



Building College-University
Partnerships for Nanotechnology
Workforce Development

X-Ray Photoelectron Spectroscopy (XPS)

Outline

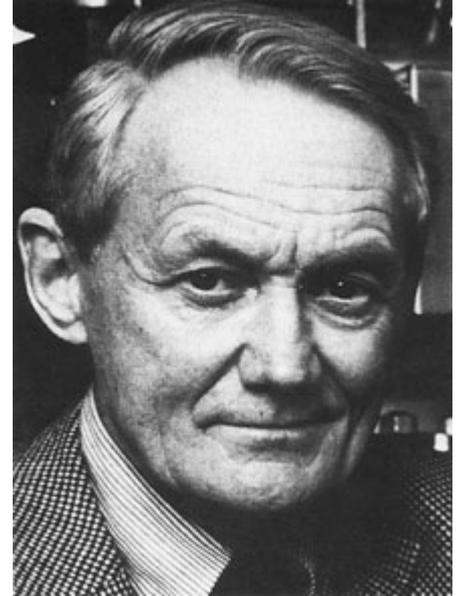
- Basic principles
- Instrumentation
- Peak characteristics
- Quantitative analysis
- Depth profiling

X-Ray Photoelectron Spectroscopy (XPS)

- X-ray Photoelectron Spectroscopy (XPS), also known as Electron Spectroscopy for Chemical Analysis (ESCA), is used to determine quantitative atomic composition and chemistry.
- A sample is irradiated with monochromatic x-rays, resulting in the emission of photoelectrons whose energies are characteristic of the elements within the sampling volume.
- An XPS spectra is created by plotting the number of electrons verses their binding energy.

Historical Notes on XPS

- Kai Siegbahn (b.1918): inventor of modern-day XPS was working at Uppsala University in Sweden in the 1950s and 1960s.
- Siegbahn was a physicist, and chose to call his method electron spectroscopy for chemical analysis (ESCA), because he understood the importance of the chemical information that XPS or ESCA can provide.
- Siegbahn shared the Nobel Prize for Physics (1981) for his work.



1918-2007

X-ray Photoelectron Spectroscopy

- Based on Einstein's photoelectric effect.
 - Many materials emit electrons when light shines upon them
- Core electrons with kinetic energy E_k are ejected by incident X-rays.

$$E_K = h\nu - E_b - \phi_{sp}$$

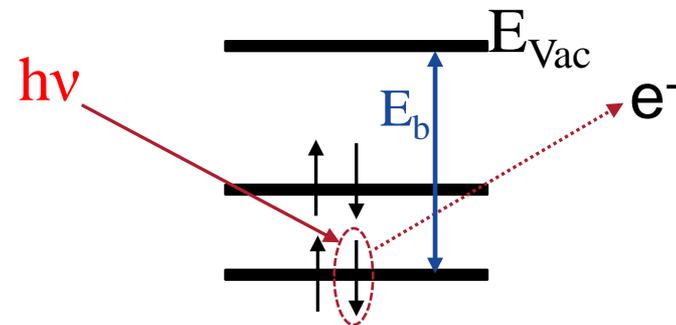
E_K = kinetic energy

E_b = binding energy

h = Planck's constant

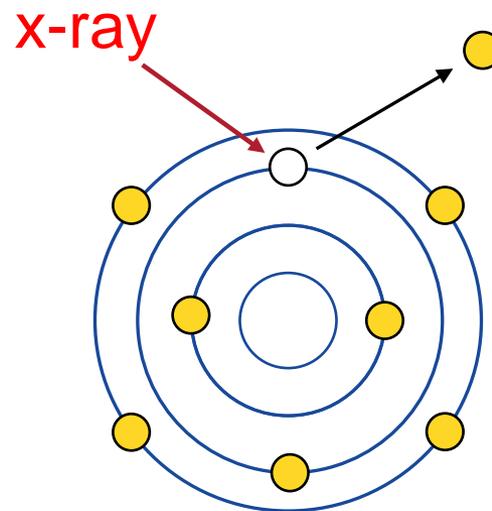
ν = frequency of X-rays

ϕ_{sp} = spectrometer work function

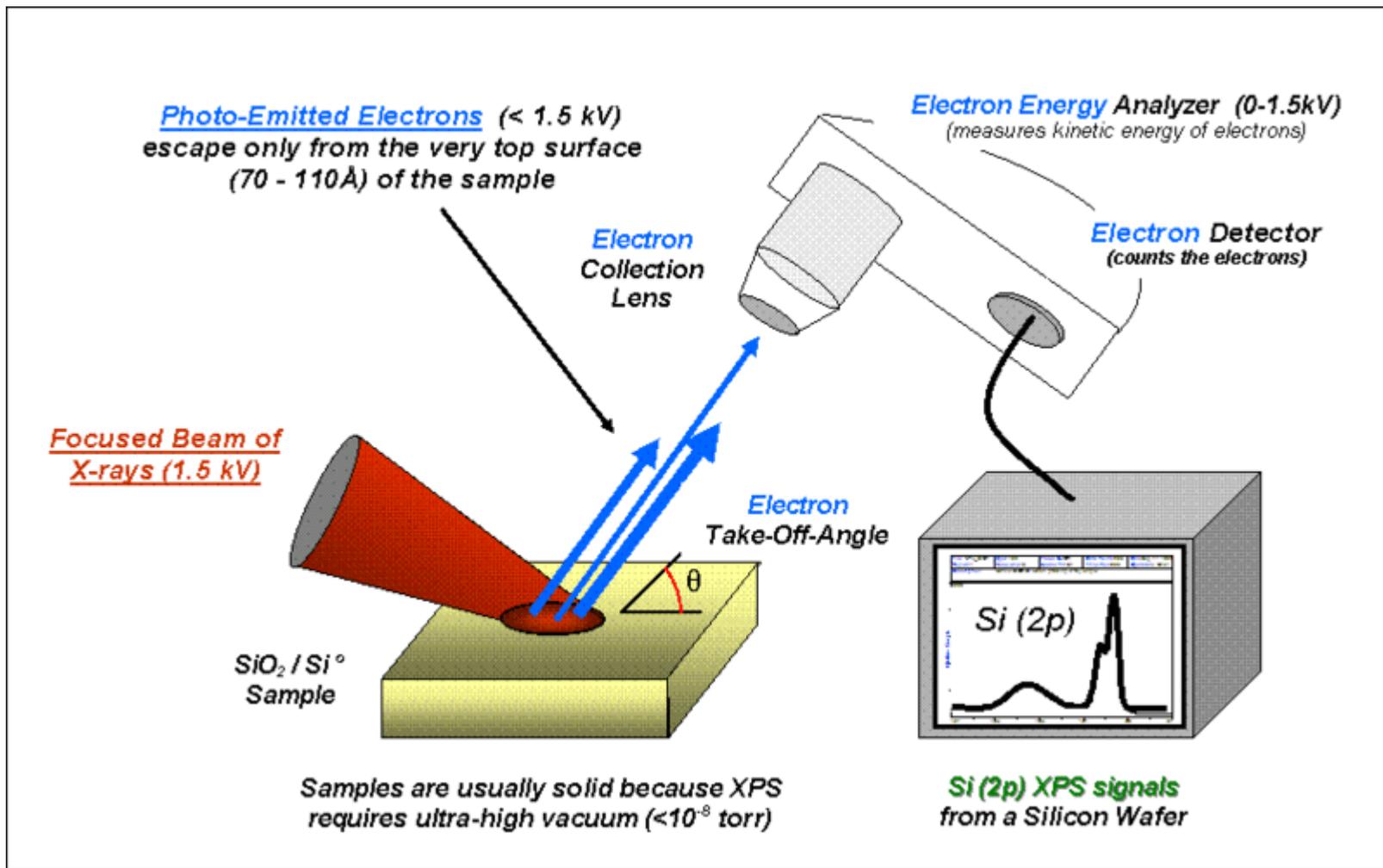


X-Ray Photoelectron Spectroscopy (XPS)

- An x-ray beam usually comprised of k-alpha x-rays is focused on the sample.
- The absorption of incident x-rays results in the ejection of electrons.
- The energy of the ejected electrons is measured by the detector.

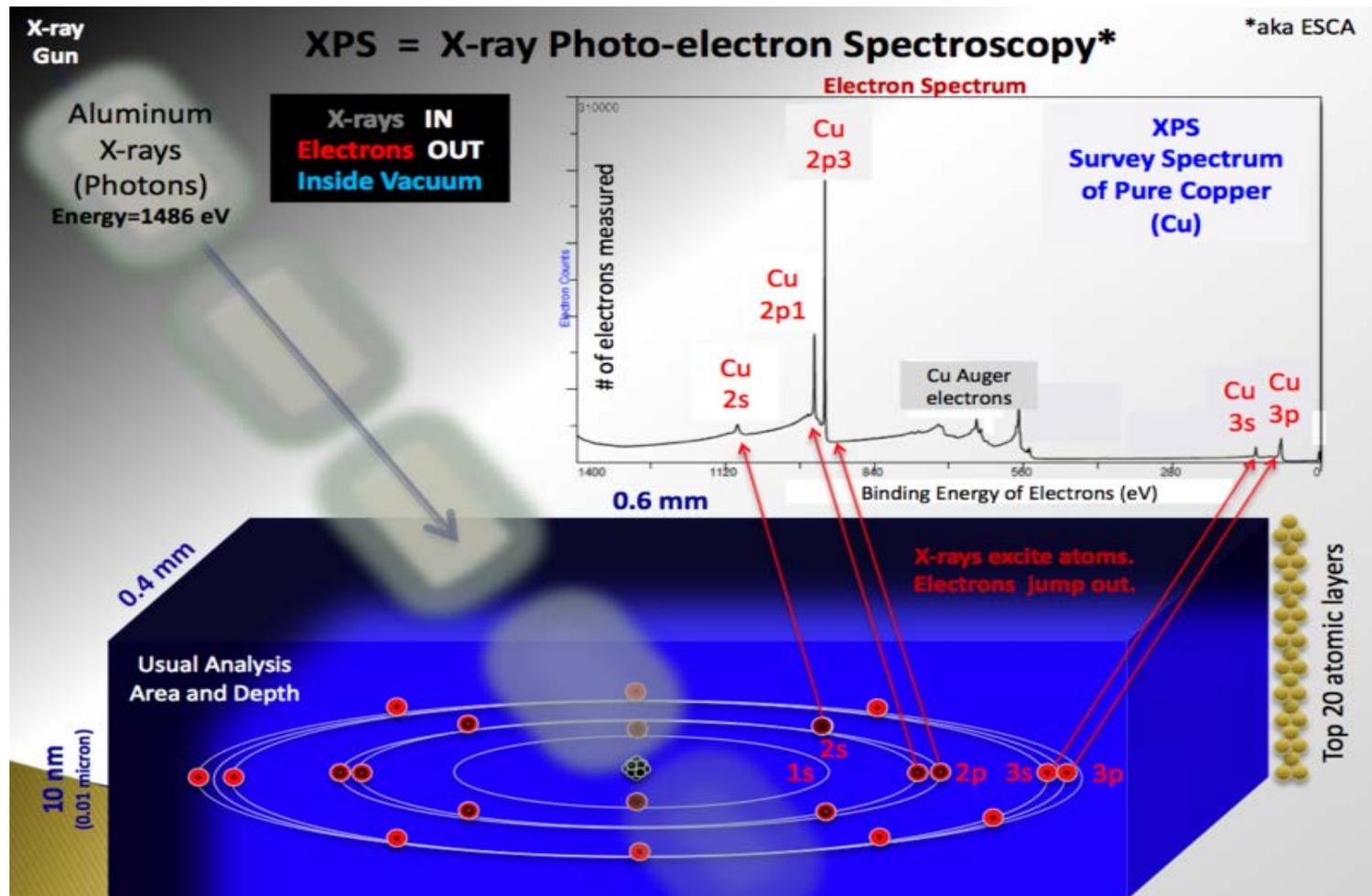


X-Ray Photoelectron Spectroscopy



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Energy of the ejected electrons



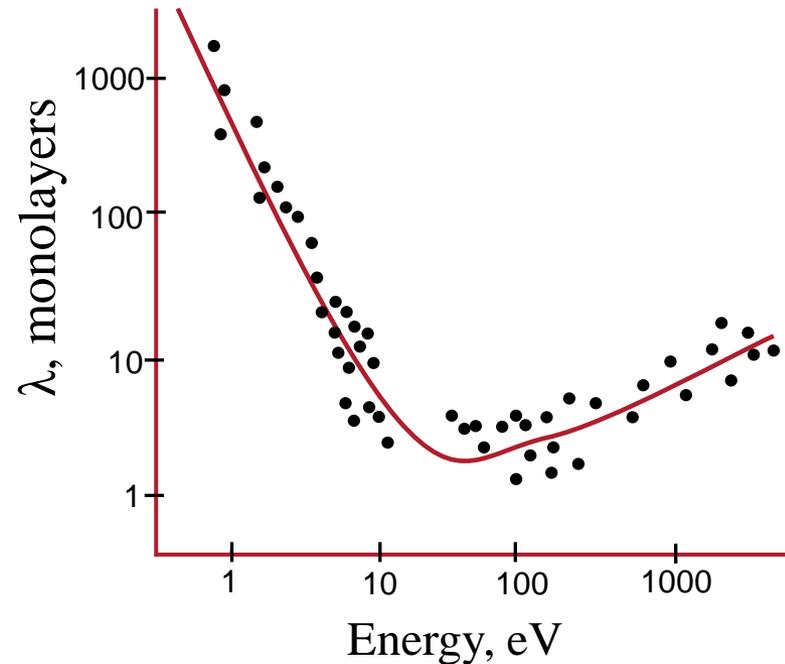
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X-Ray Photoelectron Spectroscopy (XPS)

- Each atom has a unique XPS spectra.
- XPS can determine elemental composition, stoichiometry, electrical/chemical states and examine surface contamination.
- XPS is an elemental analysis technique that is unique in providing chemical state information of the detected elements, such as distinguishing between sulfate and sulfide forms of the element sulfur.

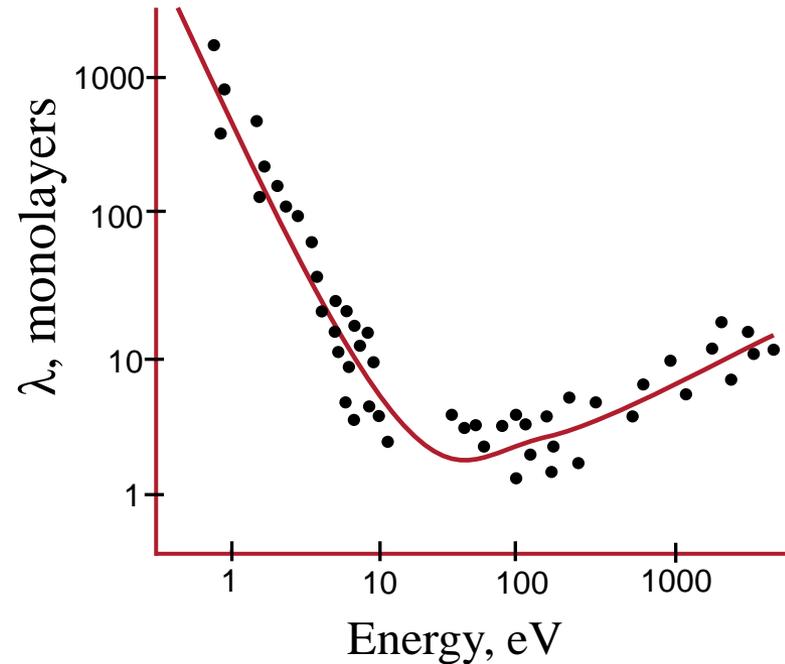
Inelastic mean free path (λ_M)

- When an electron with kinetic energy E moves through a solid matrix M , it has a probability of traveling a certain distance before losing all or part of its energy due to an inelastic collision.
- The average distance traveled before such a collision is known as the inelastic mean free path $\lambda_M(E)$.



Inelastic mean free path (λ_M)

- Since the energy ranges used in XPS analysis are typically 50–1200 eV, the values of λ are very small, corresponding to only a few monolayers.
- Photoelectrons must originate from atomic layers very close to surface to be detected.
- Therefore, the XPS technique is very surface-specific.



XPS surface analysis

What is a surface?

☐ Surfaces

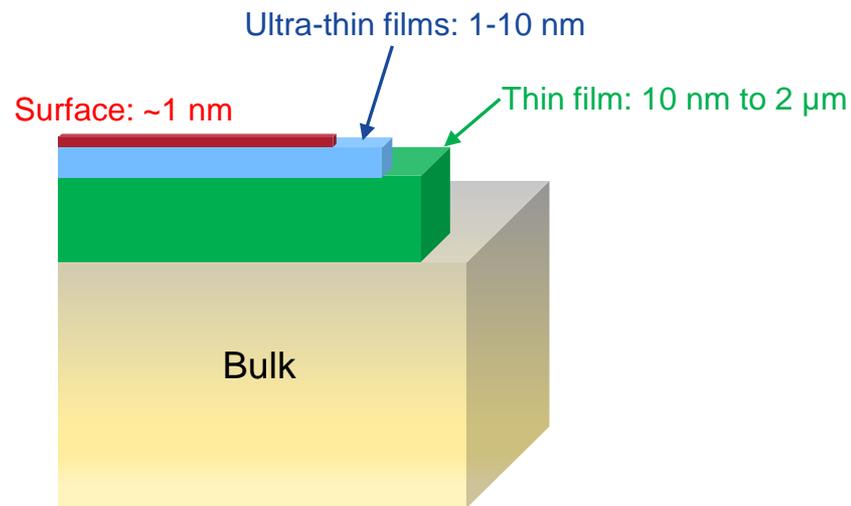
(3 atomic layers) using XPS and angle resolved XPS (ARXPS)

☐ Ultra-thin films

(3-30 atomic layers) using XPS and angle resolved XPS

☐ Thin films

(3-600 atomic layers) using XPS in combination with sputter etching for profiling

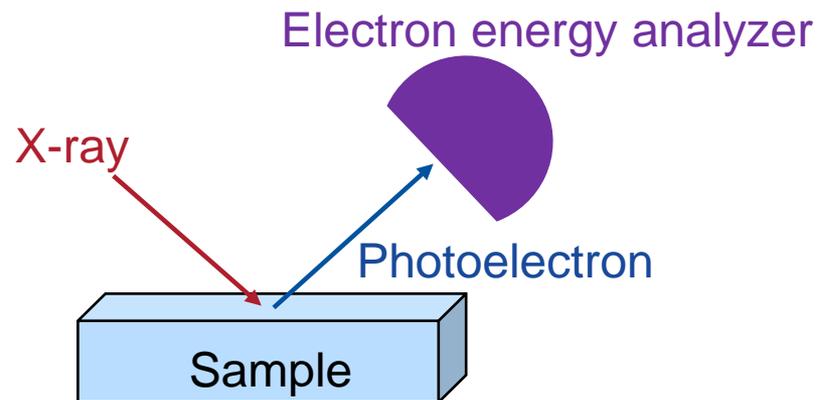


X-Ray Photoelectron Spectroscopy (XPS)

XPS is used to measure:

- elemental composition of the surface (top 1–10 nm usually)
- empirical formula of pure materials
- elements that contaminate a surface
- chemical or electronic state of each element in the surface
- uniformity of elemental composition across the top surface (or line profiling or mapping)
- uniformity of elemental composition as a function of ion beam etching (or depth profiling)

$$E_K = h\nu - E_b - \phi_{sp}$$

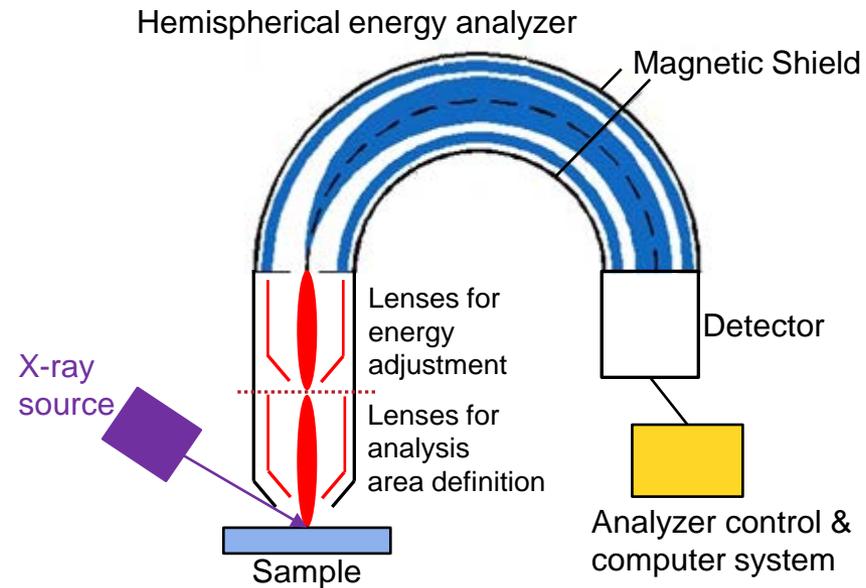


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XPS instrumentation

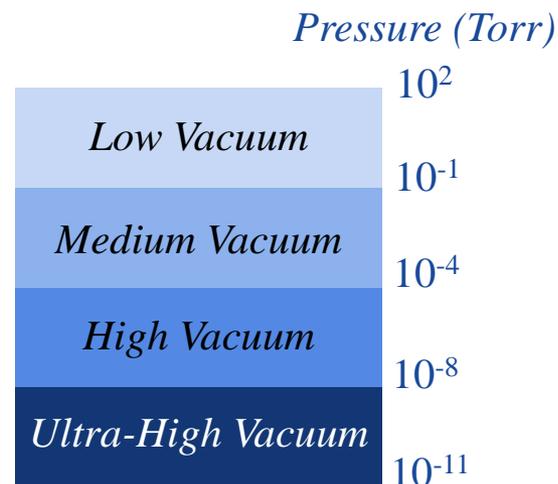
- UHV System
- X-ray source
- Electron analyzer
- Ion gun



XPS instrumentation

Ultra-High Vacuum System

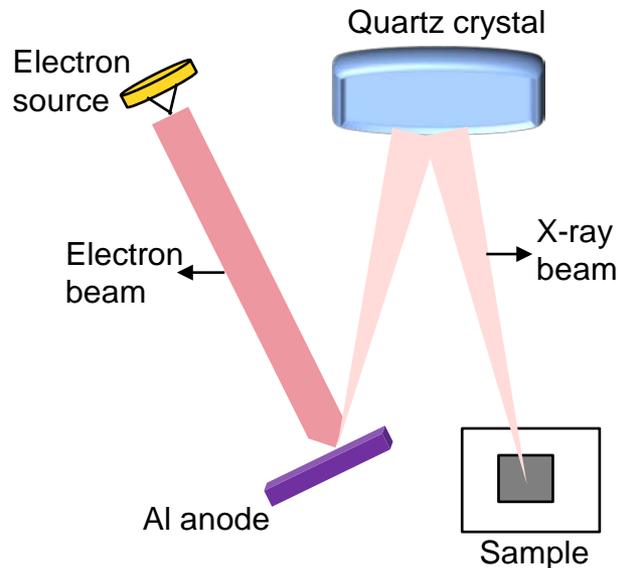
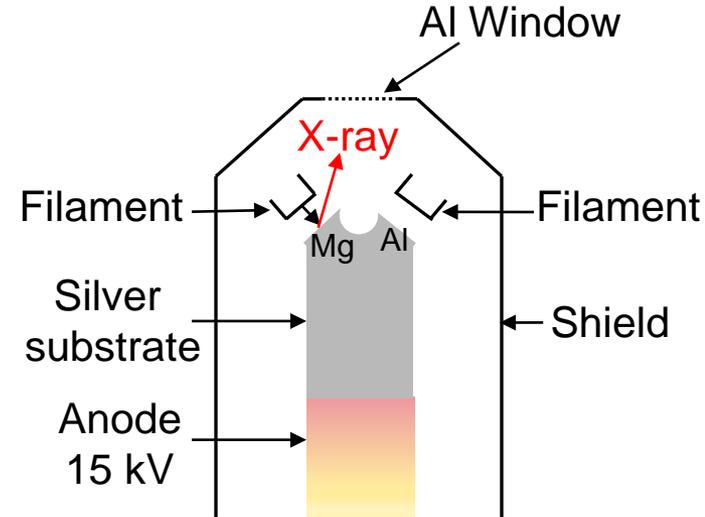
- Allows longer photoelectron path length
- Ultra-high vacuum keeps surfaces clean, preventing the contaminations to produce X-ray signal
- Pressure $< 10^{-8}$ Torr
- Vacuum pumps
 - Roughing Pump
 - Turbo Pump
 - Ion Pump



XPS instrumentation

X-ray source

- Dual Anode X-ray source
 - Mg K α radiation: $h\nu = 1253.6 \text{ eV}$
 - Al K α radiation: $h\nu = 1486.6 \text{ eV}$
- Monochromated using quartz crystal



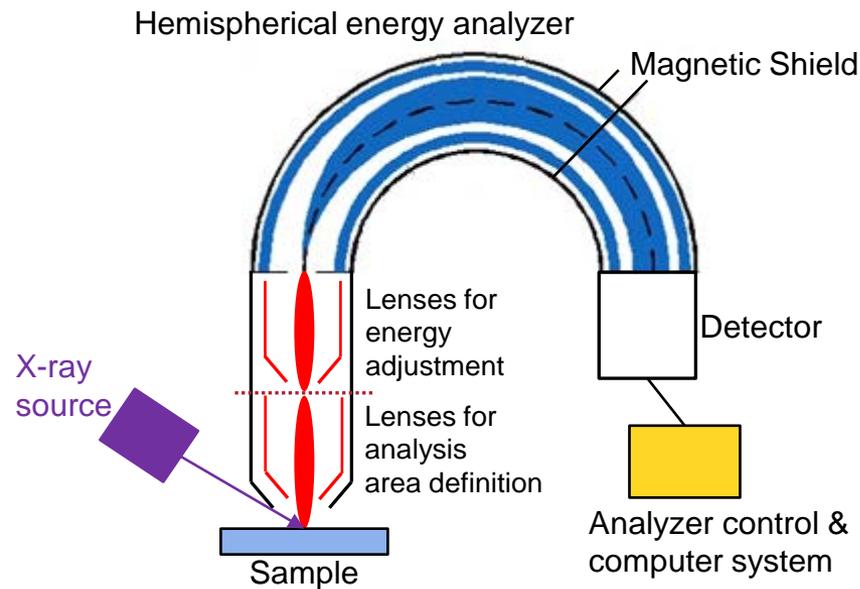
X-ray Source XR 50

http://www.specs.de/cms/front_content.php?idcat=118

XPS instrumentation

Electron analyzer

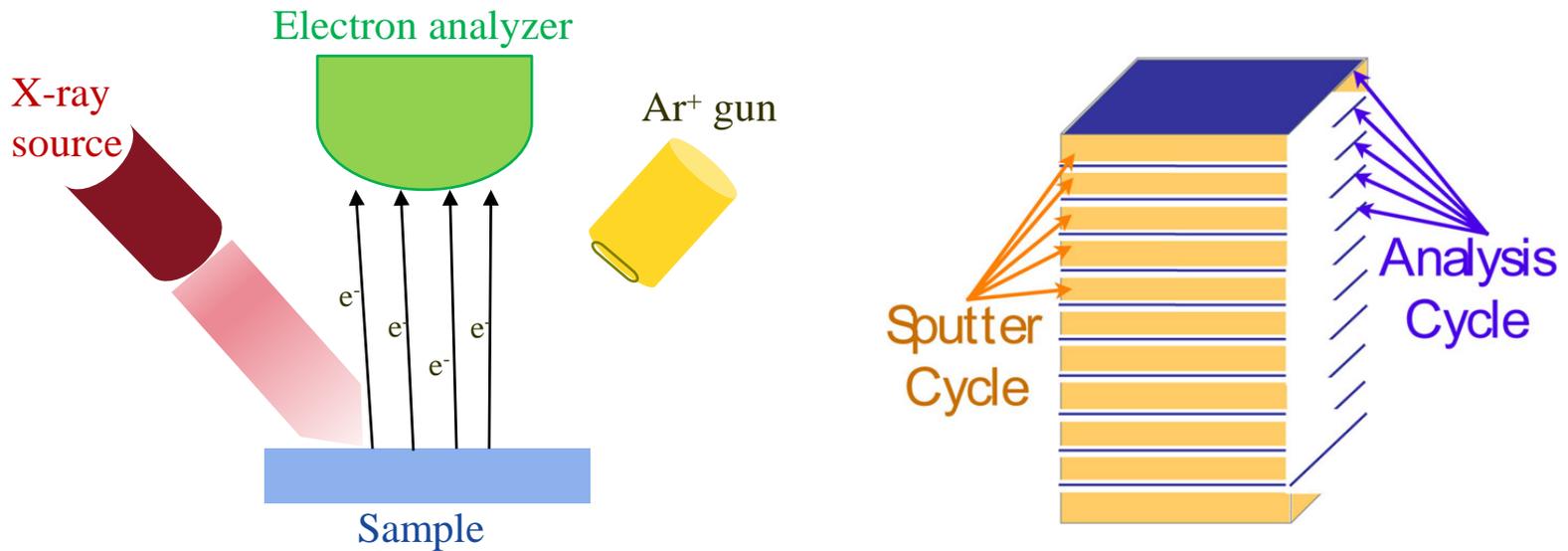
- Lens system to collect photoelectrons
- Analyzer to filter electron energies
- Detector to count electrons



XPS instrumentation

Ion gun

- Sample cleaning
- Depth profiling
- Ar^+ is the most widely used ion

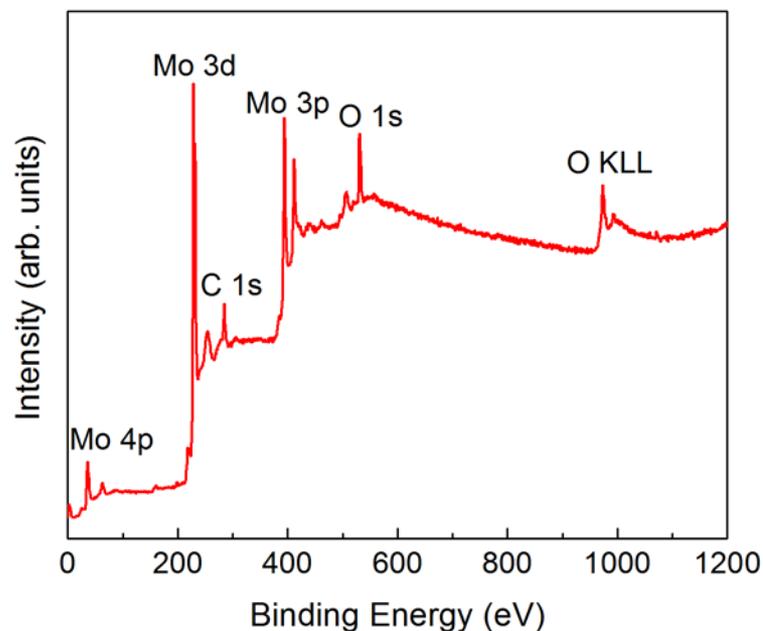


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XPS spectrum

- Photoelectron peaks reflect discrete binding energies of the electrons present in the solid
 - MoO₃ film excited by Al K α (1486.6 eV)

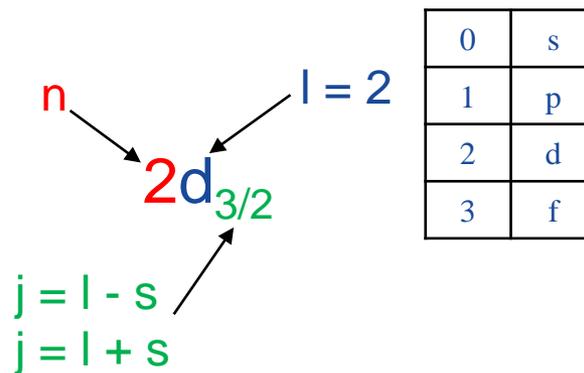


XPS Peak: spin orbit coupling

- XPS peak is originated from the photoelectrons in the core-levels and valence band.
- In the quantum mechanics, the nomenclature for a core level is nlj :
 - n : principle quantum number
 - l : orbit angular momentum quantum number
 - j : total angular momentum quantum number; $j = l + s$
 - s : spin angular momentum quantum number, $s = \pm 1/2$

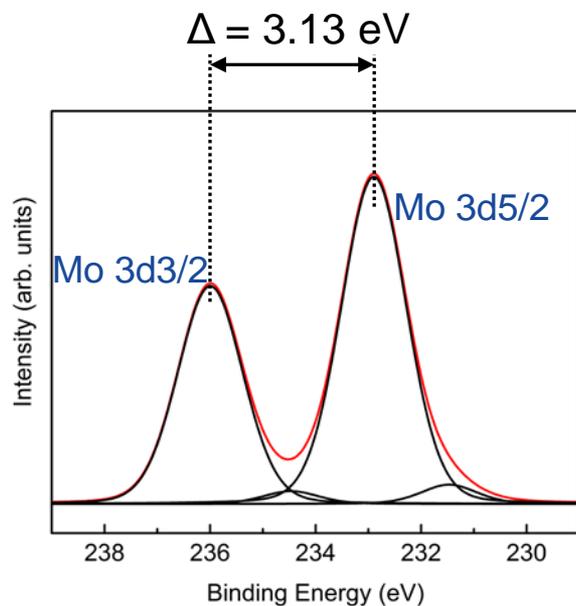
If $l=0$, single XPS peak

if $l>0$, a doublet peak-- spin orbit ($l-s$) coupling



XPS Peak: spin orbit coupling

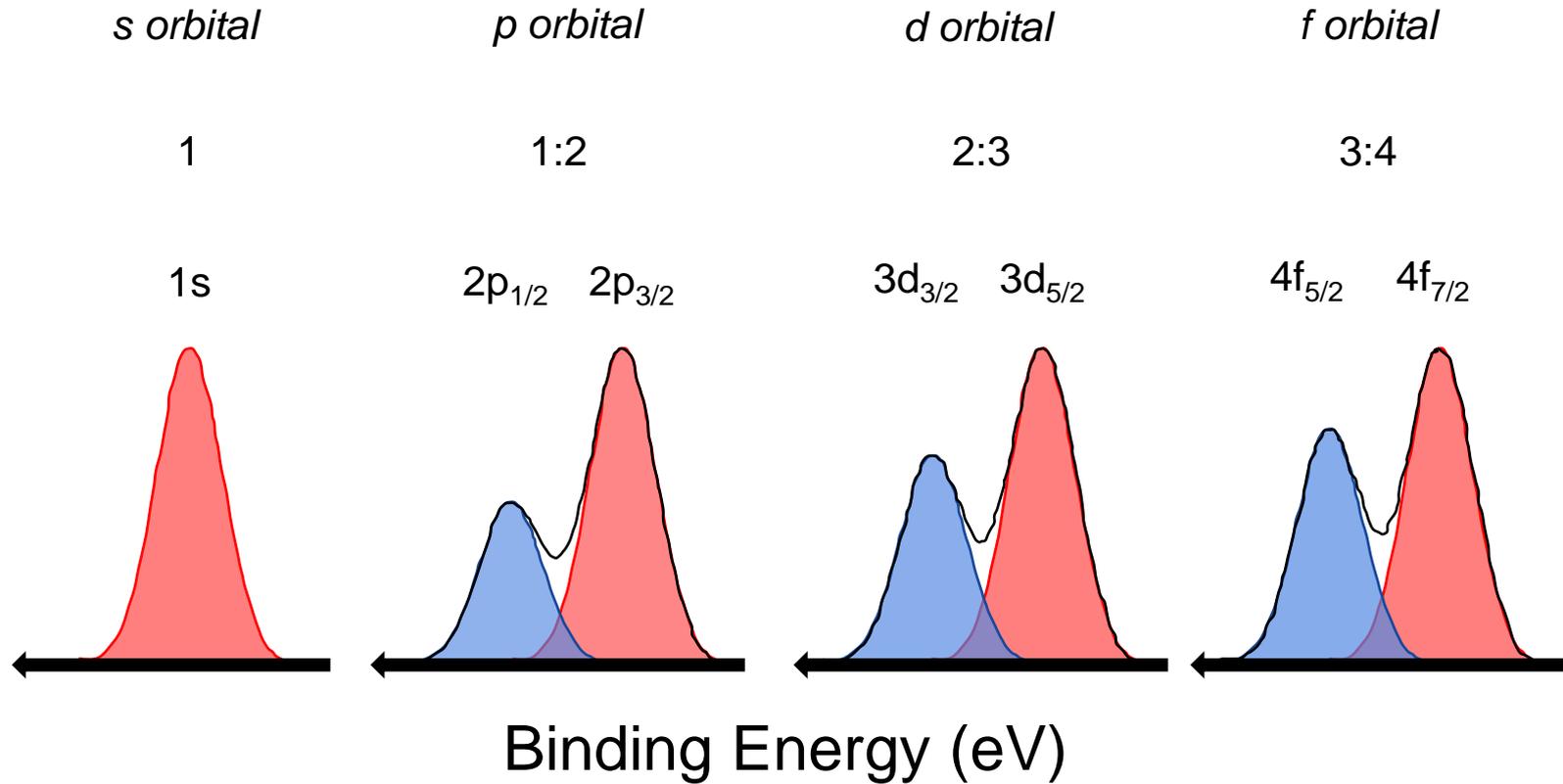
- Since s can be $\pm 1/2$, each level with $l > 0$ is split into two sublevels with an energy difference known as the spin-orbit splitting.
- The degeneracy of each of these levels is $2j+1$



MoO₃ film

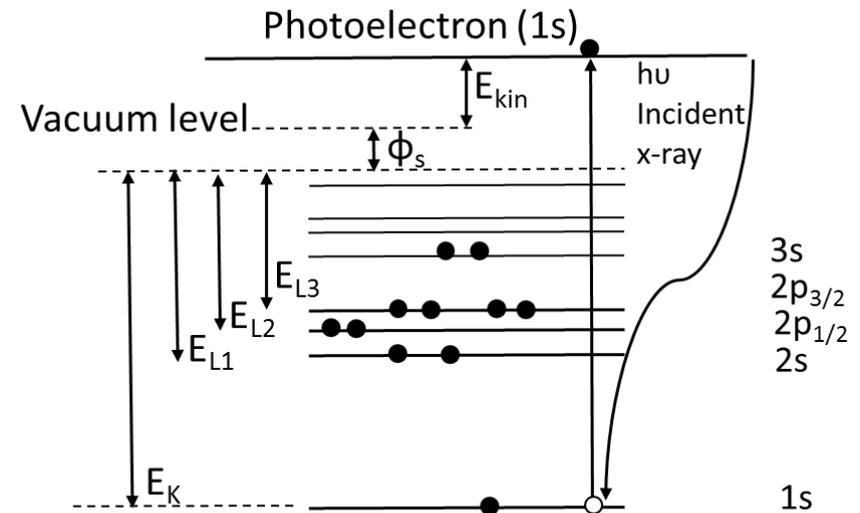
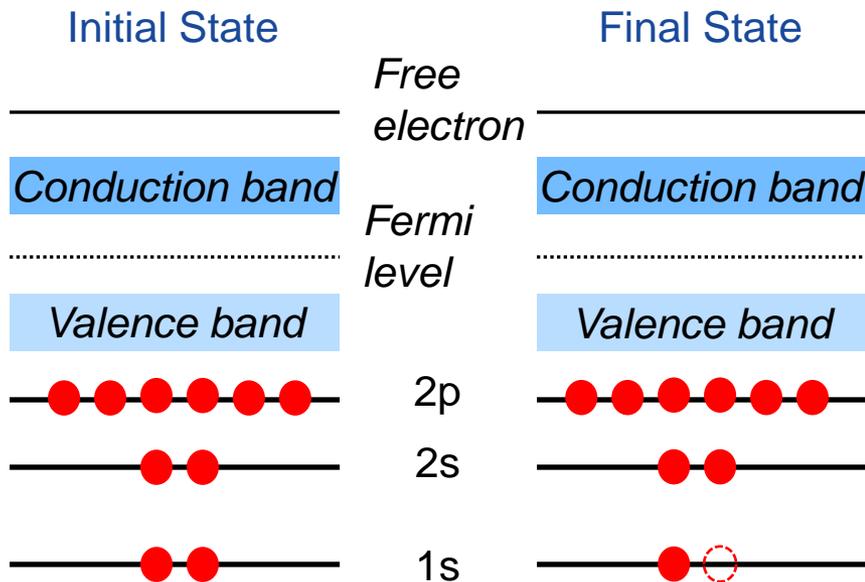
Orbital	l	J	Degeneracy	Electron level
1s	0	1/2	1	1s
2s	0	1/2	1	2s
2p	1	1/2	2	2p _{1/2}
2p	1	3/2	4	2p _{3/2}
3d	2	3/2	4	3d _{3/2}
3d	2	5/2	6	3d _{5/2}
4f	3	5/2	6	4f _{5/2}
4f	3	7/2	8	4f _{7/2}

XPS Peak intensities



XPS energy levels

- The photoelectron's binding energy will be based on the element's final-state configuration.



Energy lines

- Photon energies, in eV, of principle K- and L- shell emission lines.

Element	K α_1	K α_2	K β_1	L α_1	L α_2	L β_1	L β_2	L γ_1
3 Li	54.3							
4 Be	108.5							
5 B	183.3							
6 C	277							
7 N	392.4							
8 O	524.9							
9 F	676.8							
10 Ne	848.6	848.6						
11 Na	1,040.98	1,040.98	1,071.1					
12 Mg	1,253.60	1,253.60	1,302.2					
13 Al	1,486.70	1,486.27	1,557.45					
14 Si	1,739.98	1,739.38	1,835.94					
15 P	2,013.7	2,012.7	2,139.1					
16 S	2,307.84	2,306.64	2,464.04					
17 Cl	2,622.39	2,620.78	2,815.6					
18 Ar	2,957.70	2,955.63	3,190.5					
19 K	3,313.8	3,311.1	3,589.6					
20 Ca	3,691.68	3,688.09	4,012.7	341.3	341.3	344.9		
21 Sc	4,090.6	4,086.1	4,460.5	395.4	395.4	399.6		
22 Ti	4,510.84	4,504.86	4,931.81	452.2	452.2	458.4		
23 V	4,952.20	4,944.64	5,427.29	511.3	511.3	519.2		
24 Cr	5,414.72	5,405.509	5,946.71	572.8	572.8	582.8		
25 Mn	5,898.75	5,887.65	6,490.45	637.4	637.4	648.8		
26 Fe	6,403.84	6,390.84	7,057.98	705.0	705.0	718.5		
27 Co	6,930.32	6,915.30	7,649.43	776.2	776.2	791.4		
28 Ni	7,478.15	7,460.89	8,264.66	851.5	851.5	868.8		
29 Cu	8,047.78	8,027.83	8,905.29	929.7	929.7	949.8		
30 Zn	8,638.86	8,615.78	9,572.0	1,011.7	1,011.7	1,034.7		
31 Ga	9,251.74	9,224.82	10,264.2	1,097.92	1,097.92	1,124.8		
32 Ge	9,886.42	9,855.32	10,982.1	1,188.00	1,188.00	1,218.5		
33 As	10,543.72	10,507.99	11,726.2	1,282.0	1,282.0	1,317.0		
34 Se	11,222.4	11,181.4	12,495.9	1,379.10	1,379.10	1,419.23		
35 Br	11,924.2	11,877.6	13,291.4	1,480.43	1,480.43	1,525.90		
36 Kr	12,649	12,598	14,112	1,586.0	1,586.0	1,636.6		
37 Rb	13,395.3	13,335.8	14,961.3	1,694.13	1,692.56	1,752.17		
38 Sr	14,165	14,097.9	15,835.7	1,806.56	1,804.74	1,871.72		
39 Y	14,958.4	14,882.9	16,737.8	1,922.56	1,920.47	1,995.84		
40 Zr	15,775.1	15,690.9	17,667.8	2,042.36	2,039.9	2,124.4*	2,219.4	2,302.7

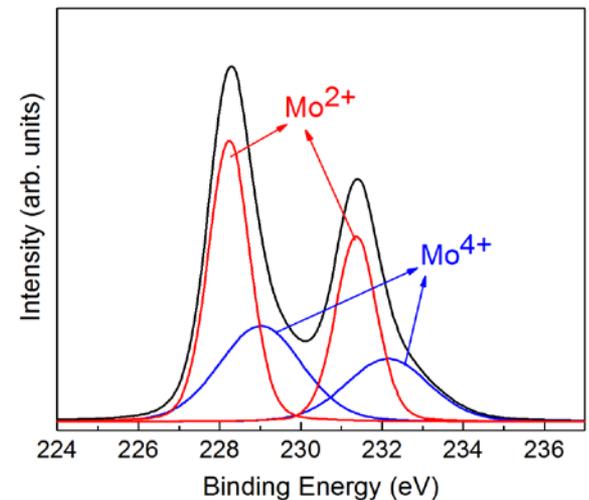
X-ray data booklet, Lawrence Berkeley National Laboratory, 3rd edition, 2009

XPS energy: chemical shifts

- When an atom makes a bond with another atom, the valence electron density changes resulting in an adjustment of the electrostatic potential affecting the core electrons.
- Change in the binding energies of the core electrons cause shifts in the corresponding photoelectron peaks

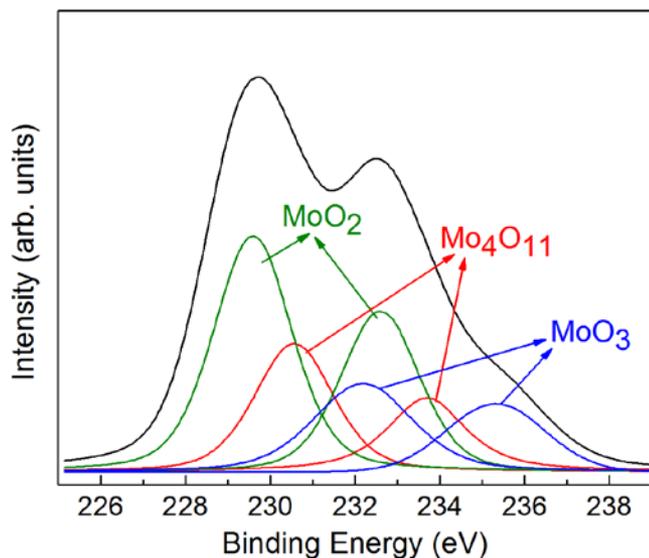
$$E_K = h\nu - E_b - \phi_{sp}$$

- Atom loses valence charge, BE increases
 - (Mo \rightarrow MoO₂)
- Atom gains valence charge, BE decreases
 - (MoO₃ \rightarrow MoO₂)



XPS energy: chemical shifts

- Atoms of higher positive oxidation state show a higher binding energy
 - Extra coulombic interaction between the photo-emitted electron and the ion core



Element	level	Compound	Binding Energy (eV)
Mo	3d _{5/2}	Mo ₂ C	227.8
Mo	3d _{5/2}	Mo	228.0
Mo	3d _{5/2}	MoO ₂	229.4
Mo	3d _{5/2}	MoS ₂	229.4
Mo	3d _{5/2}	MoCl ₃	230.0
Mo	3d _{5/2}	MoCl ₄	231.0
Mo	3d _{5/2}	MoCl ₅	232.2
Mo	3d _{5/2}	MoO ₃	232.6

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Quantitative analysis

- Atomic concentration of elements can be calculated:

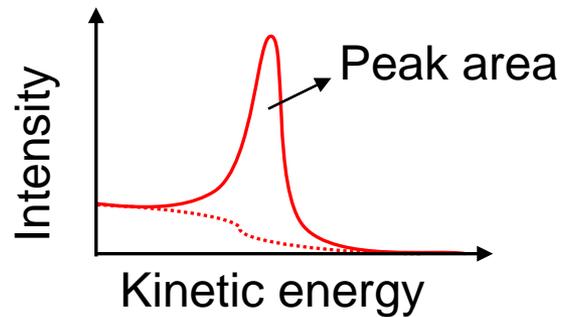
$$n_i = n_i / \sum n_i$$

- We define sensitivity factors: $S_i = \sigma_{ij} \lambda(KE)$

- σ_{ij} : Photoionization cross-section of peak j of element i
- $\lambda(KE)$: Inelastic mean free path length

- Therefore, n_i is dependent on the peak area (I_{ij}) and sensitivity factor

$$n_i = \frac{I_{ij}/S_i}{\sum I_i/S_i}$$



Quantitative analysis

➤ Atomic sensitivity factors for X-ray sources at 54.7°

Element	Line	ASF									
Ag	3d	5.987	Eu	4d	2.488	Na	1s	1.685	Si	2p	0.339
Al	2p	0.234	F	1s	1.000	Nb	3d	2.921	Sm	3d _{5/2}	3.611
Ar	2p	1.155	Fe	2p	2.957	Nd	3d	5.671	Sn	3d _{5/2}	4.725
As	3d	0.677	Ga	2p _{3/2}	3.720	Ne	1s	1.340	Sr	3d	1.843
Au	4f	6.250	Gd	4d	2.484	Ni	2p	4.044	Ta	4f	3.082
B	1s	0.159	Ge	2p _{3/2}	3.457	O	1s	0.711	Tb	4d	2.477
Ba	3d _{5/2}	7.469	Hf	4f	2.639	Os	4f	4.461	Tc	3d	3.776
Be	1s	0.074	Hg	4f	6.915	P	2p	0.486	Te	3d _{5/2}	5.705
Bi	4f	9.140	Ho	4d	2.469	Pb	4f	8.329	Th	4f _{7/2}	9.089
Br	3d	1.053	I	3d _{5/2}	6.206	Pd	3d	5.356	Ti	2p	2.001
C	1s	0.296	In	3d _{5/2}	4.359	Pm	3d	4.597	Tl	4f	7.691
Ca	2p	1.833	Ir	4f	5.021	Pr	3d	7.627	Tm	4d	2.454
Cd	3d _{5/2}	3.974	K	2p	1.466	Pt	4f	5.575	U	4f _{7/2}	10.315
Ce	3d	8.808	Kr	3d	1.287	Rb	3d	1.542	V	2p	2.116
Cl	2p	0.891	La	3d	9.122	Re	4f	3.961	W	4f	3.523
Co	2p	3.590	Li	1s	0.025	Rh	3d	4.822	Xe	3d _{5/2}	6.64
Cr	2p	2.427	Lu	4d	2.441	Ru	3d	4.273	Y	3d	2.175
Cs	3d _{5/2}	7.041	Mg	2s	0.252	S	2p	0.666	Yb	4d	2.451
Cu	2p	5.321	Mn	2p	2.659	Sb	3d _{5/2}	5.176	Zn	2p _{3/2}	3.726
Dy	4d	2.474	Mo	3d	3.321	Sc	2p	1.875	Zr	3d	2.576
Er	4d	2.463	N	1s	0.477	Se	3d	0.853			

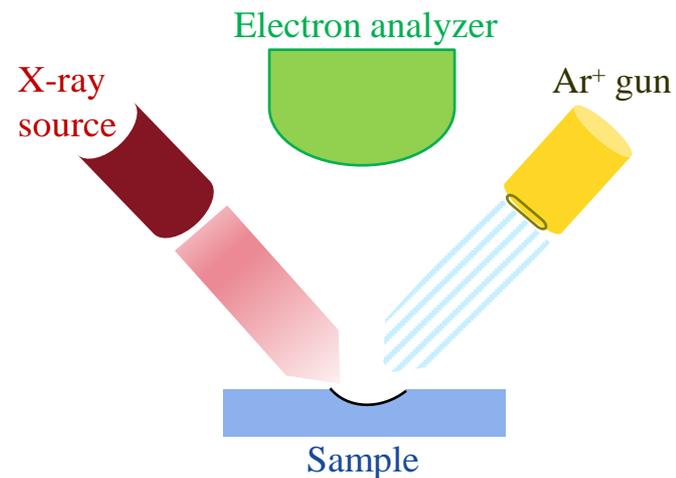
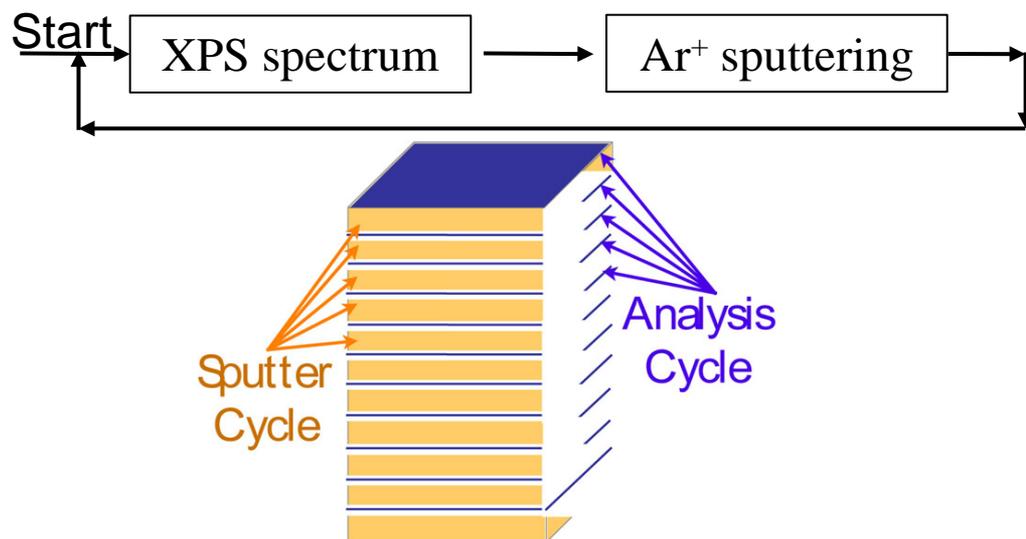
C.D. Wagner, et al, Surf. Interface Anal. 3, (1981) 211.

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Depth profiling

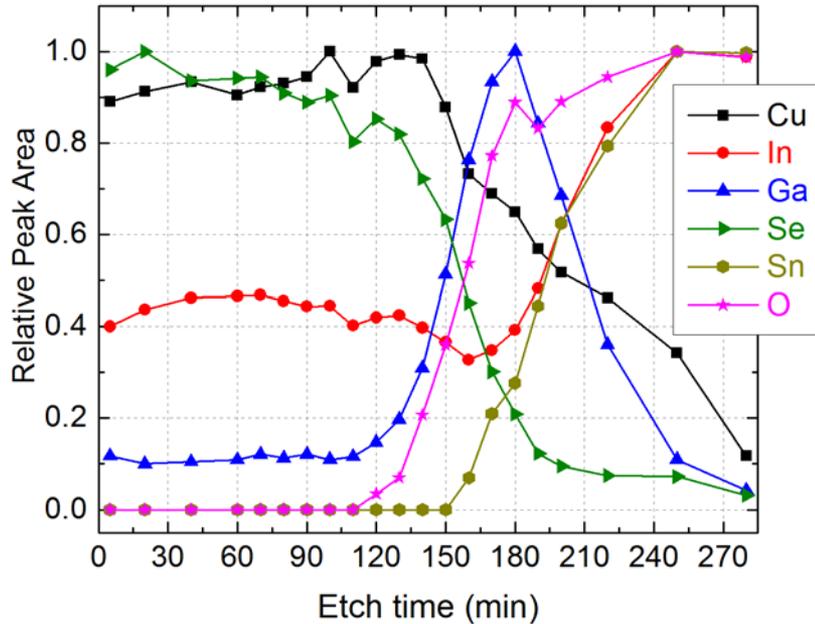
- To remove surface contaminations or find elemental distribution throughout the film thickness
 - Ar⁺ energy: 1-3 KV
 - Sample rotation



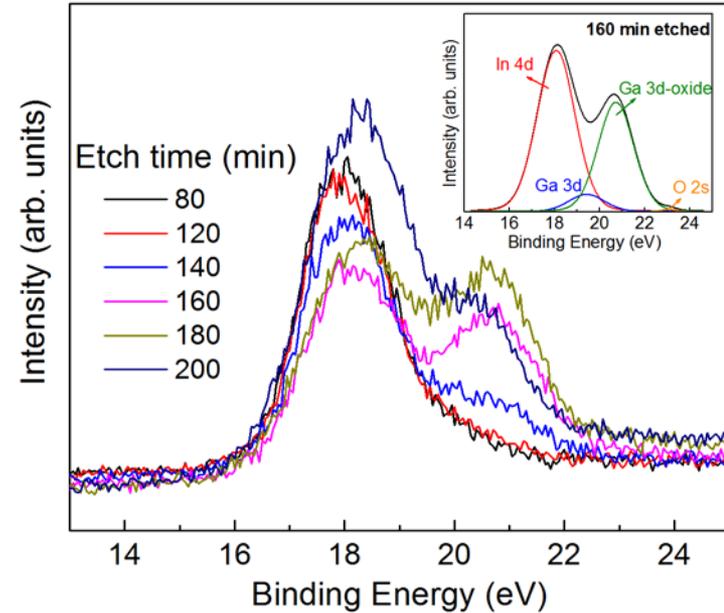
Depth profiling

➤ Cu(In,Ga)Se₂ film deposited on ITO

Elemental distribution



Ga 3d analysis



➤ Ga accumulation at the interface
➤ Cu diffusion into the ITO layer

➤ Formation of Ga oxide at the interface

Summary

Vacuum Range

- Requires ultra high vacuum
- Sample compatibility with UHV environment may be an issue with biological samples

Sensitivity

- Measures the elemental composition of the top 10 nm
- Can detect all elements except H and He
- Detection limits typically ~ 0.1 atomic percent
- Typically the smallest analytical area ~10 μm

Material analysis

- Can analyze metals, inorganic, polymers
- Sample compatibility with UHV environment

Online sources

- PNNL EMSL: www.emsl.gov
- AVS Science & Technology Society: www.avs.org
- AVS Surface Science Spectra: www.avs.org/literature.sss.aspx
- Evans Analytical Group: www.cea.com
- NIST X-ray Photoelectron Spectroscopy Database: www.srdata.nist.gov/sps/
- NIST Electron Inelastic-Mean-Free-Path Database: www.nist.gov/srd/nist71.htm
- QUASES-IMFP-TPP2M QUASES-Tougaard Inc.: www.quases.com
- Surfaces & Interfaces Section, National Physical Lab. www.npl.co.uk/npl/cmmt/sis
- XPS MultiQuant www.chemres.hu/aki/XMQpages/XMQhome.htm
- ASTM International: www.astm.org