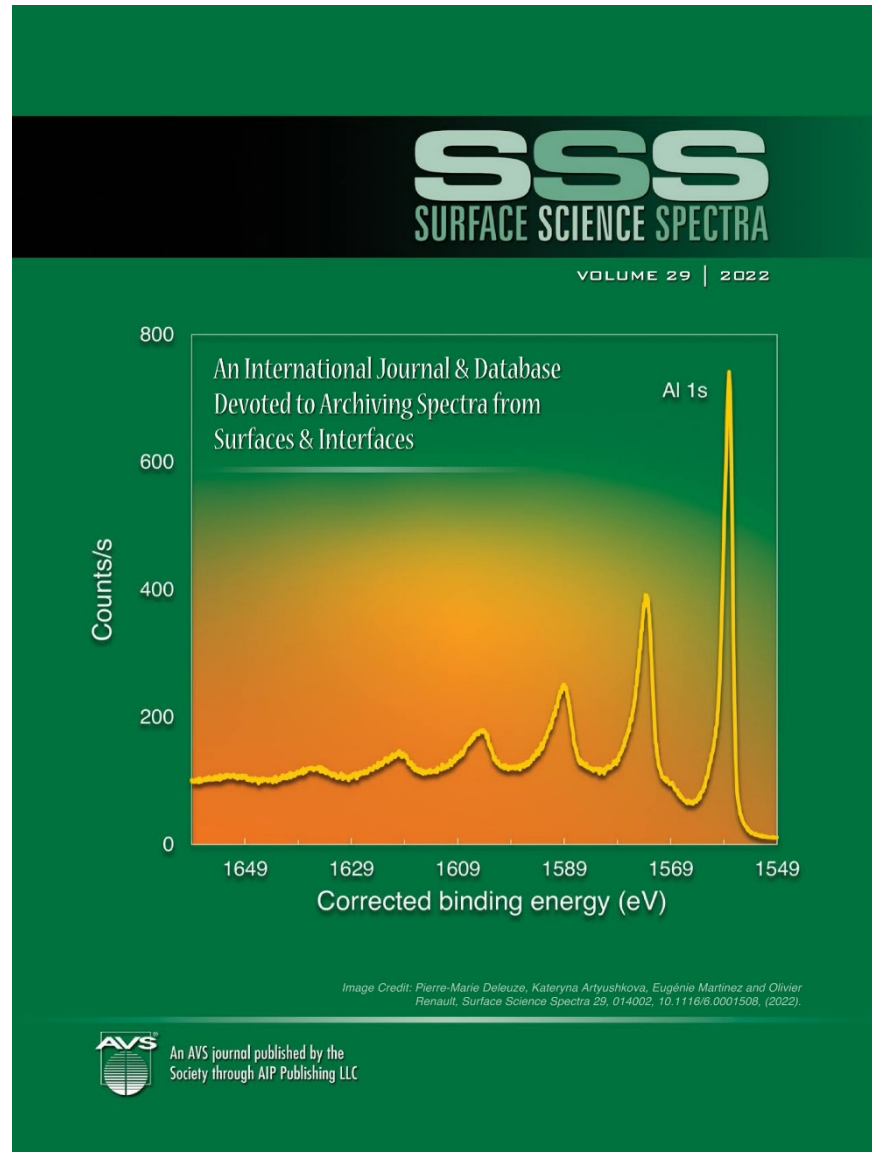


Elemental Shifts

Core Level Binding Energies



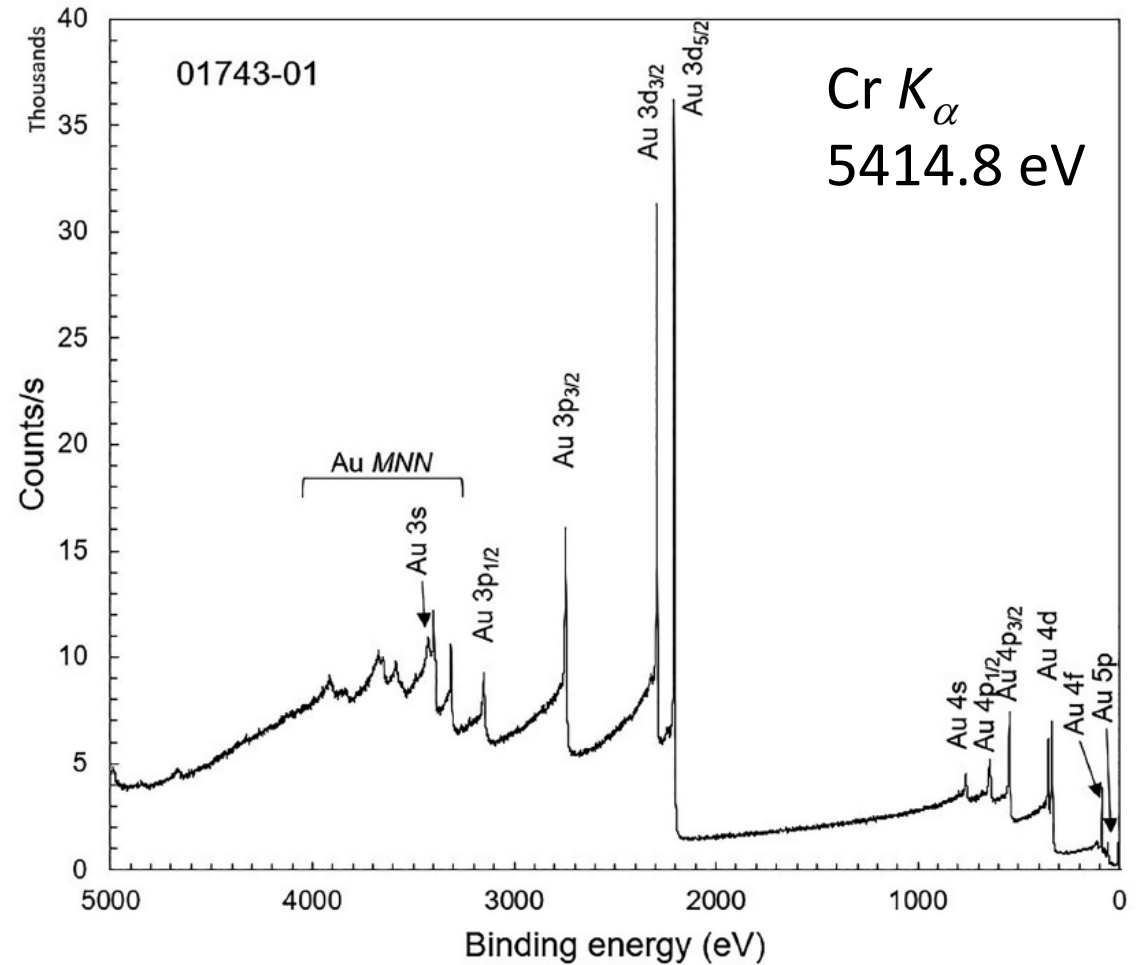
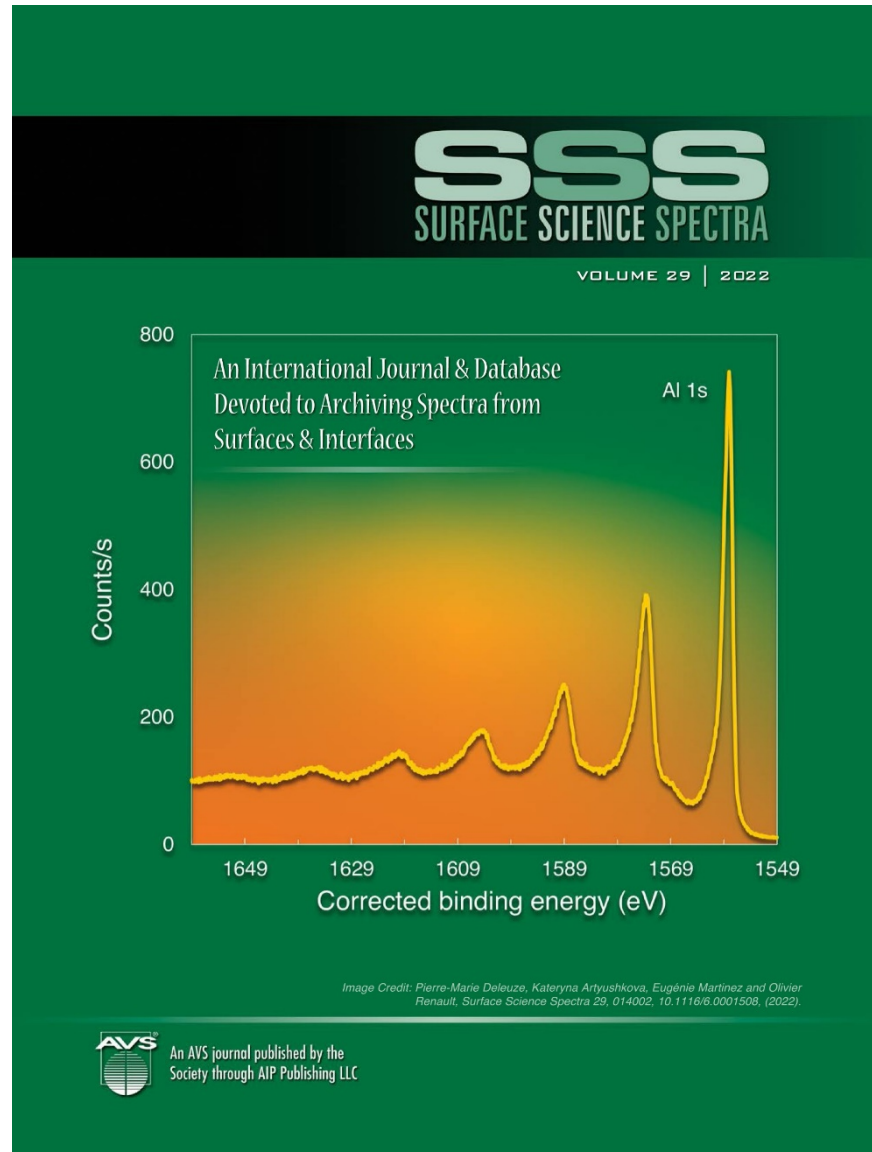
Elemental Shifts – Higher Energy X-ray Sources



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
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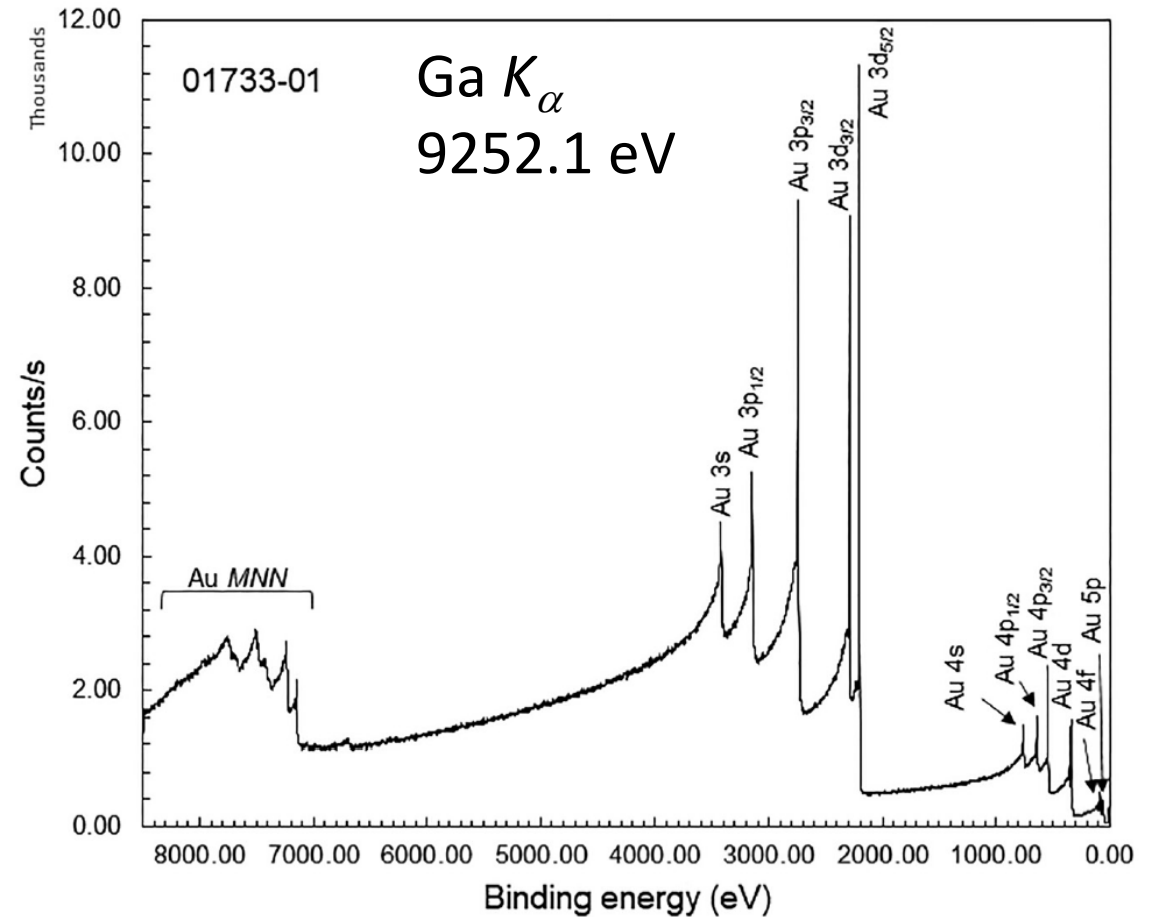
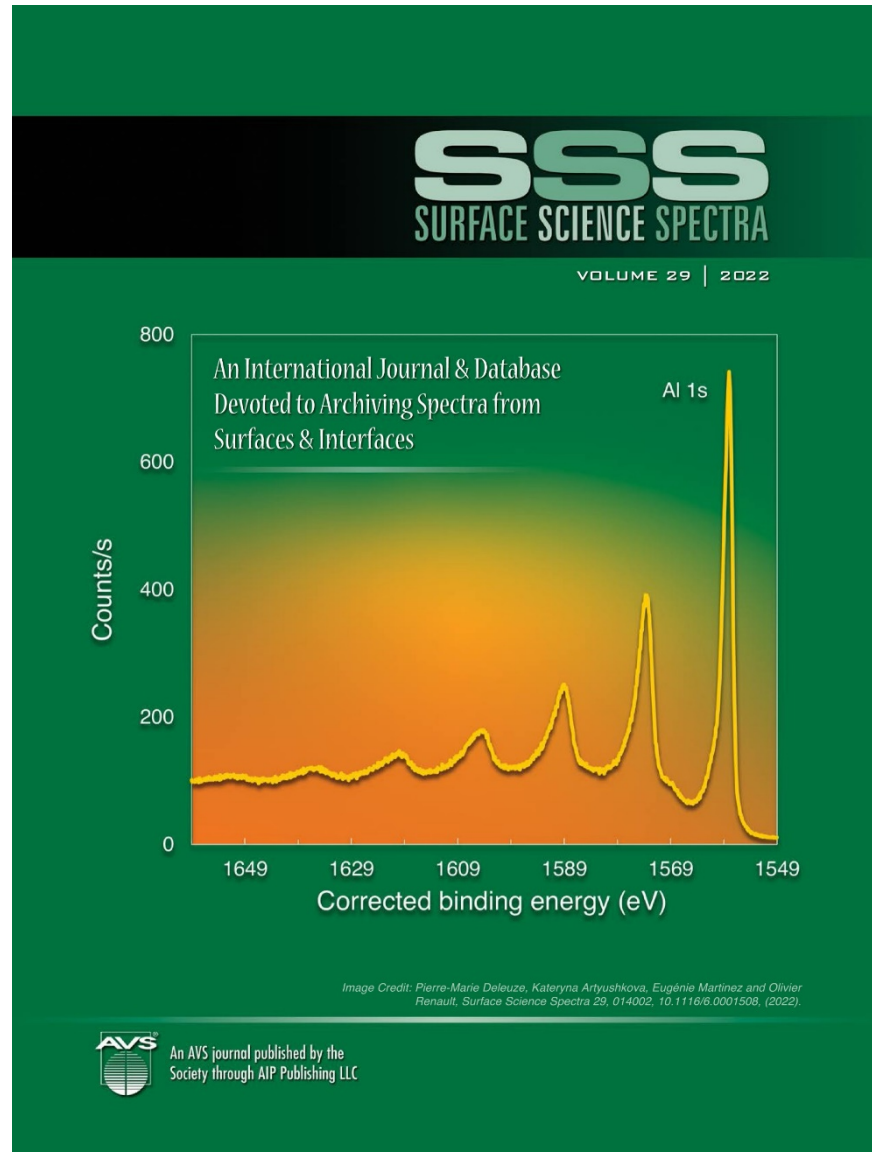
Elemental Shifts – Higher Energy X-ray Sources



I. Hoflijk, A. Vanleenhove, I. Vaesen, C. Zborowski, K. Artyushkova, T. Conard; High energy x-ray photoelectron spectroscopy spectra of Si_3N_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 SiO₂ with Ga K α 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 Sc Scandium 44.95591	22 Ti Titanium 47.88	23 V Vanadium 50.9415	24 Cr Chromium 51.9961	25 Mn Manganese 54.938	26 Fe Iron 55.847	27 Co Cobalt 58.9332	28 Ni Nickel 58.6934	29 Cu Copper 63.546	30 Zn Zinc 65.39

Binding Energy (eV)			
Element	2p _{3/2}	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

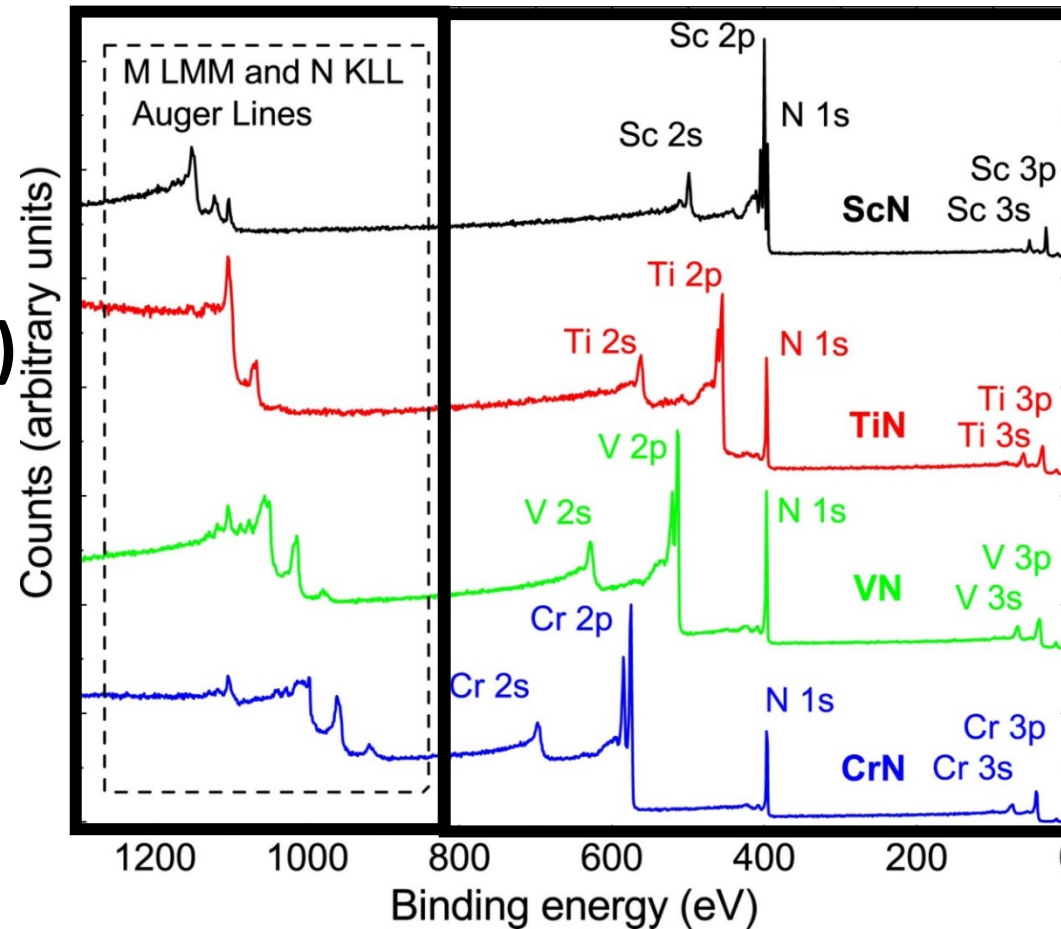


Elemental Shifts: Transition Metal Nitrides

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)

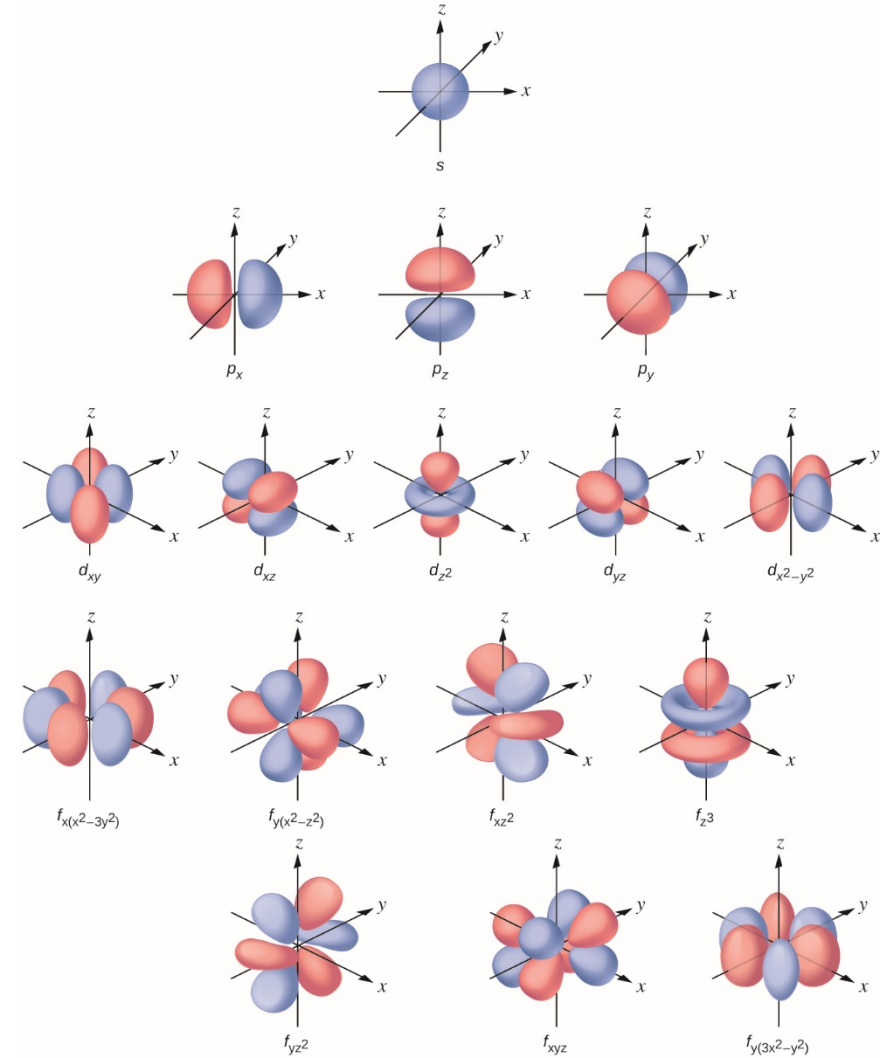
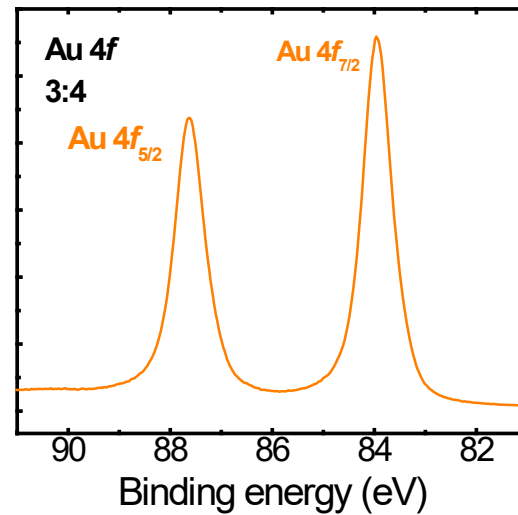
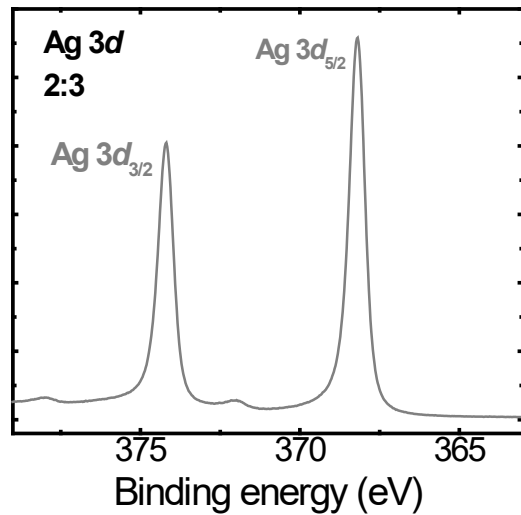
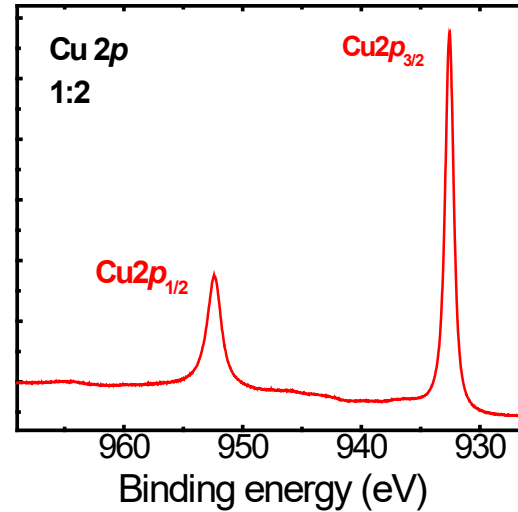
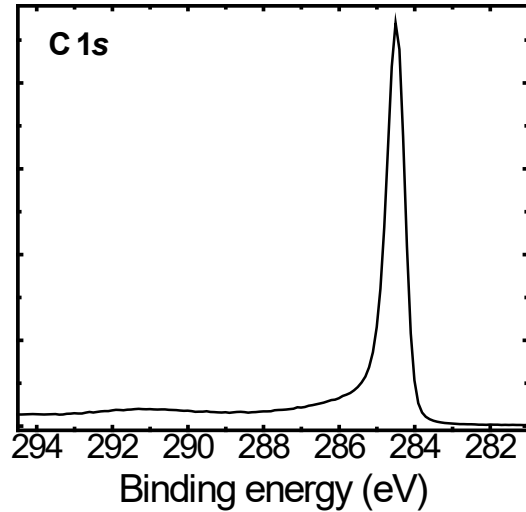


XPS Core-level binding energies increase



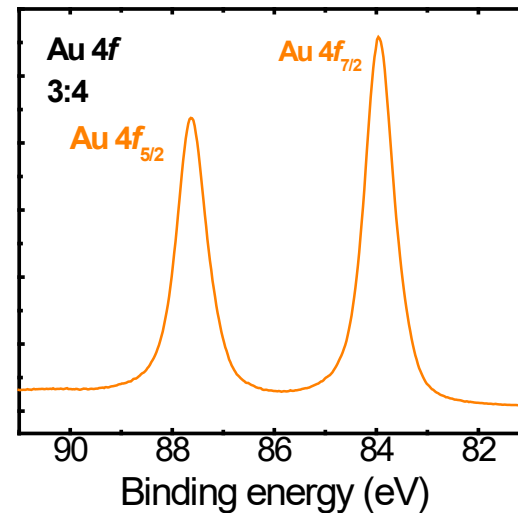
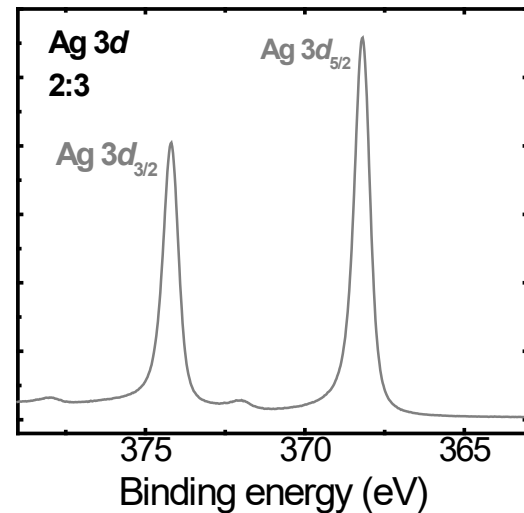
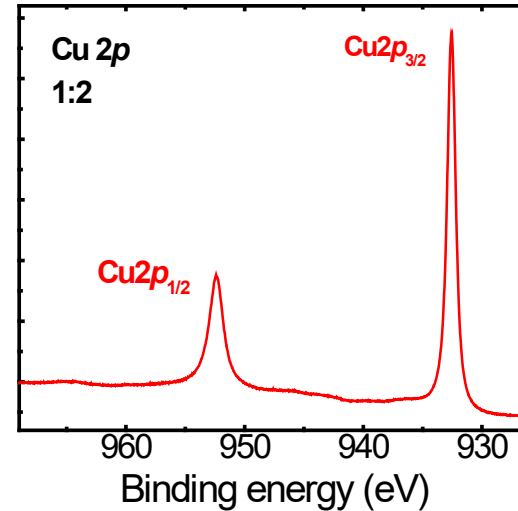
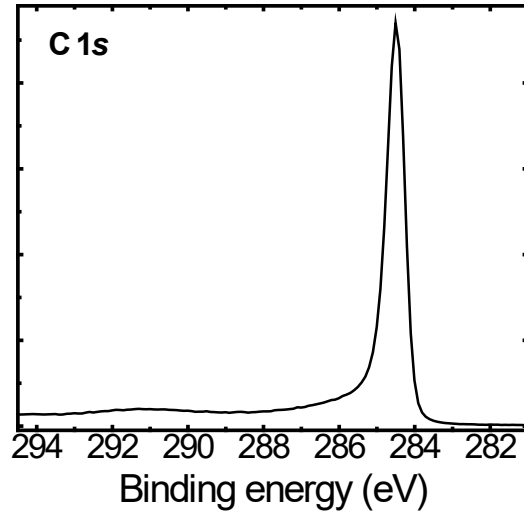
R. T. Haasch, T.-Y. Lee, D. Gall, C.-S. Shin, J. E. Greene, I. Petrov, *Surf. Sci. Spectra*, **7**, 169 (2000), *Surf. Sci. Spectra*, **7**, 193 (2000), *Surf. Sci. Spectra*, **7**, 221 (2000), *Surf. Sci. Spectra*, **7**, 250 (2000).

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

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

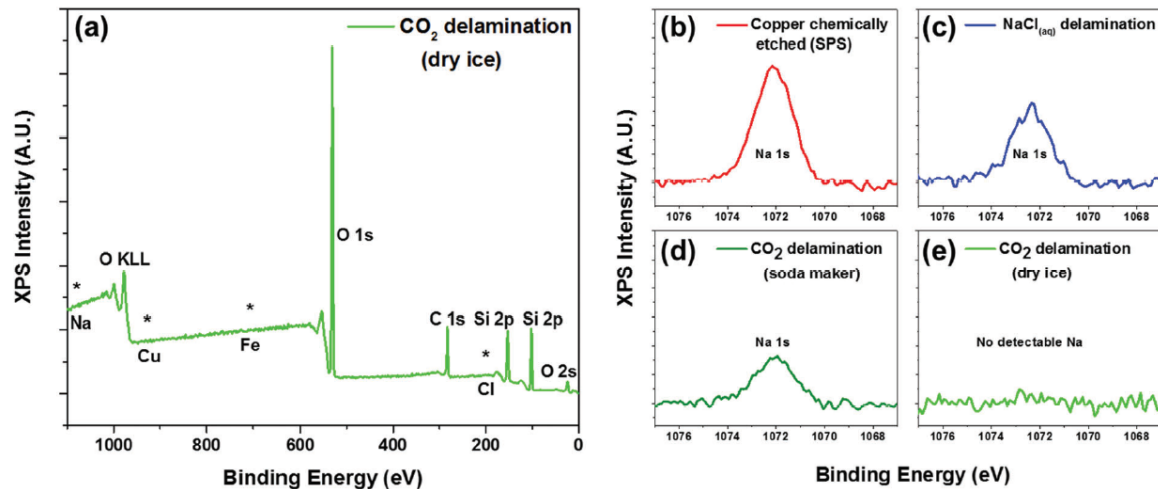
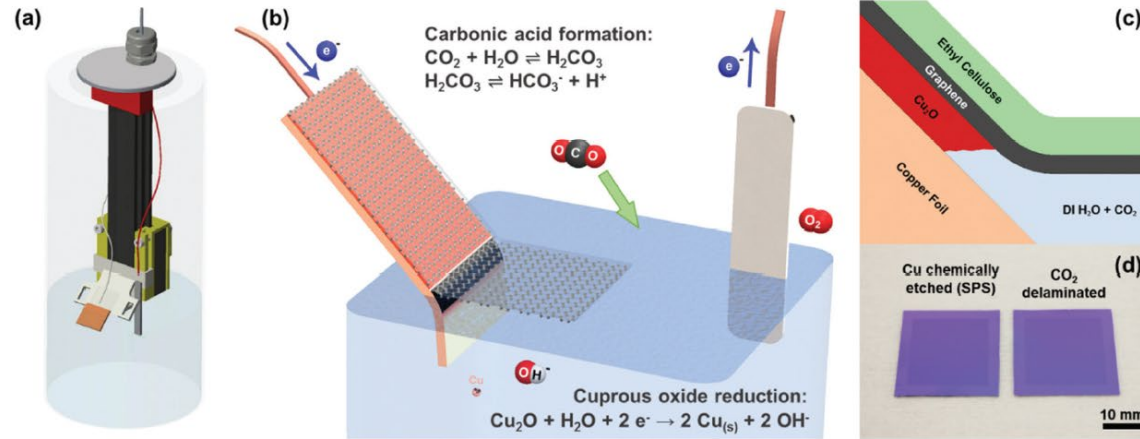
Momentum quantum number:
 $m_j, -j$ to j ($2j + 1$ states)



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



- XPS survey of CO_2 delamination (from dry ice)
- Chemically etched (sodium persulphate)
- $\text{NaCl}_{(aq)}$ delaminated
- CO_2 delamination using compressed CO_2 from soda maker
- Delamination using carbonic acid generated from dry ice pellets

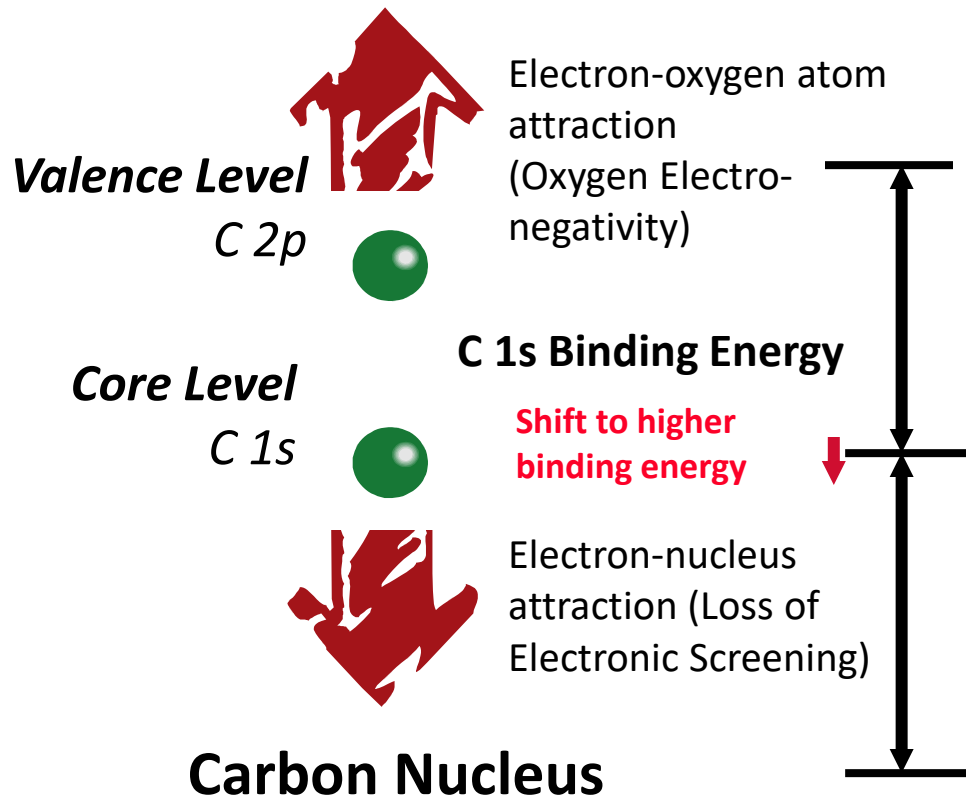


M. C. Wang, W. Moestopo, S. Takekuma, S. Farabi, R. T. Haasch, S.-W. Nam, "Sustainable approach for large area transfer of graphene and recycle of the catalyst substrate," *J. Mater. Chem. C*, **5**, 11226 (2017). [doi:10.1039/c7tc02487h](https://doi.org/10.1039/c7tc02487h).

Electronegativity Effects

Carbon-Oxygen Bond

Oxygen Atom



Electronegativity

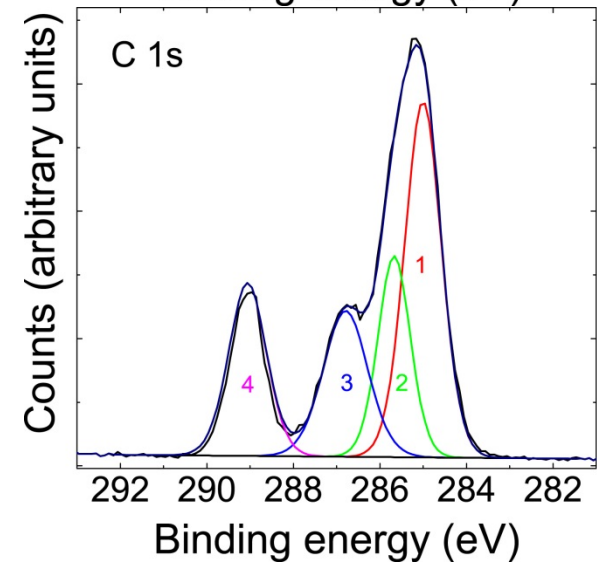
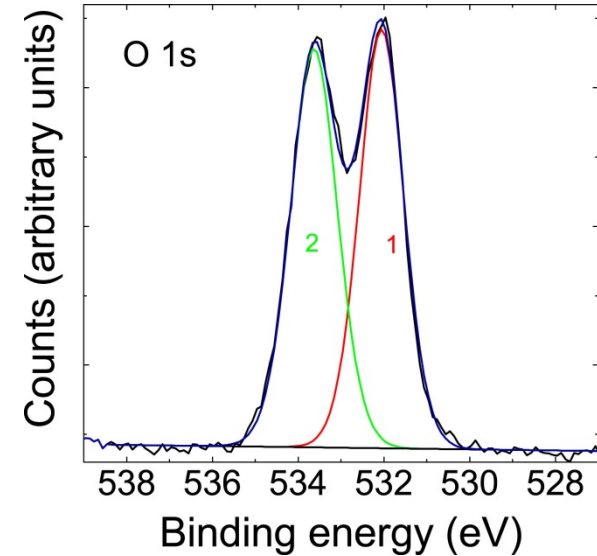
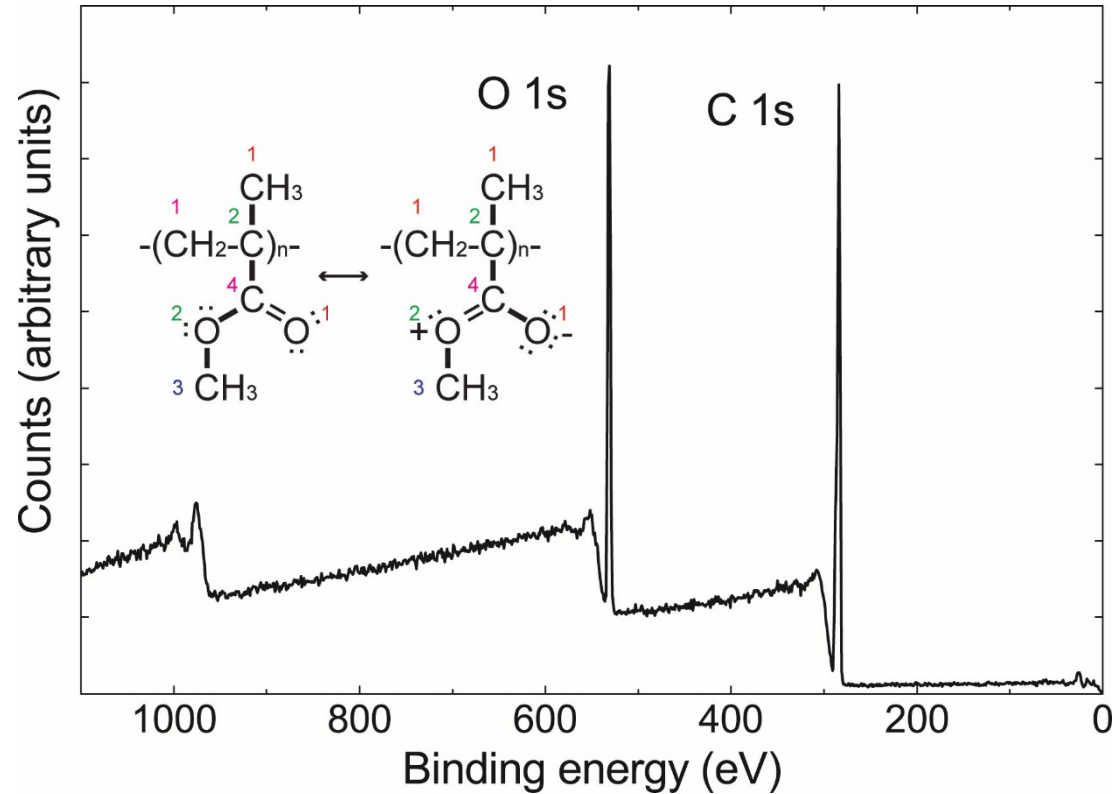
13 IIIA 3A	14 IVA 4A	15 VA 5A	16 VIA 6A	17 VIIA 7A
5 B Boron 10.811	6 C Carbon 12.011	7 N Nitrogen 14.00674	8 O Oxygen 15.9994	9 F Fluorine 18.998403

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

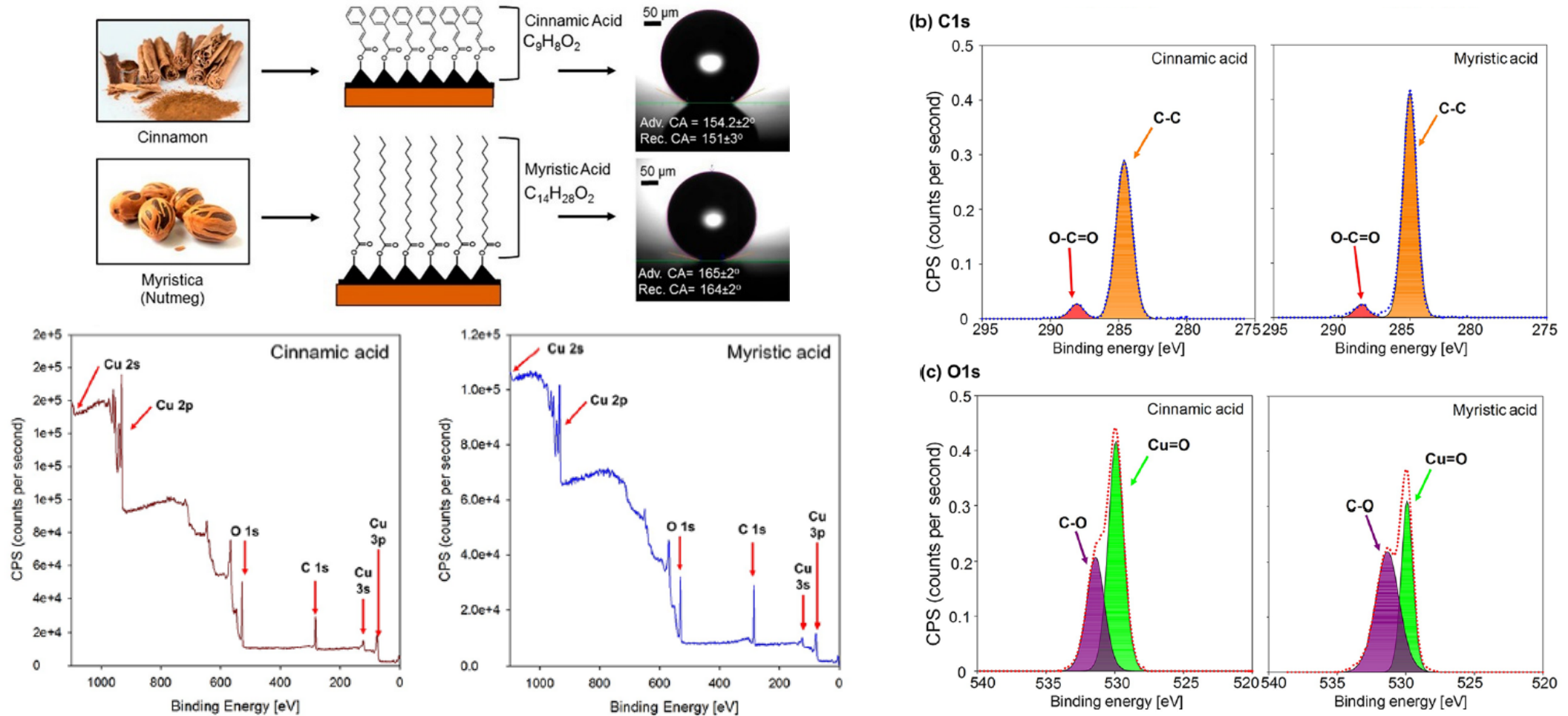


R. T. Haasch, "X-ray Photoelectron Spectroscopy (XPS) and Auger Electron Spectroscopy (AES)," in *Practical Materials Characterization*, M. Sardela, ed., (Springer Science + Business Media, New York, 2014). ISBN 978-1-4614-9280-1. doi: 10.1007/978-1-4614-9281-8_3.

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Superhydrophobic Materials

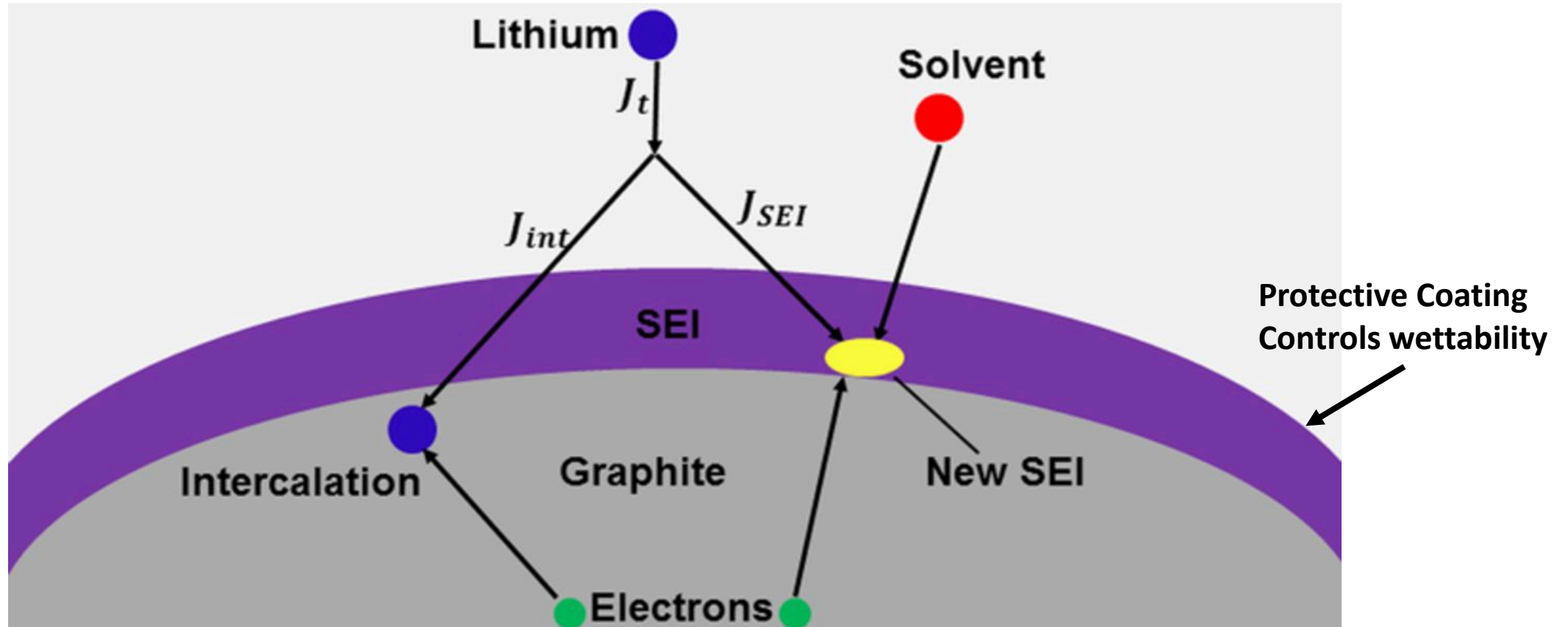
Superhydrophobic Surfaces from Naturally Derived Hydrophobic Materials



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.



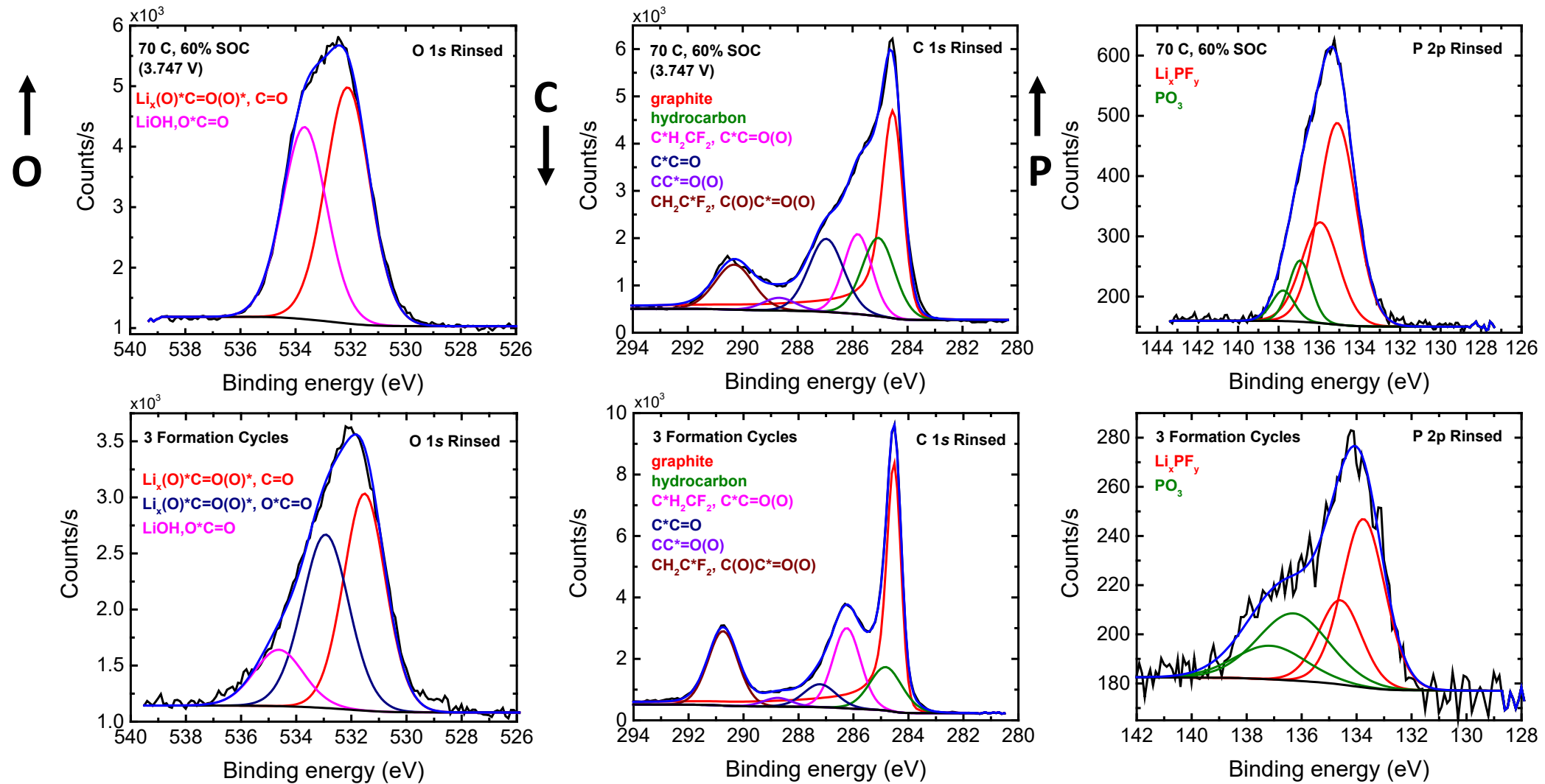
A. A. Tahmasbi et al. J. Electrochem. Soc. 2017;164:A1307-A1313

Journal of The Electrochemical Society

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



70 °C,
60% SOC

3 Formation
Cycles

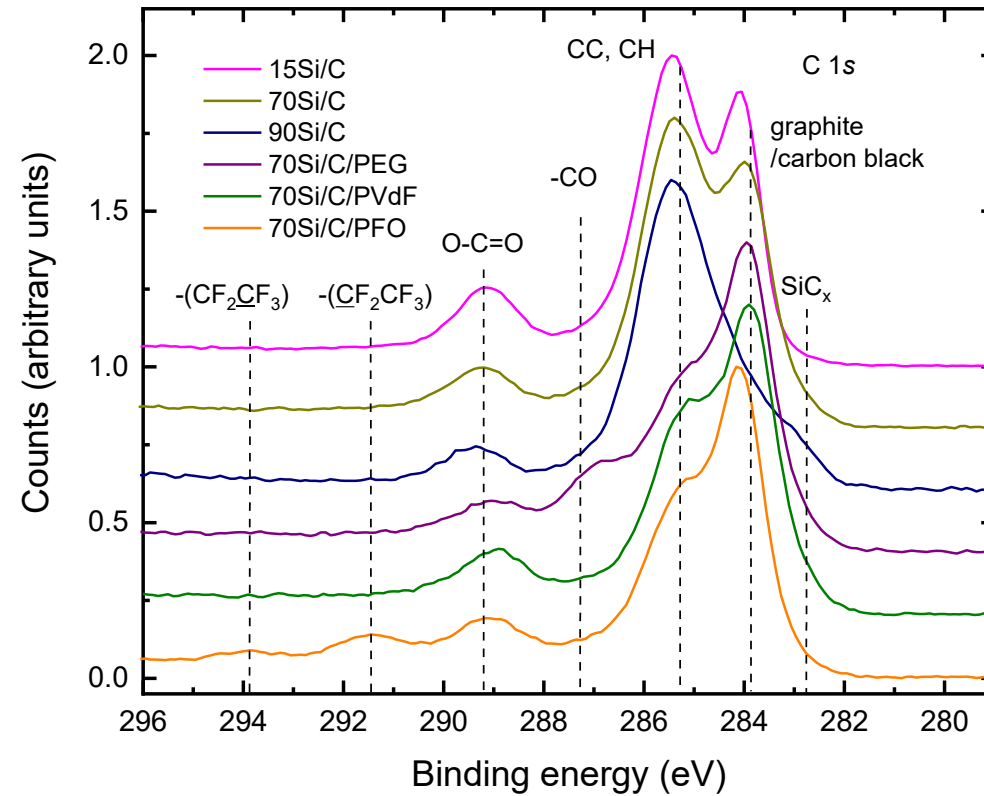
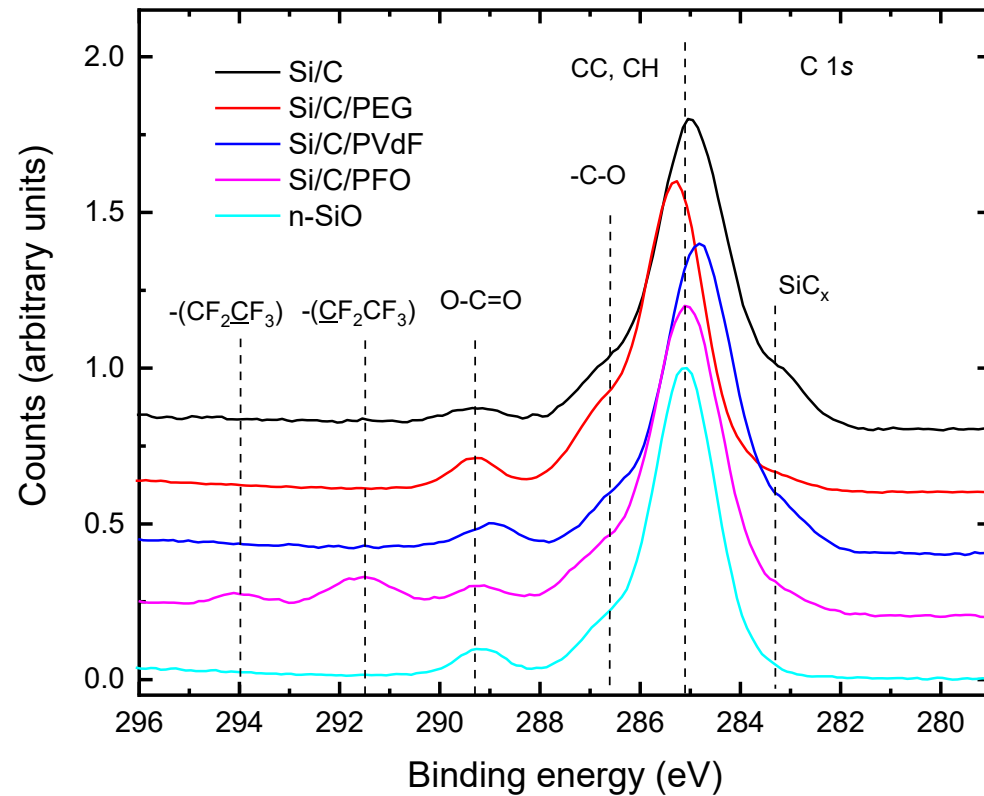


D. P. Abraham, J. Liu, C. H. Chen, Y. E. Hyung, M. Stoll, N. Elsen, S. Maclaren, R. Twisten, R. Haasch, E. Sammann I. Petrov, K. Amine, G. Henriksen, "Diagnosis of power fade mechanisms in high-power lithium-ion cells," *J. Power Sources*, **119-121**, 511-516 (2003).

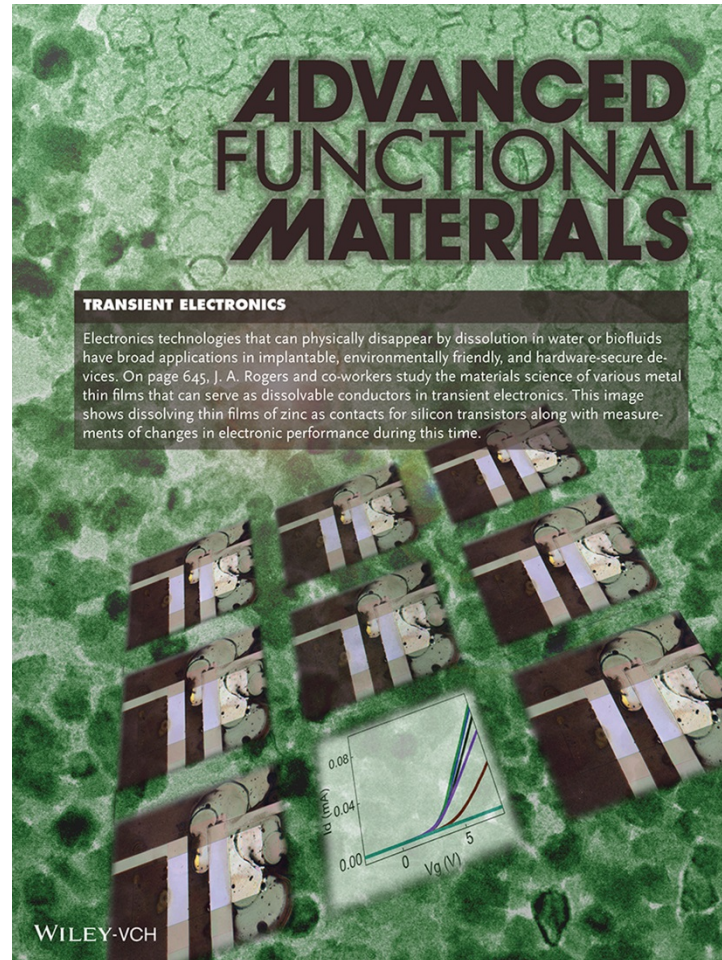
R. T. Haasch, D. P. Abraham, "LiNi_{0.8}Co_{0.2}O₂-based high-power lithium-ion battery positive electrodes analyzed by X-ray photoelectron spectroscopy," *Surface Science Spectra*, **23**, 112-172 (2016).

Anode (negative electrode)- Si Based Materials

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

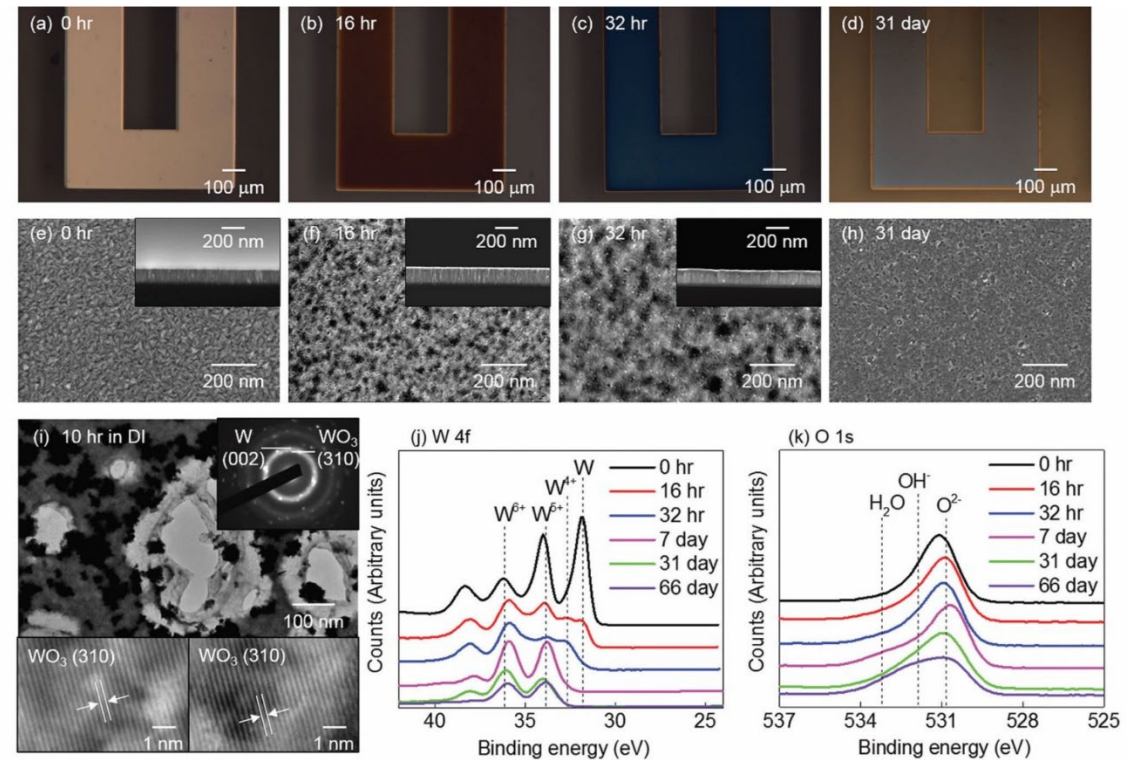


R. T. Haasch, D. P. Abraham, "Si powders and electrodes for high-energy lithium-ion cells," *Surf. Sci. Spectra*, **26**, 016801 (2020). [doi:10.1116/1.5130764](https://doi.org/10.1116/1.5130764).



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).

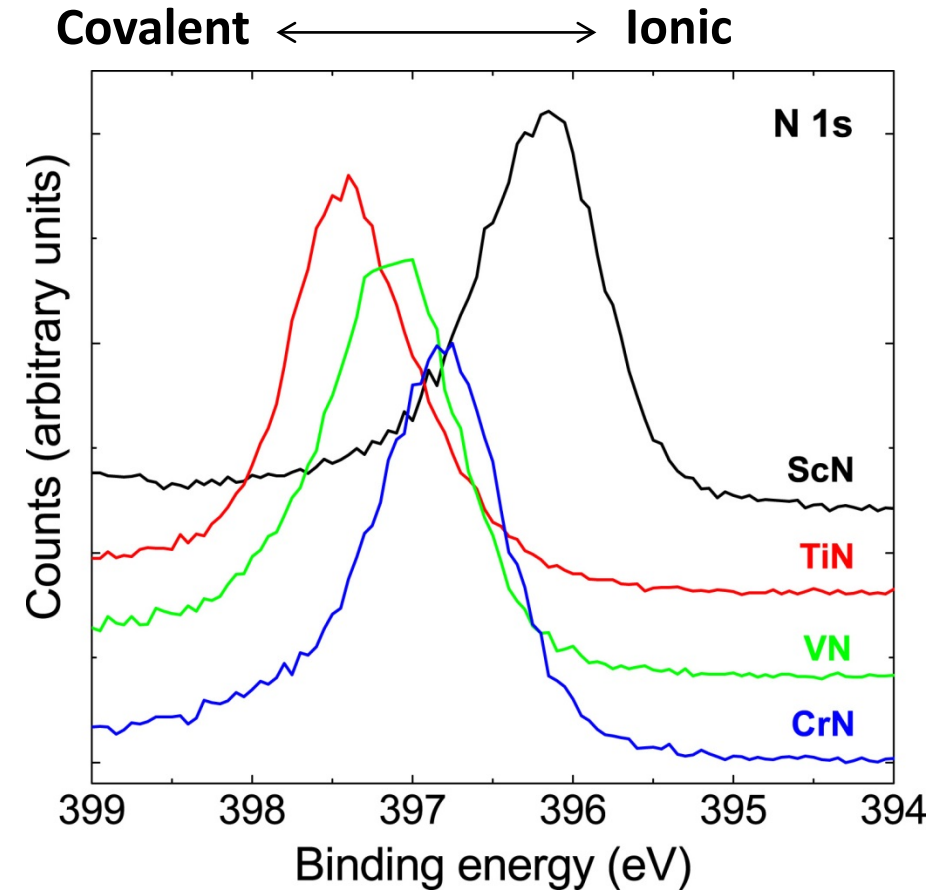


Transition Metal Nitrides

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

p-d hybridization 8 MO's

	Anti-bonding e ⁻ /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

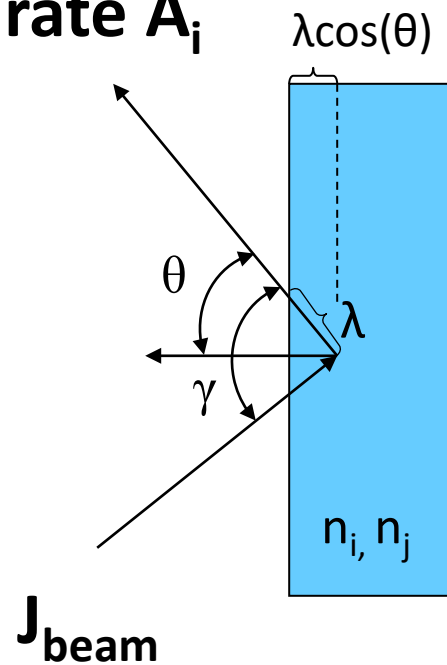


R. T. Haasch, T.-Y. Lee, D. Gall, C.-S. Shin, J. E. Greene, I. Petrov, *Surf. Sci. Spectra*, **7**, 169 (2000), *Surf. Sci. Spectra*, **7**, 193 (2000), *Surf. Sci. Spectra*, **7**, 221 (2000), *Surf. Sci. Spectra*, **7**, 250 (2000).

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/cm³

$\sigma(\gamma)$ = photoelectric (scattering) cross-section, cm²

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

Instrument Dependent Terms

J = X-ray flux, photon/cm²-sec

$T(E_i)$ = analyzer transmission function

a = analysis area, cm²

θ = 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 λ_i so it is usually neglected. Modern acquisition and analysis software can account for the transmission function.

$$N_i = A_i / S_i$$

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

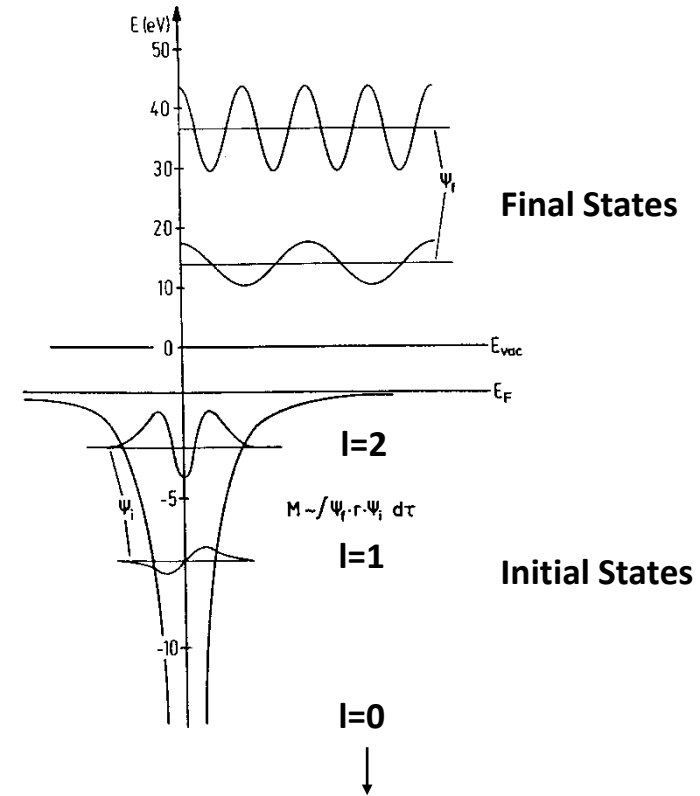
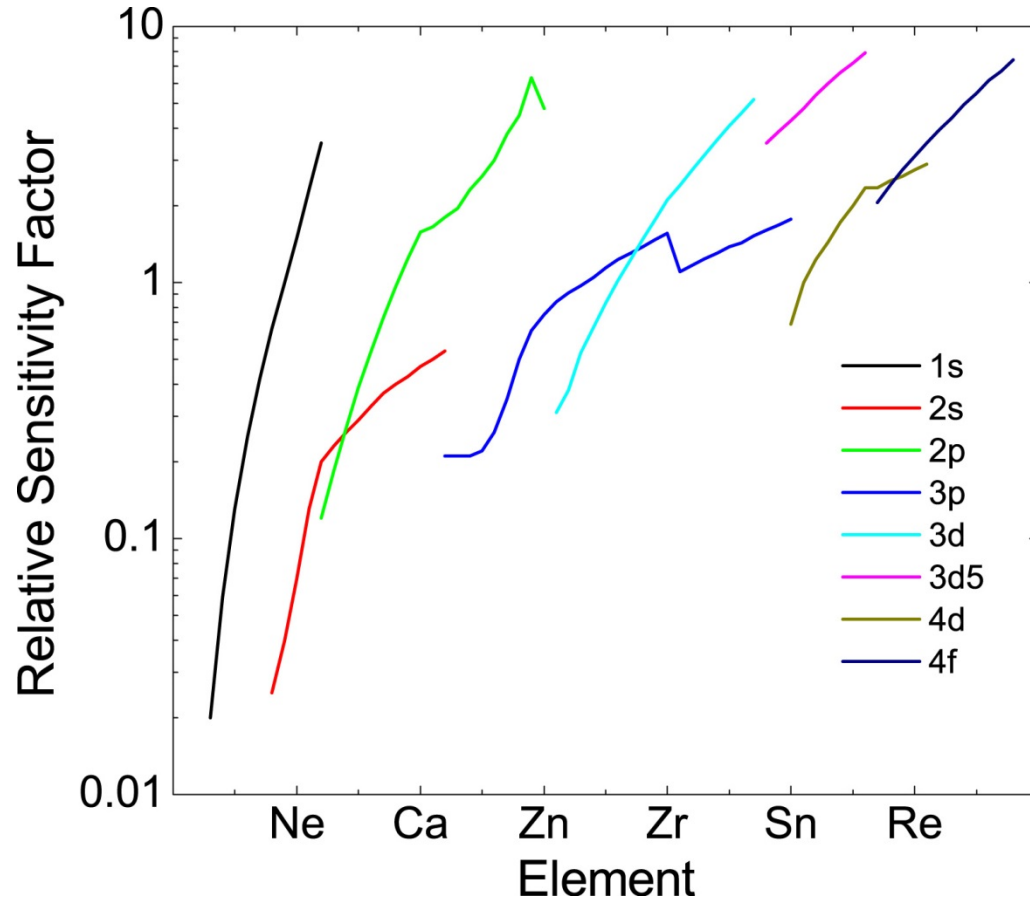
The values of S are determined theoretically or empirically with standards.

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



Quantitative Surface Analysis: XPS

XPS Relative Elemental Sensitivities

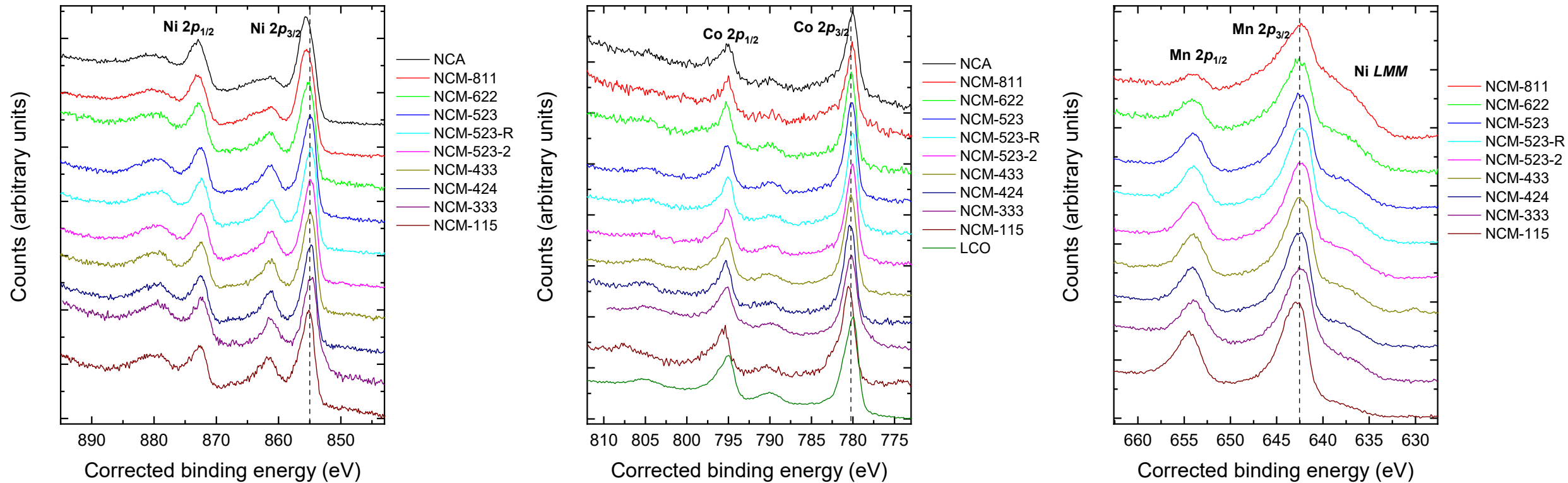


S. Hüfner, *Photoelectron Spectroscopy Principles and Applications*, Second Edition, (Springer, Berlin Heidelberg, 1996). ISBN 3-540-60875-3.



NCM Family of Oxide Materials - Raw Powder

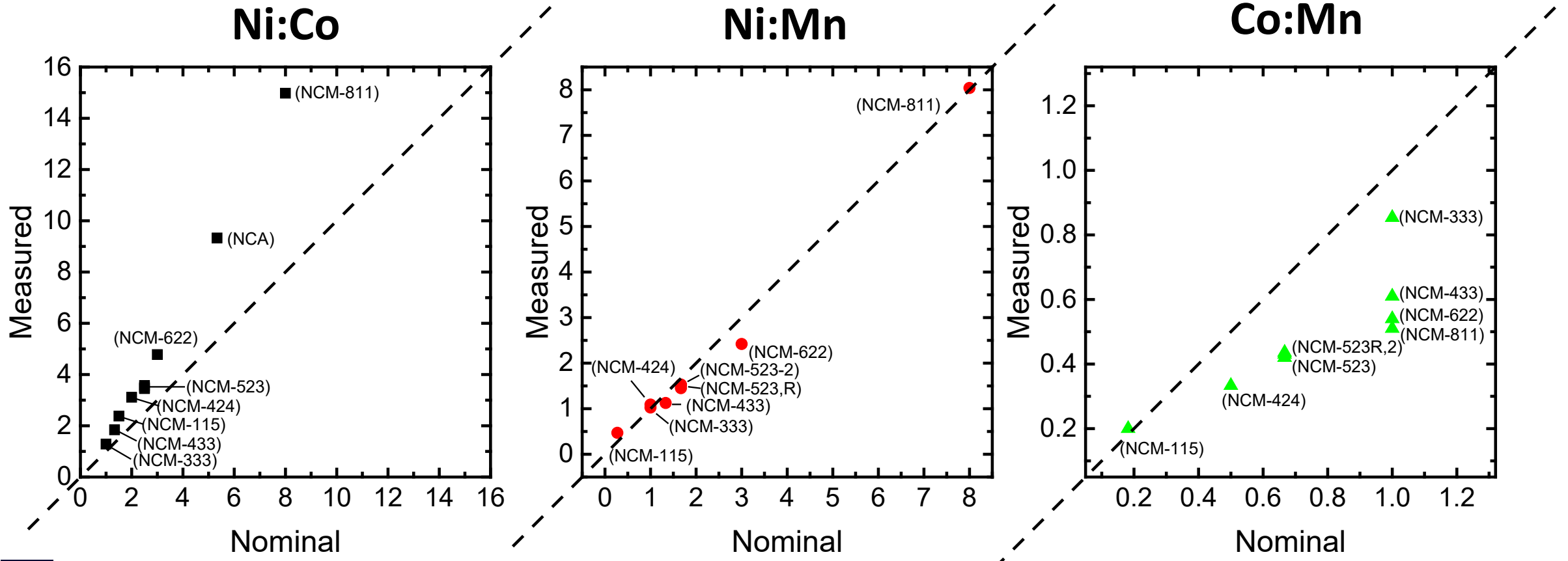
Lithium-bearing Oxides for Rechargeable Li-ion Batteries:



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

XPS Analysis		ScN	TiN	VN	CrN	
Binding energy (eV)	Metal 2p _{3/2}	Major peak	400.4	455.1	513.2	574.4
		Satellite ^a		457.9	515.5	575.5
	Metal 2p _{1/2}	Major peak	404.9	461.0	520.7	584.0
		Satellite ^a		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 ^b	
	After ion bombardment	0.99	0.73	0.46	0.55 ^b	
	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).

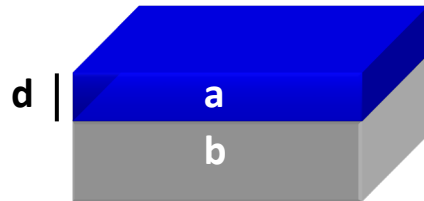
Layer Thickness Measurement

Layer thickness calculation: Two-Layer Model

Assuming only inelastic scattering

Beer-Lambert relationship:

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



$$\frac{I_a}{I_b} \xrightarrow{\int} \ln \left(\frac{N_a n_b \rho_b \lambda_b MW_a}{N_b n_a \rho_a \lambda_a MW_b} + 1 \right) = \frac{d}{\lambda_a \cos \theta}$$

Where: η = number of atoms per molecule unit,
 ρ = molecular density,
 λ = inelastic mean-free path,
MW = molecular weight,
N = atomic concentration.

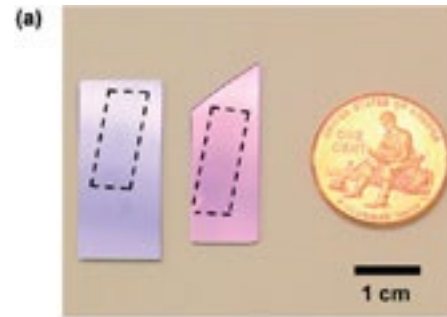
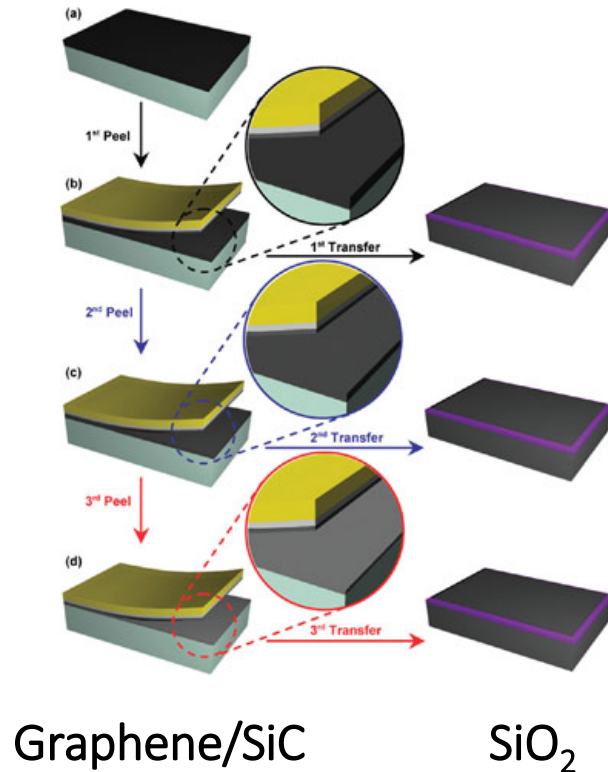


R. T. Haasch, "X-ray Photoelectron Spectroscopy (XPS) and Auger Electron Spectroscopy (AES)," in *Practical Materials Characterization*, M. Sardela, ed., (Springer Science + Business Media, New York, 2014). ISBN 978-1-4614-9280-1. doi: 10.1007/978-1-4614-9281-8_3.

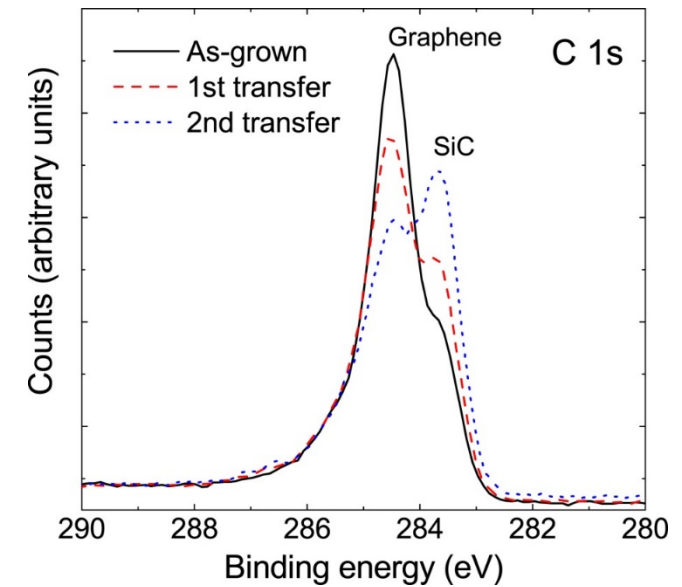
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Graphene Transfer

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 st Transfer	1.5
2 nd Transfer	0.8

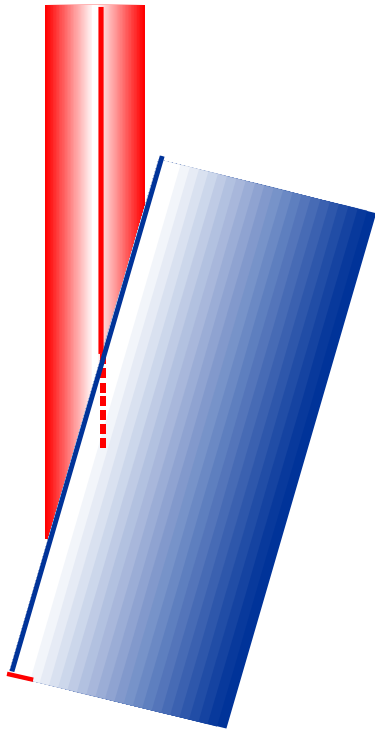


S. Unarunotai, J. Koepke, C.-L. Tsai, F. Du, C. Chialvo, Y. Murata, R. Haasch, I. Petrov, N. Mason, M. Shim, J. Lyding, J. A. Rogers, *ACS Nano*, **4**(10), 5591-5598, (2010).

Angle-resolved XPS

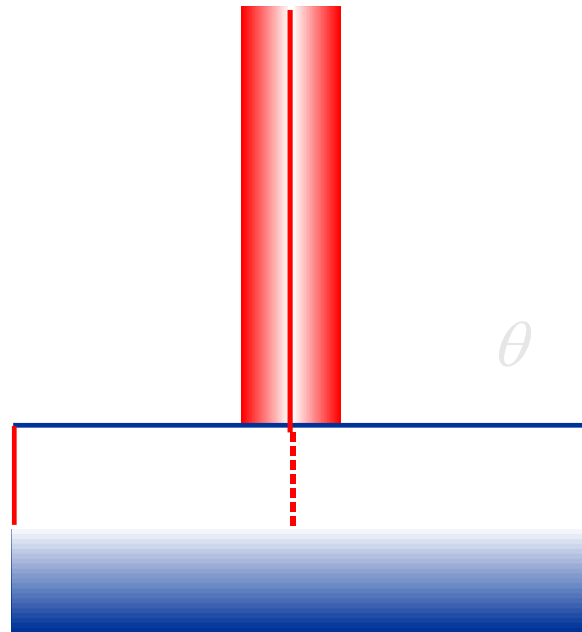
More Surface Sensitive

$$\theta = 75^\circ$$



Less Surface Sensitive

$$\theta = 0^\circ$$

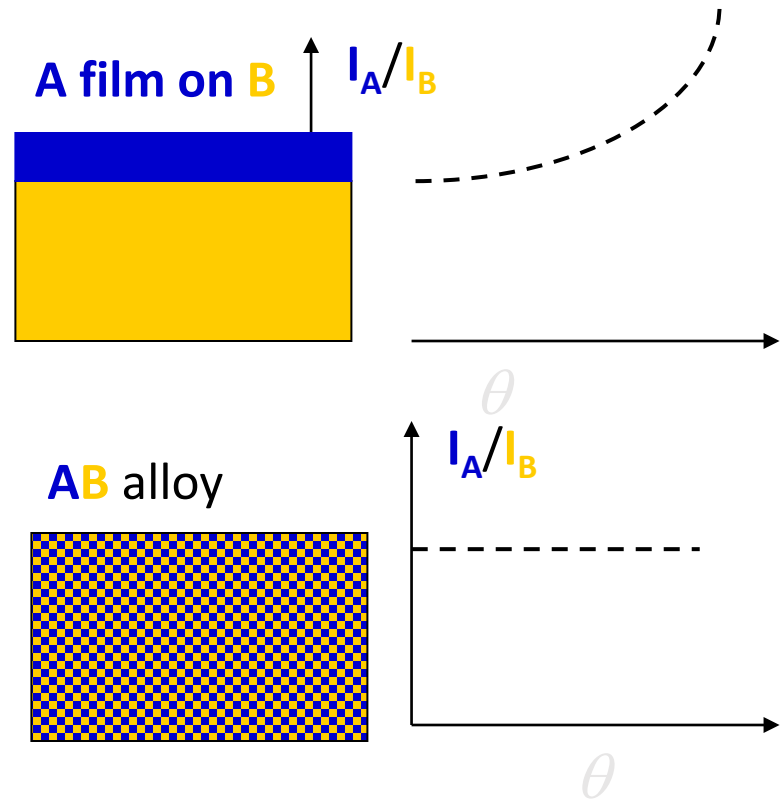


Information depth = $d \cos \theta$

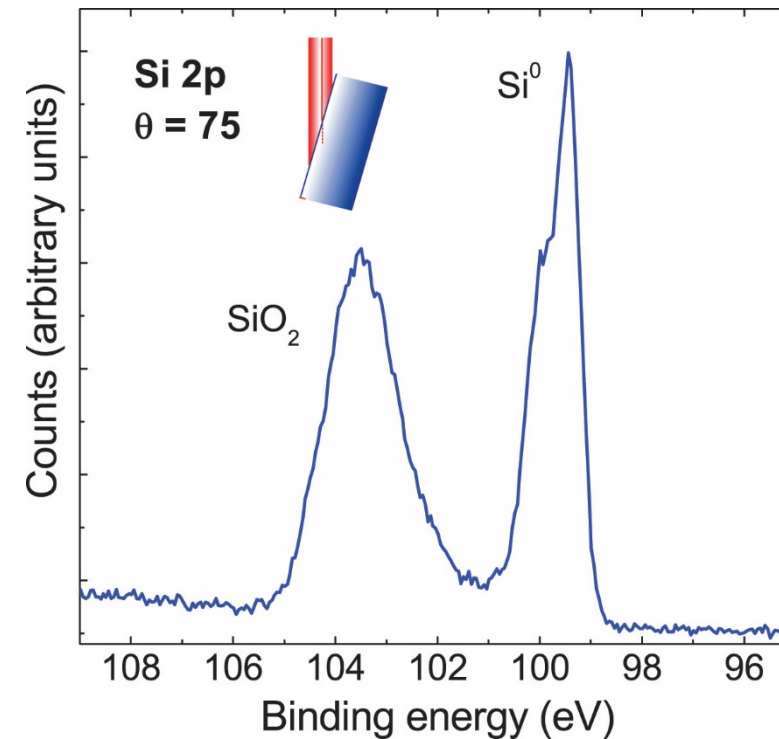
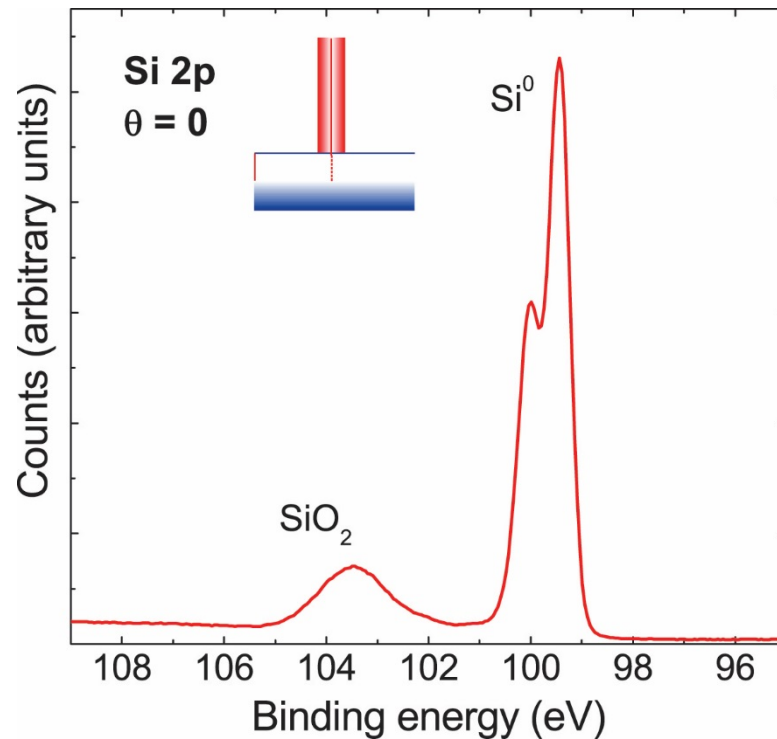
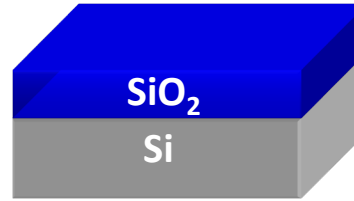
d = Escape depth $\sim 3 \lambda$

θ = Emission angle (relative to surface normal)

λ = Inelastic Mean Free Path



Angle-resolved XPS - SiO₂/Si

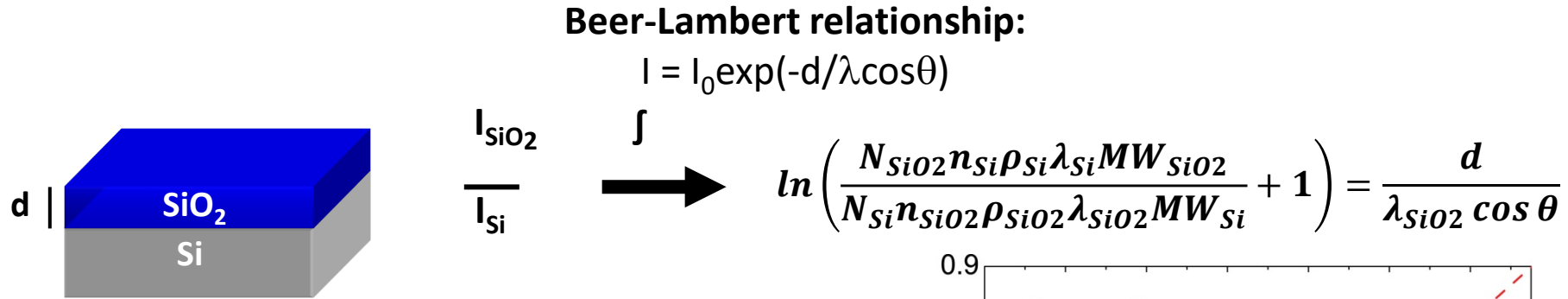


R. T. Haasch, "X-ray Photoelectron Spectroscopy (XPS) and Auger Electron Spectroscopy (AES)," in *Practical Materials Characterization*, M. Sardela, ed., (Springer Science + Business Media, New York, 2014). ISBN 978-1-4614-9280-1. doi: 10.1007/978-1-4614-9281-8_3.

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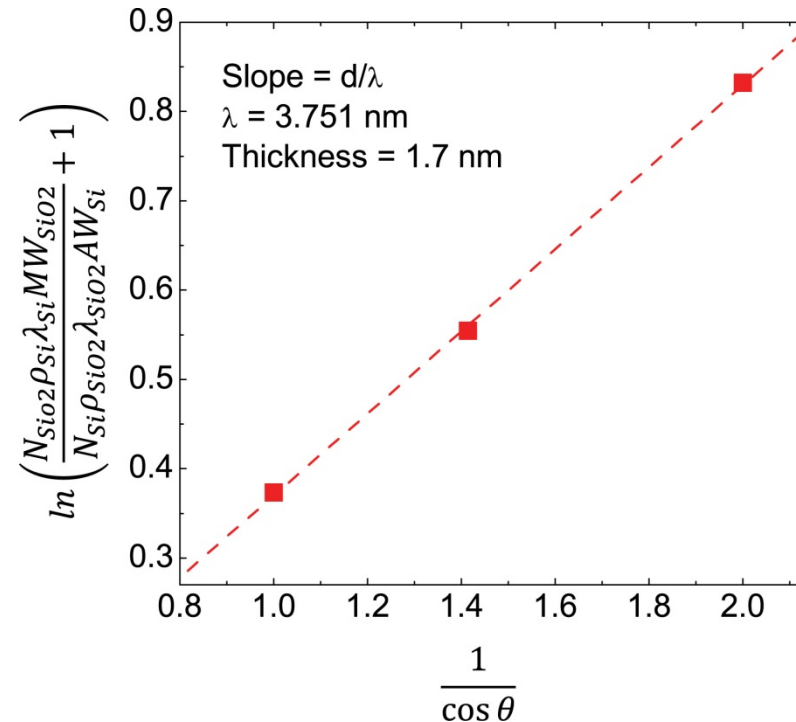
Angle-resolved XPS - SiO₂/Si

Layer thickness calculation: Angle-resolved XPS



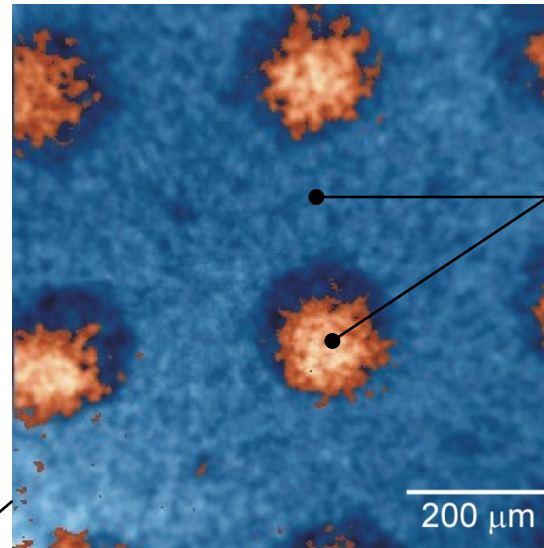
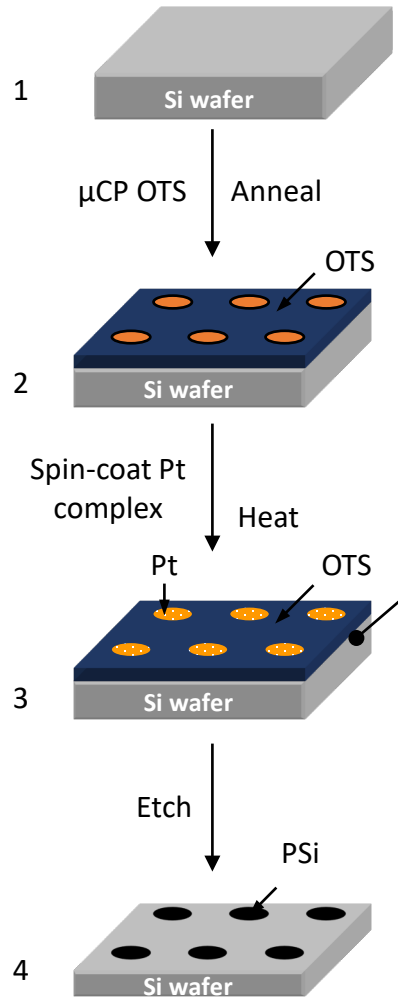
Plot:

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

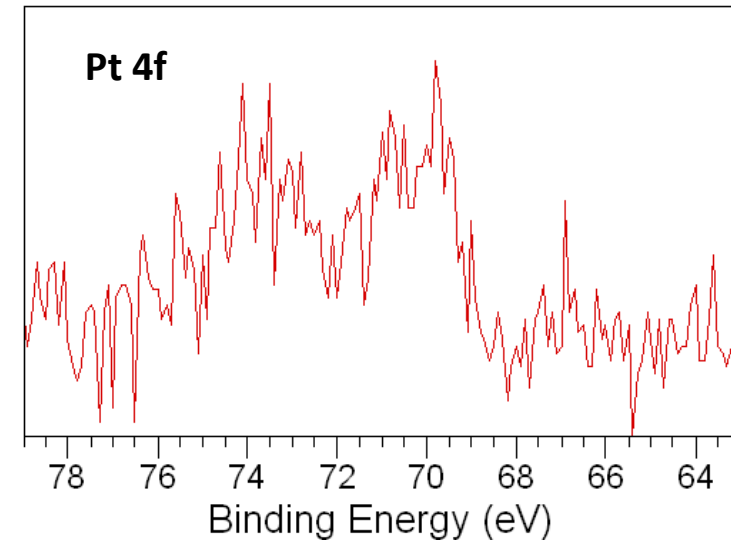
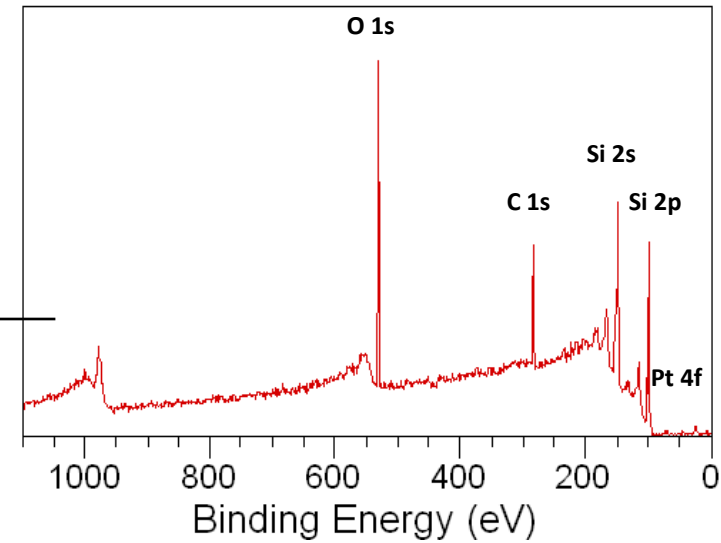


XPS Imaging: Porous Silicon Pixel Array

Pt catalyzed etching of patterned porous silicon



Cross-correlated, low-magnification XPS image after step 3 for the Pt 4f_{7/2} (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

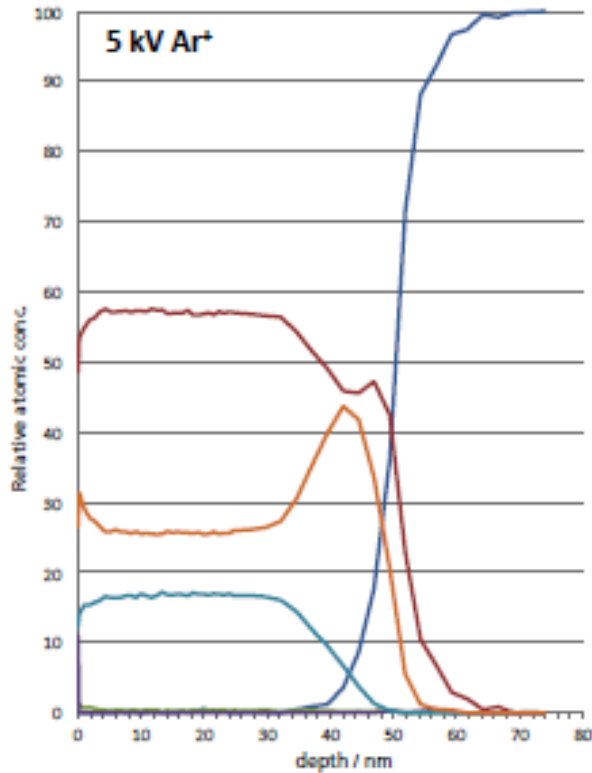


Figure 1(a) Sputter depth profile through ALD LiPON thin film using 5 keV Ar⁺

Cluster ion

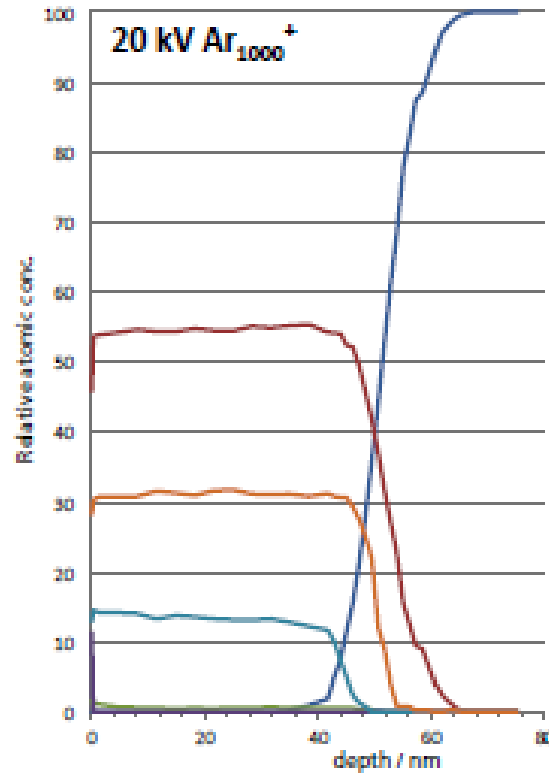


Figure 1(b) Sputter depth profile through ALD LiPON thin film using 20 keV Ar₁₀₀₀⁺

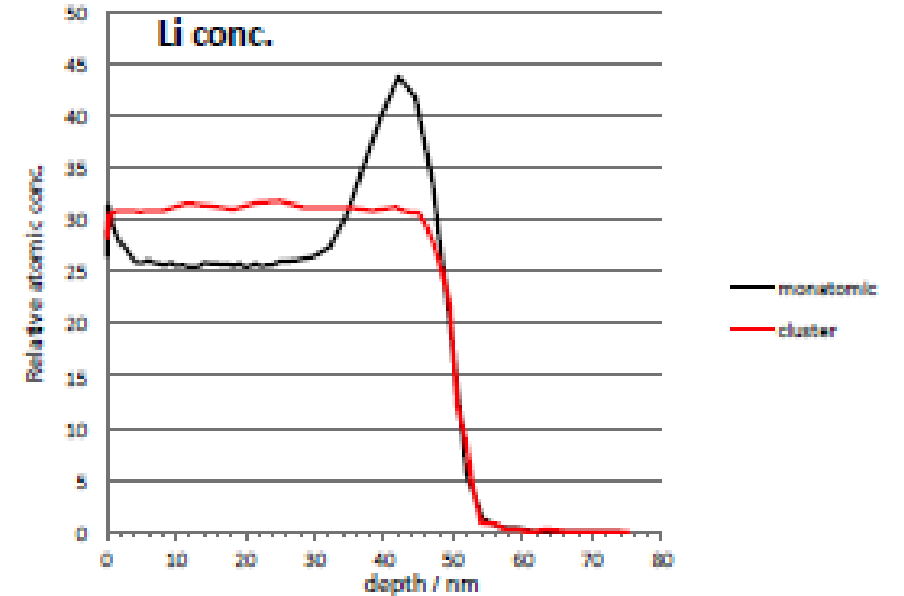


Figure 1(c) comparison of the Li concentration through the same sample generated using monoatomic and cluster ion projectiles.



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

Technique Comparison: Resolution vs. Detection Limit

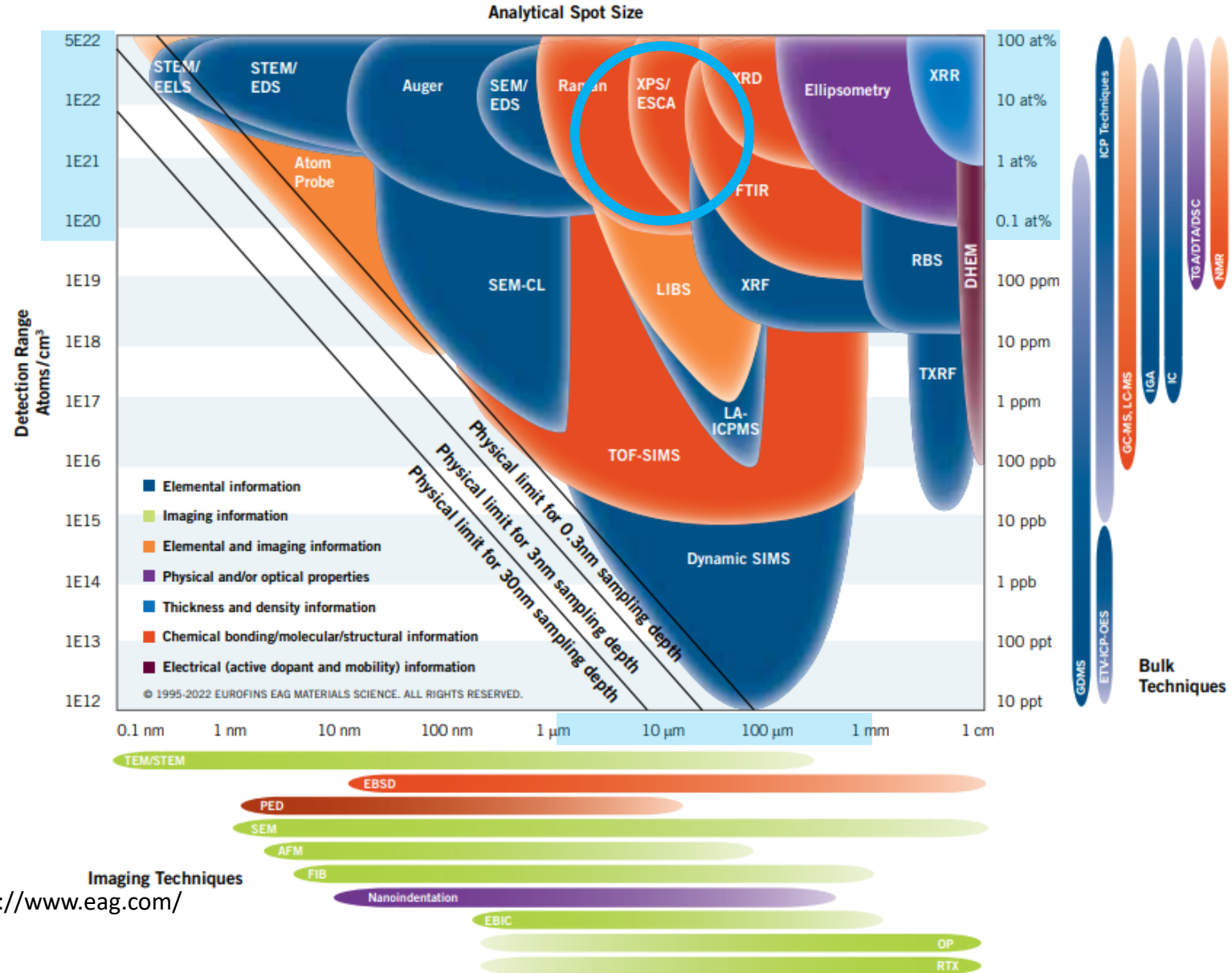


Image credit: <https://www.eag.com/>

Technique Comparison: Typical Analysis Depth

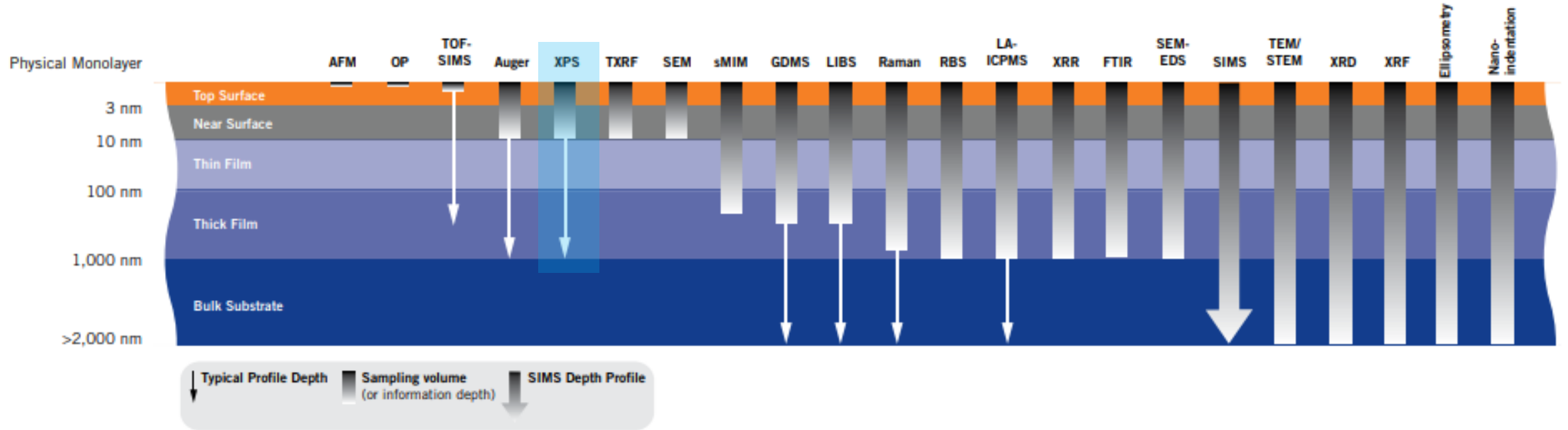


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