

Nanoparticle Technology

Lecture 09: Nanomaterials Characterization II

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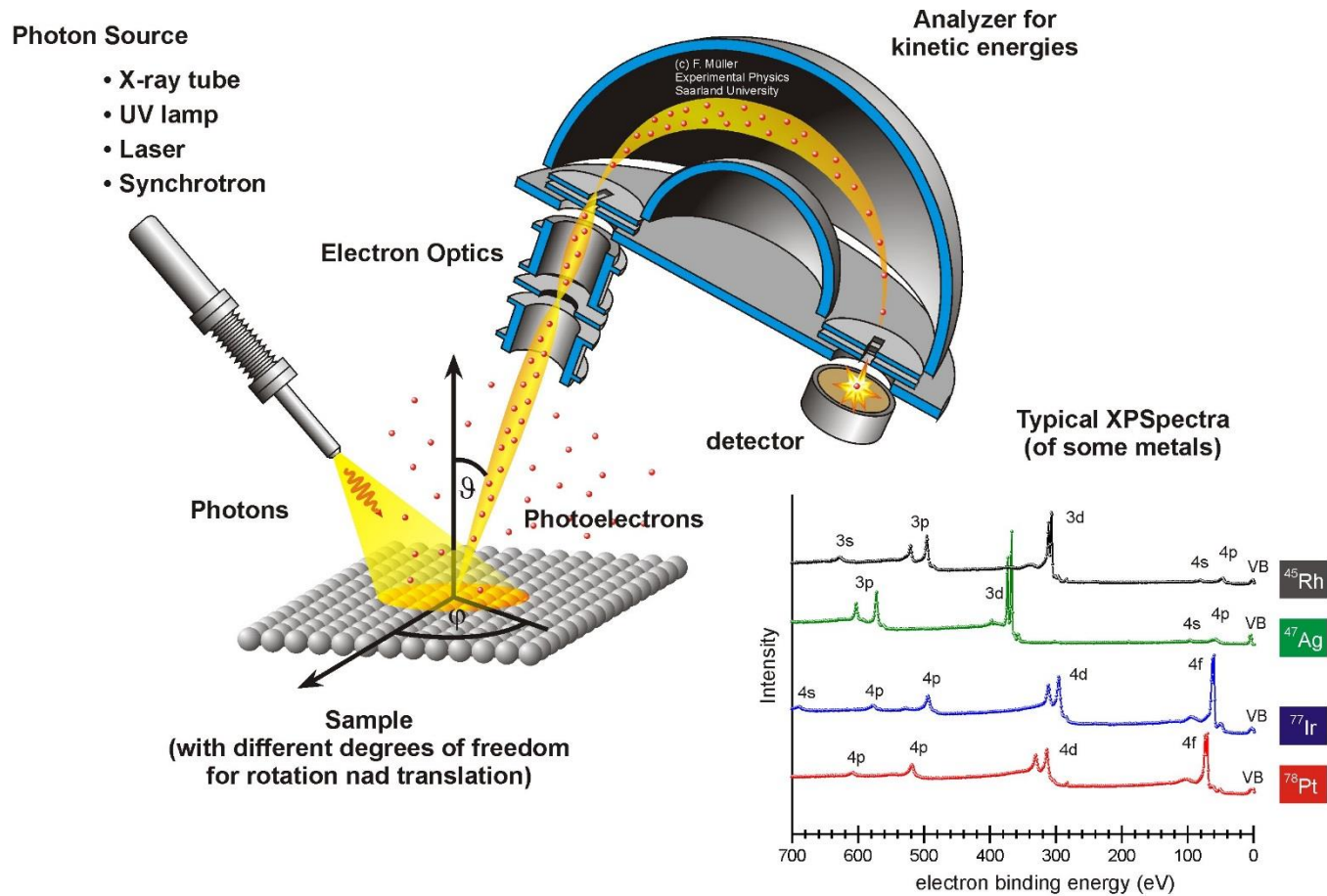
X-ray photoelectron spectroscopy

Electron spectroscopy

Classification

Spectroscopy	In/Out	Incident energy	Information
X-ray photoelectron spectroscopy (XPS)	In: X-ray Out: electron	1 ~ 4 keV	Chemical states Composition
UV photoelectron spectroscopy (UPS)	In: UV photon Out: electron	5 ~ 500 eV	Valence band
Auger electron spectroscopy (AES)	In: electron Out: electron	1 ~ 5 keV	Depth profile Composition
Inverse photoelectron spectroscopy (IPS)	In: electron Out: photon	8 ~ 20 eV	Unoccupied states
Electron energy loss spectroscopy (EELS)	In: electron Out: electron	1 ~ 5 eV	Vibrations

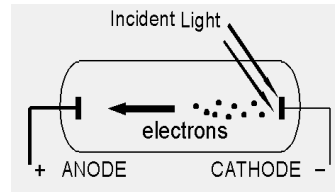
Electron spectroscopy



X-ray photoelectron spectroscopy

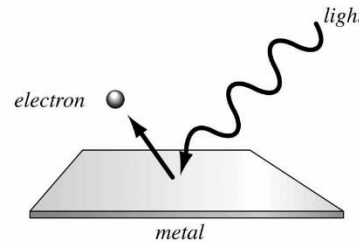
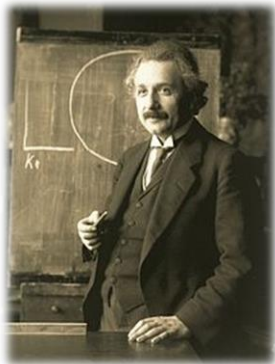
History of X-ray photoelectron spectroscopy (XPS)

Heinrich Hertz (1857 ~ 1894)



In 1887,
Heinrich Hertz discovered photoelectric effect, but could not explain.
“Ionization occurs when matter interacts with light of sufficient energy.”

Albert Einstein (1879 ~ 1955)



Albert Einstein received the Nobel Prize in Physics (1921) for his “services to theoretical physics”, in particular his discovery of the law of the photoelectric effect, a pivotal step in the evolution of quantum theory.

History of X-ray photoelectron spectroscopy (XPS)

Kai Siegbahn (1918 ~ 2007)



Precision Method for Obtaining Absolute Values of Atomic Binding Energies

CARL NORDLING, EVELYN SOKOLOWSKI, AND KAI SIEGBAHN
Department of Physics, University of Uppsala, Uppsala, Sweden
(Received January 10, 1957)

WE have recently developed a precision method of investigating atomic binding energies, which we believe will find application in a variety of problems in atomic and solid state physics. In principle, the method

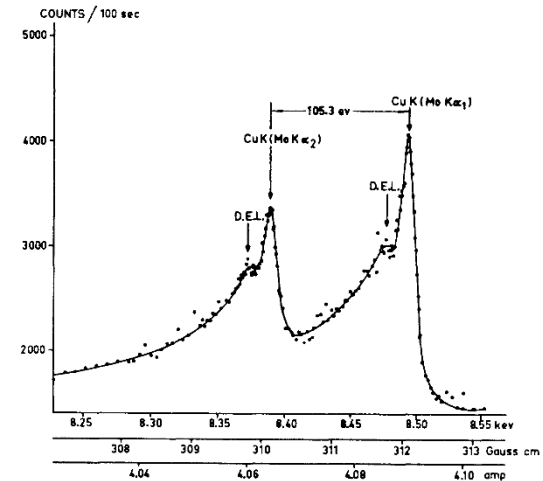


FIG. 1. Lines resulting from photoelectrons expelled from Cu by Mo $K\alpha_1$ and Mo $K\alpha_2$ x-radiation. The satellites marked D.E.L. are interpreted as due to electrons which have suffered a discrete energy loss when scattered in the source.

Nobel Prize in Physics (1981)

(His father, Manne Siegbahn, won the Nobel Prize in Physics in 1924 for development of X-ray spectroscopy.)

What can we do with XPS?

1. What elements are present in the surface region.

- Different elements have different binding energies of the inner (core) levels.

2. Often, also the chemical state of the elements can be determined,

- ex) Al-metal can be distinguished from Al-oxide.
- The exact binding energy of a core level depends on the chemical state. Chemical shifts.

3. The surface geometry can be qualitatively determined.

- Using diffraction effects and/or the chemical shifts of the binding energies (and imagination)

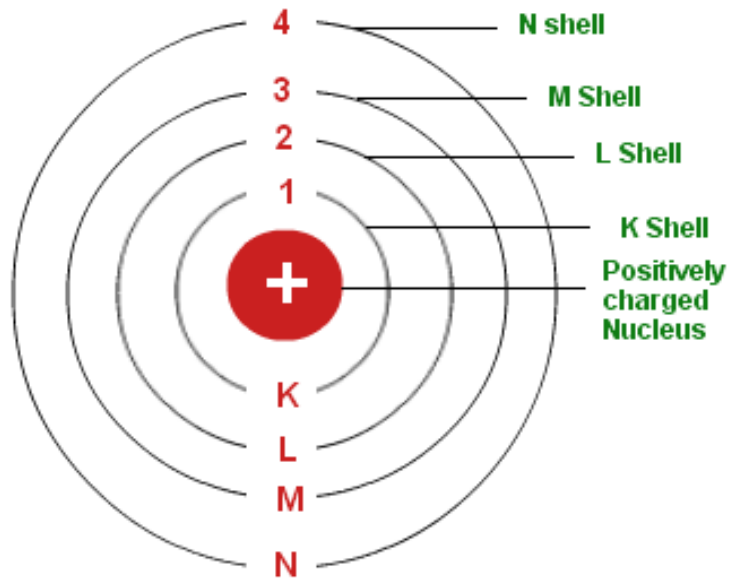
4. The band-structure of the solid can be measured.

- Measuring the emission from the valence band in an angle resolved manner

5. Chemically sensitive microscopy is possible.

In other words, chemical composition, geometrical structure and electronic structure can be analyzed by XPS measurement.

Valence shell



Hydrogen
(valence = 1)



H·

Nitrogen
(valence = 3)



·N·

Oxygen
(valence = 2)



·Ö·

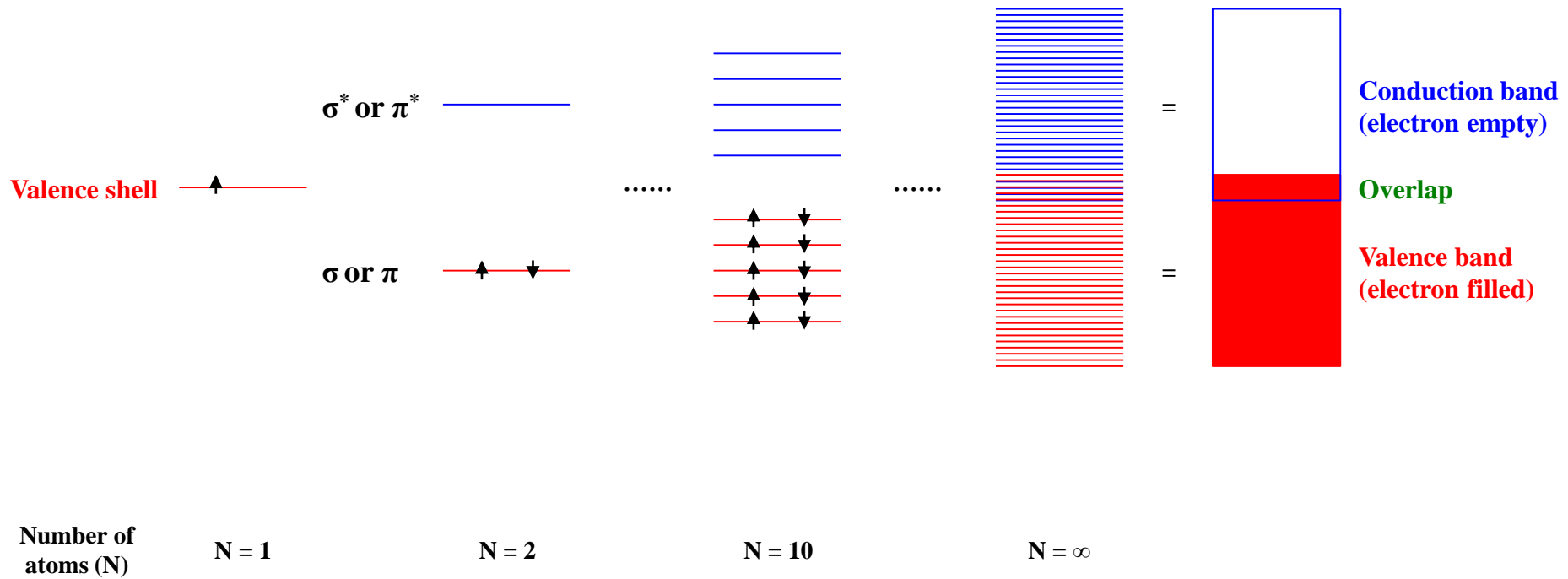
Carbon
(valence = 4)



·C·

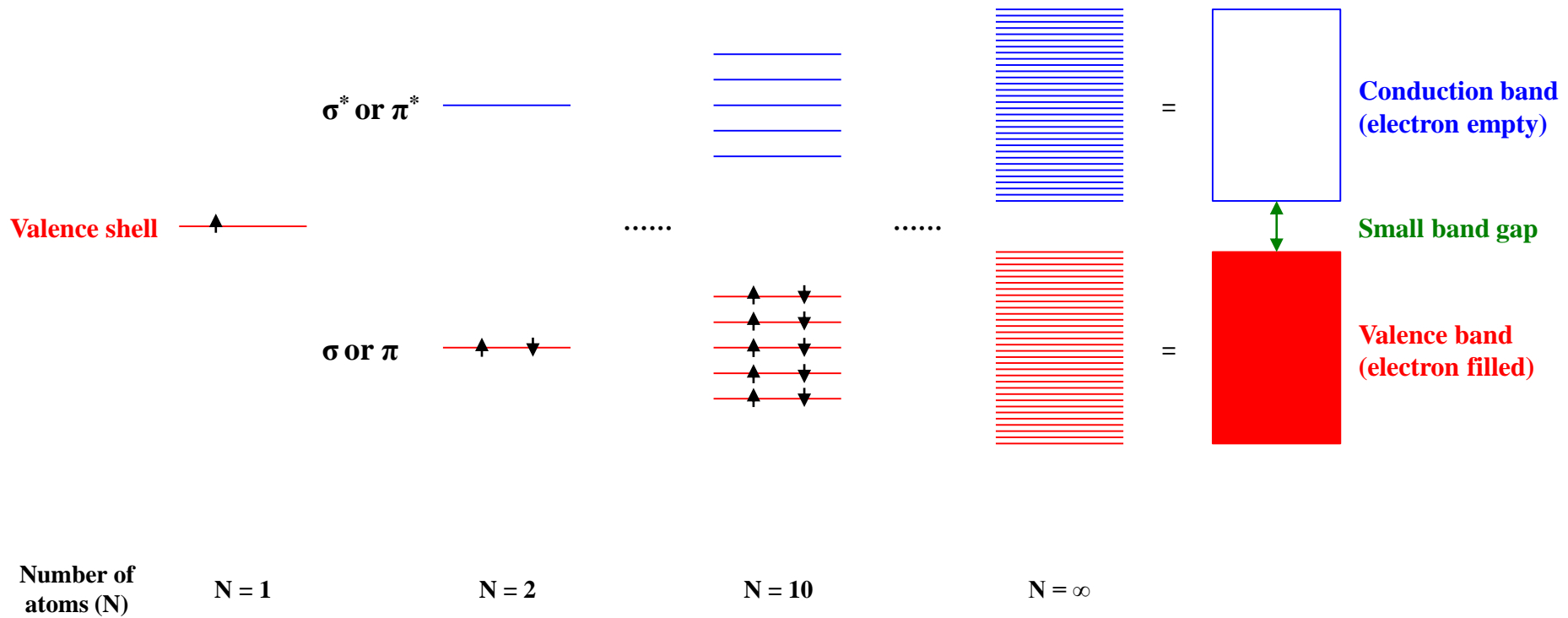
Energy levels: conduction and valence band

Conductors (metals)



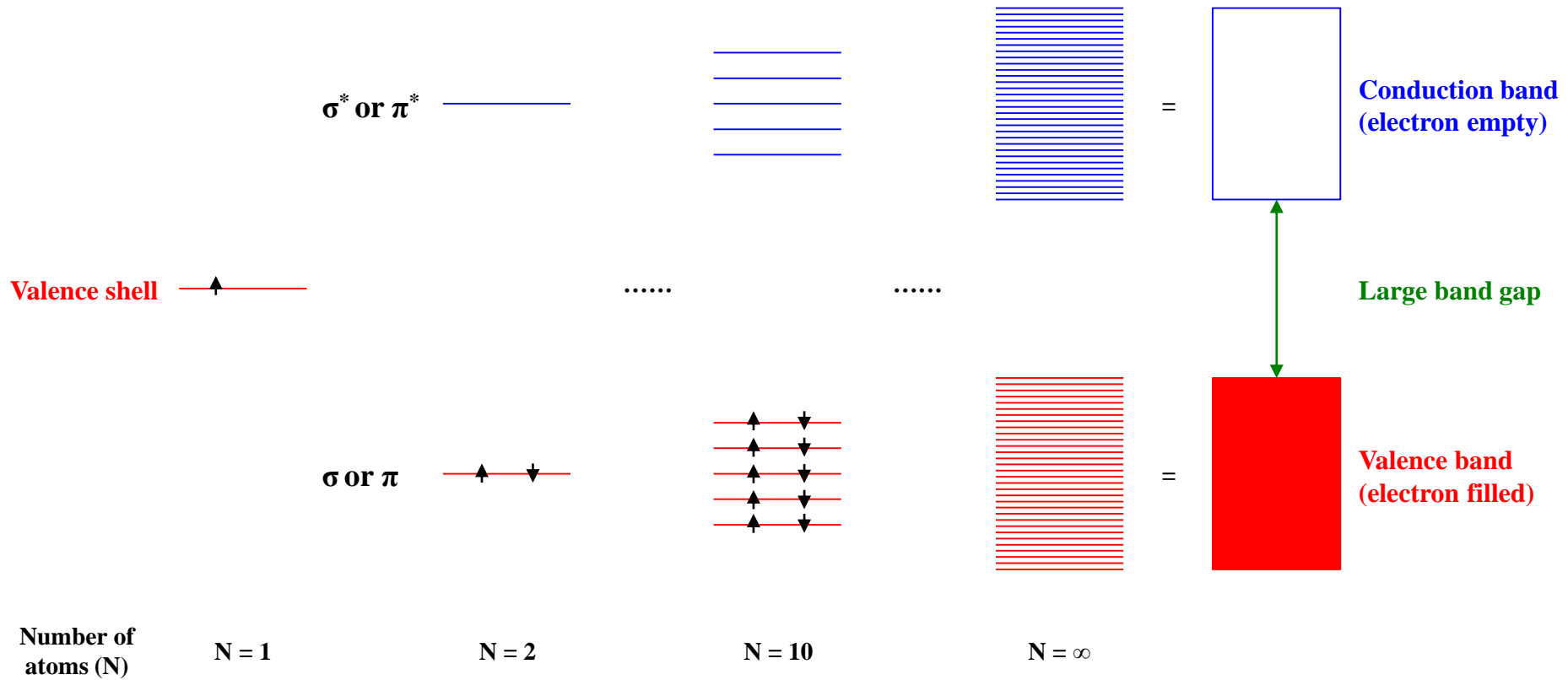
Energy levels: conduction and valence band

Semiconductors

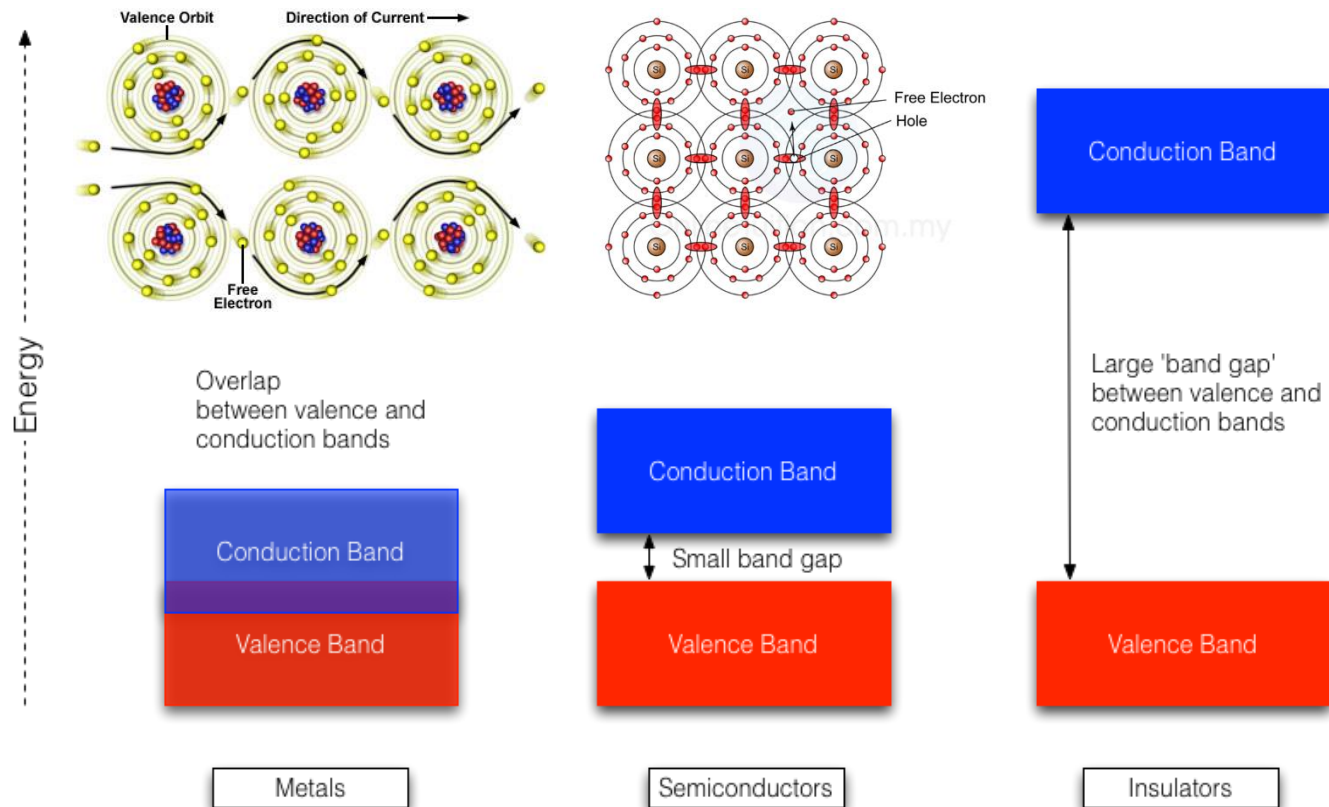


Energy levels: conduction and valence band

Insulators

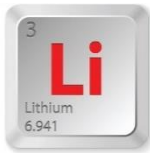
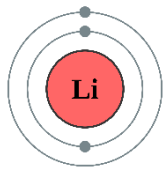


Energy levels: conduction and valence band

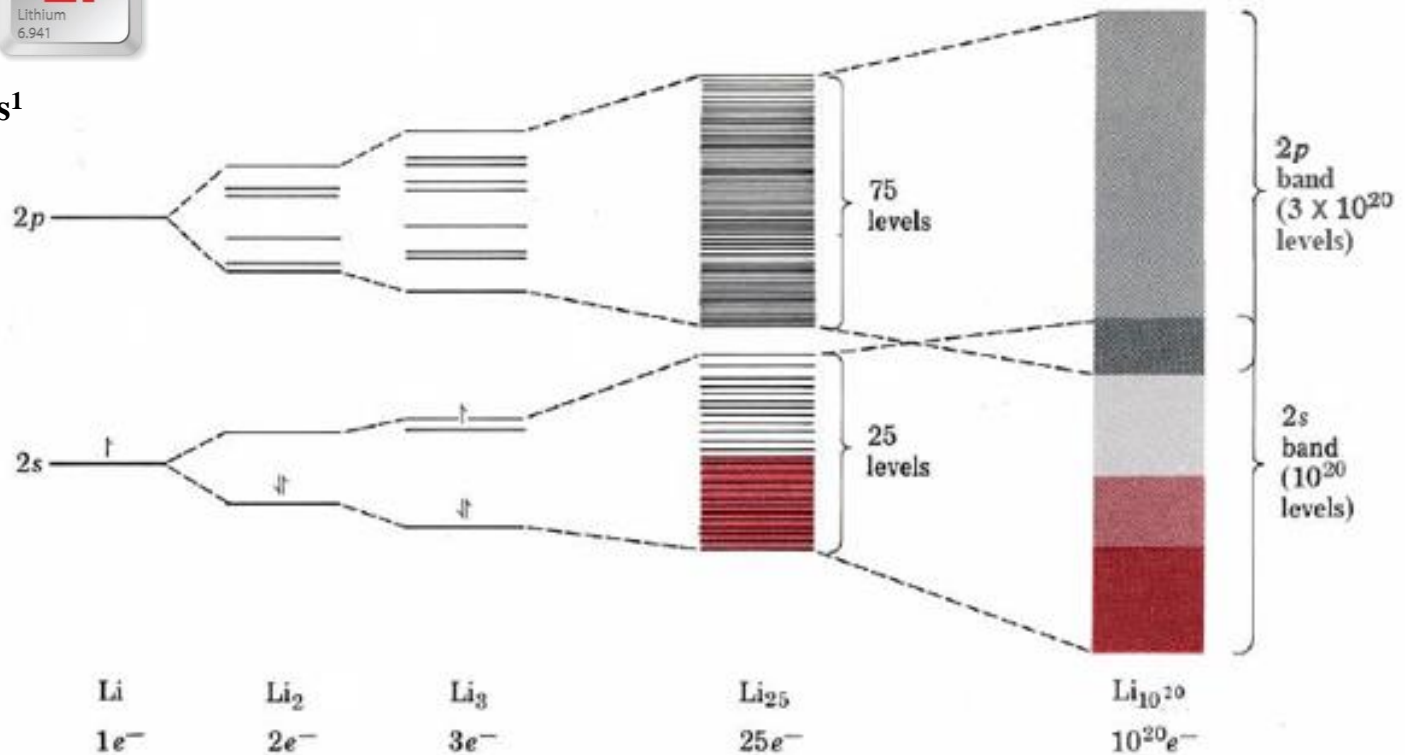


- Conduction band: the lowest-energy empty band
- Valence band: highest-energy filled band (which may be only partially filled)

Energy levels: core level

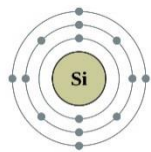


$1s^2 2s^1$

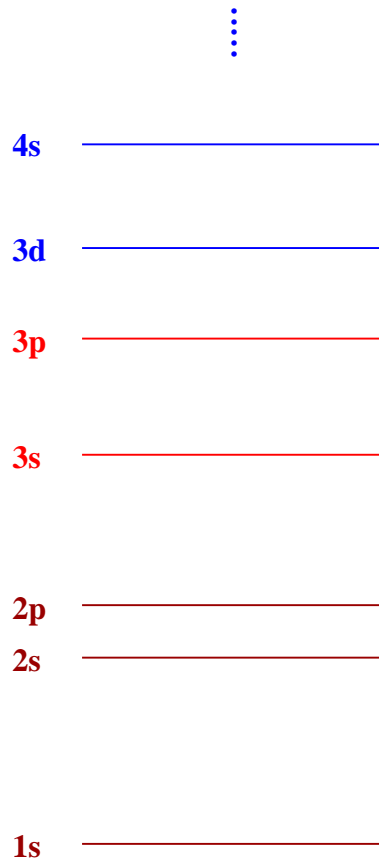


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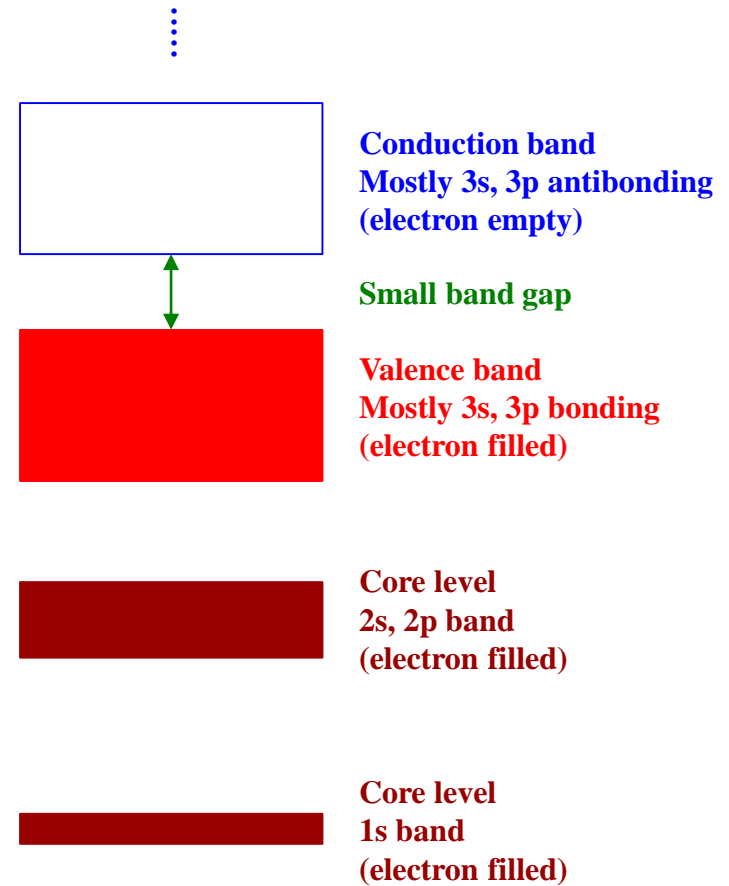
Energy levels: core level



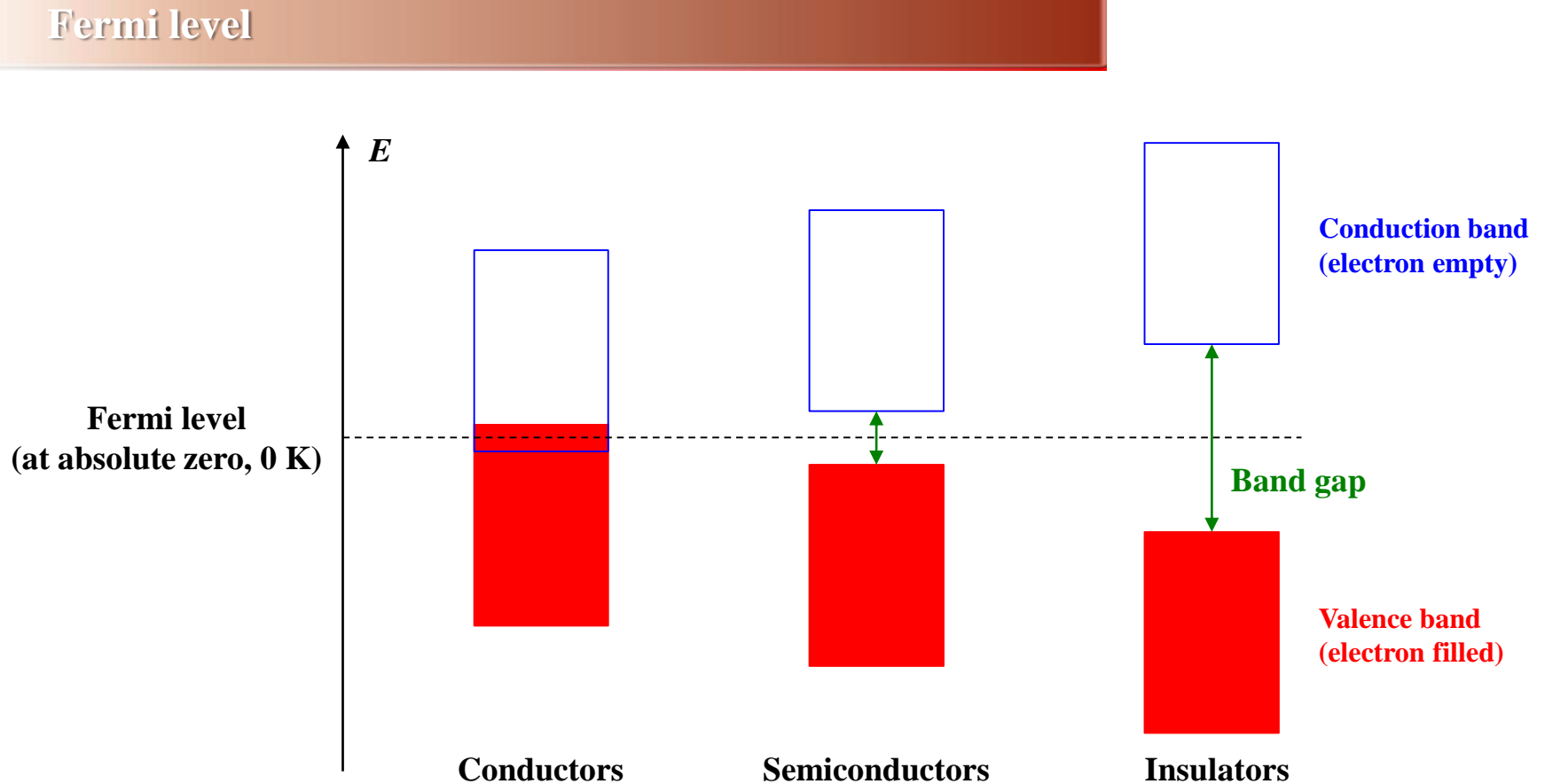
$1s^2 2s^2 2p^6 3s^2 3p^2$



Silicon atom

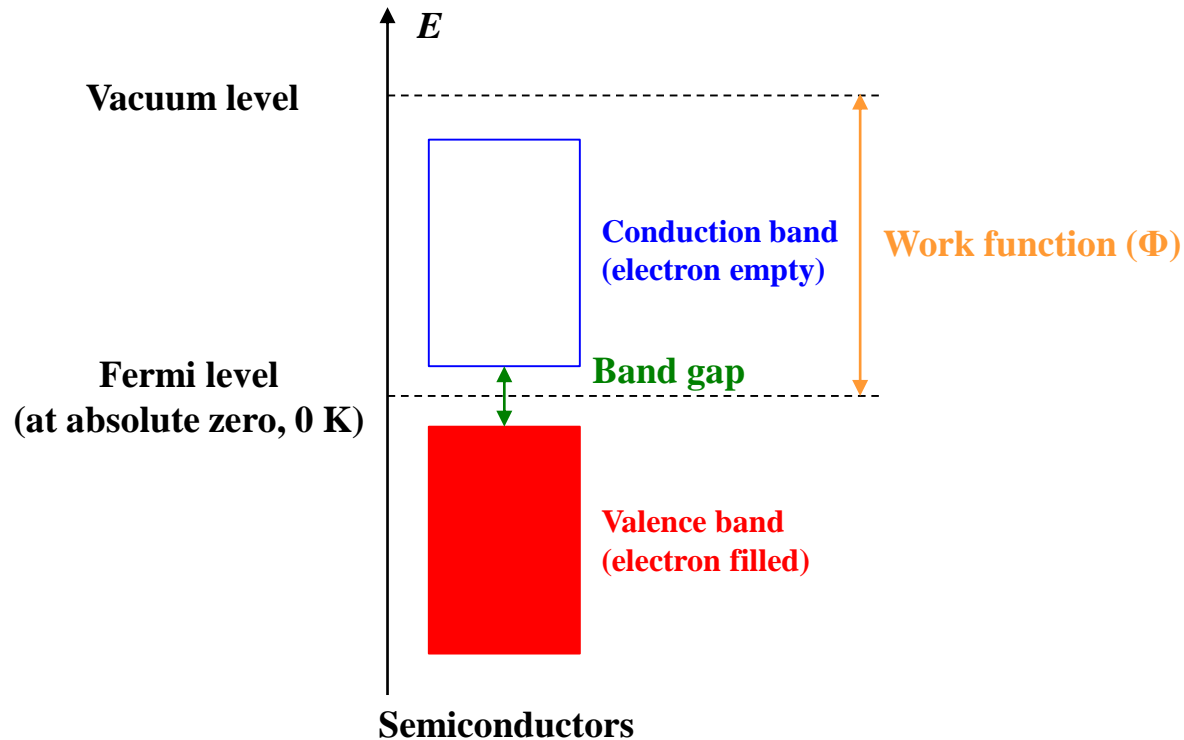


Silicon bulk



Fermi level is the highest energy level of electron in valence band at absolute zero (0 K).

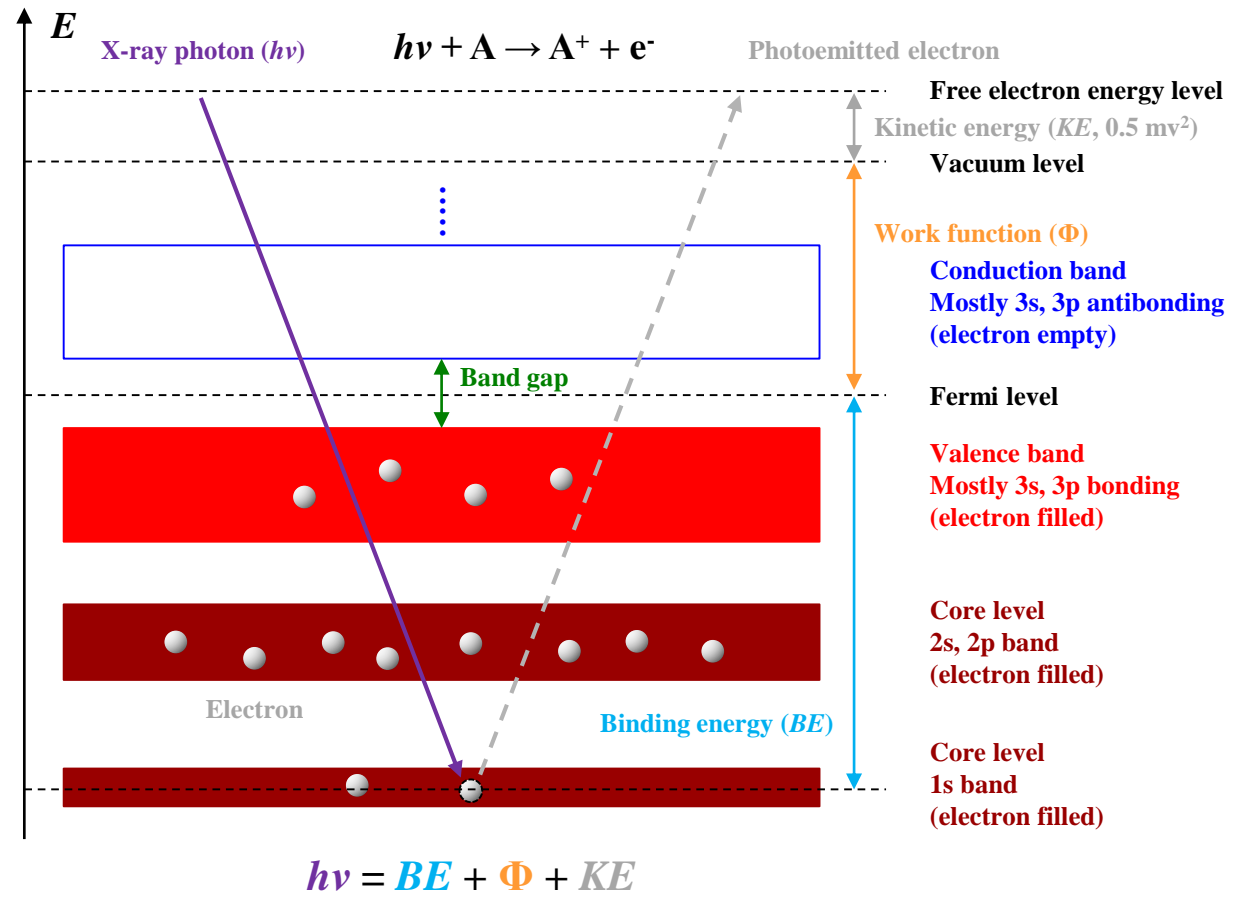
Vacuum level and work function



In solid-state physics, the work function is the minimum thermodynamic work (i.e. energy) needed to remove an electron from a solid to the vacuum level immediately (outside the solid surface).

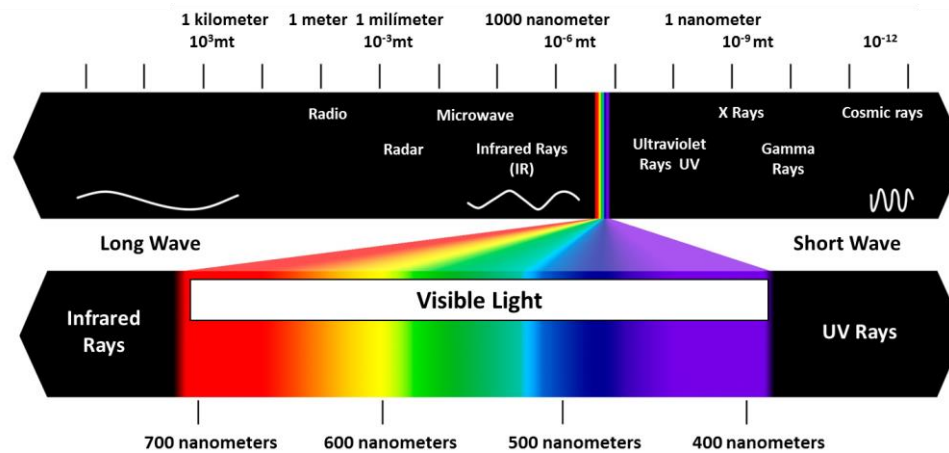
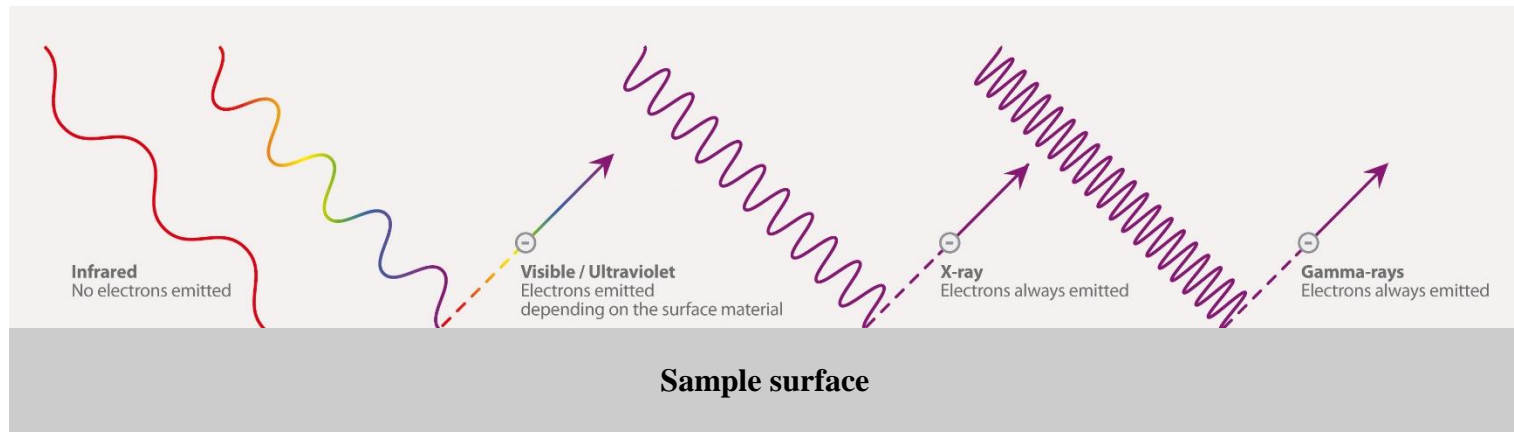
Period	Element	Work Function by eV Group
2	Boron	~4.5
	Carbon	4.5-5.0
3	Aluminum	4.0-4.5
4	Vanadium	4.0-4.5
	Chromium	4.5-5.0
	Iron	4.0-4.5
	Cobalt	4.0-4.5
	Nickel	~4.5
	Copper	4.0-4.5
	Zinc	4.0-4.5
	Germanium	4.5-5.0
	Arsenic	5.0-5.5
	Selenium	4.5-5.0
5	Molybdenum	4.0-4.5
	Technetium	4.0-4.5
	Ruthenium	4.5-5.0
	Rhodium	4.5-5.0
	Palladium	4.5-5.0
	Silver	4.0-4.5
	Cadmium	4.0-4.5
	Tin	4.0-4.5
	Antimony	4.0-4.5
	Tellurium	4.5-5.0
6	Tantalum	4.0-4.5
	Tungsten	~4.5
	Rhenium	~5.0
	Osmium	4.5-5.0
	Iridium	3.5-4.0
	Platinum	5.5-6.0
	Gold	4.5-5.0
	Mercury	~4.5
	Lead	~4.0
	Bismuth	4.0-4.5
	Polonium	4.5-5.0

Photoelectric effect



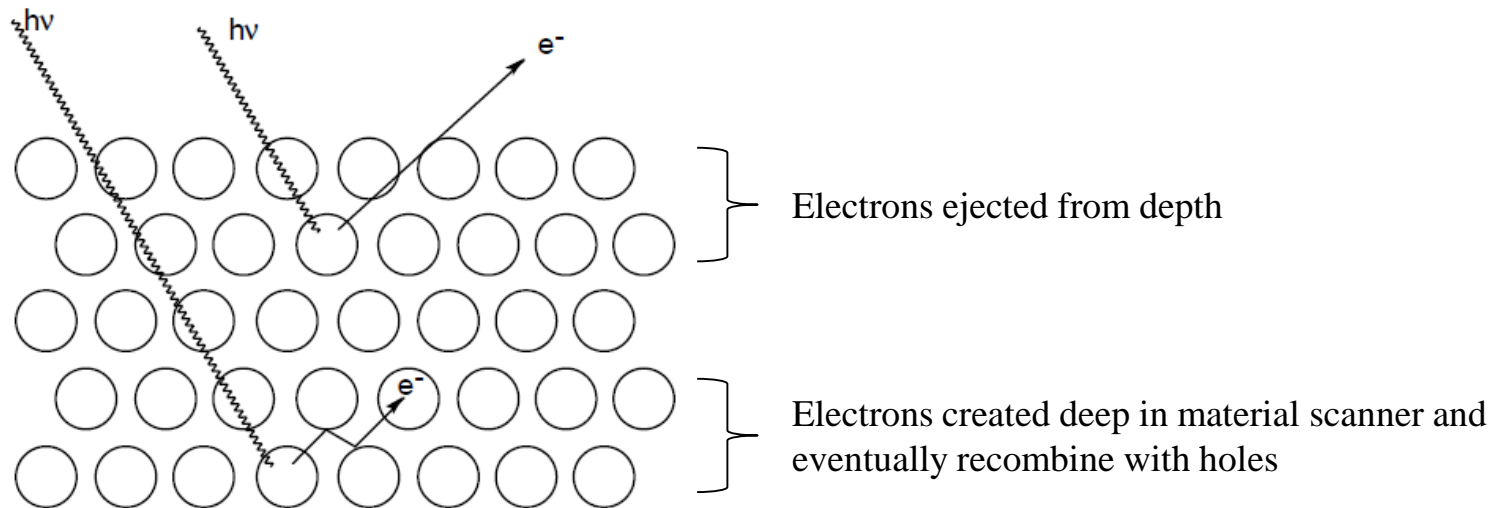
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Photoelectric effect



Photoelectric effect

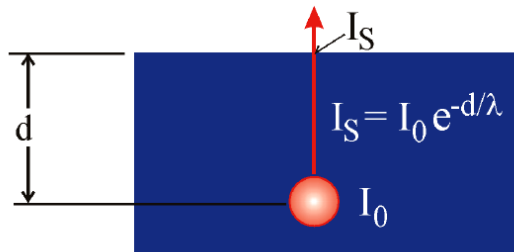
Inelastic mean free path (IMFP)



- The inelastic mean free path (IMFP) is an index of how far an electron on average travels through a solid before losing energy.

Photoelectric effect

Inelastic mean free path (IMFP)



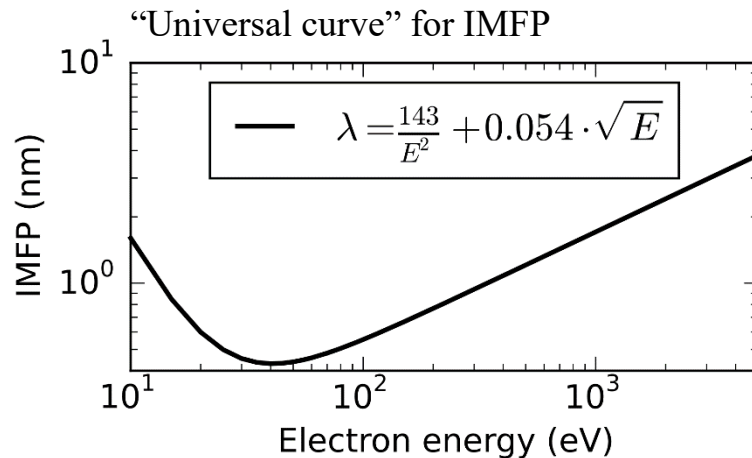
$$I_s = I_0 e^{-d/\lambda}$$

I_s = electron intensity at the surface

I_0 = electron intensity emitted at a depth d below the surface

d = depth

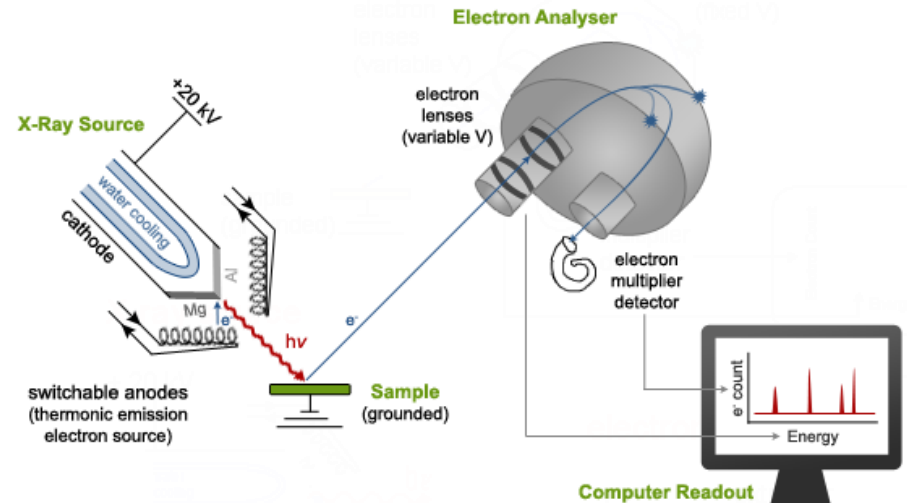
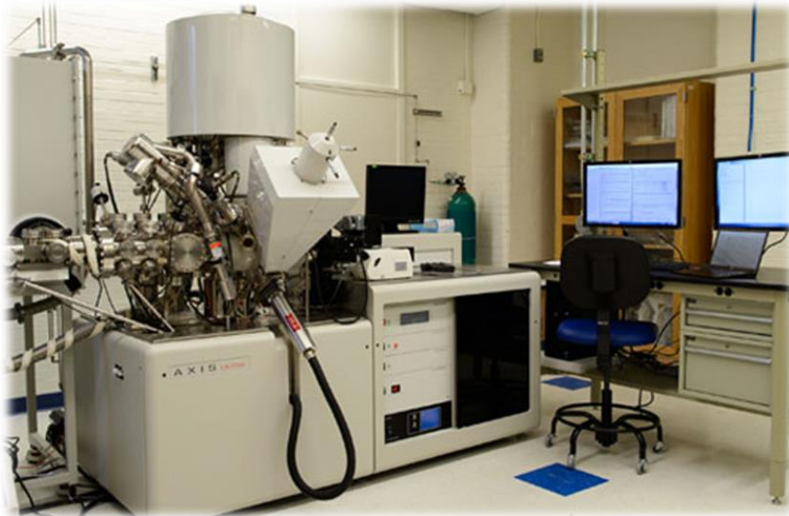
λ = inelastic mean free path



- Sampling depth is defined as the depth from which 95 % of all photoelectrons are scattered by the time they reach the surface (3λ).
- Most λ 's are in the range of 1.0 ~ 3.5 nm for Al K α radiation.
- The sampling depth (3λ) for X-ray photoelectron spectroscopy under these conditions is 3 ~ 10 nm.

Instrument

Typical X-ray photoelectron spectroscopy (XPS)

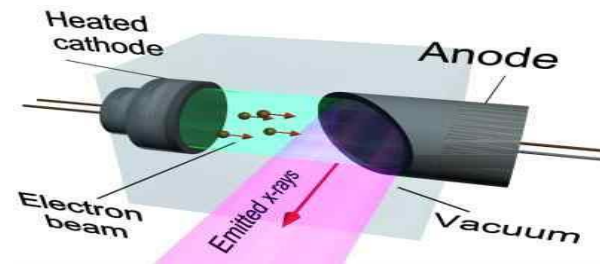


1. Sources
 - X-ray: aluminum (1486.6 eV) or magnesium (1253.6 eV)
 - Vacuum UV: He(I) (21.2 eV), He(II) (40.8 eV)
2. Sample size: centimeter scaled area
3. Chamber: ultrahigh vacuum ($< 10^{-8}$ Torr or $< 10^{-11}$ atm)
4. Electron analyzer: kinetic energy measurement
5. Detector: electron multiplier

Instrument

X-ray generation

Wilhelm Röntgen (1845 ~ 1923)

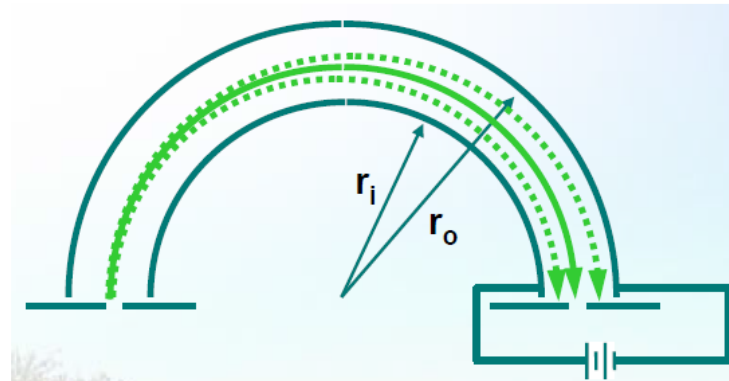


Energy and line widths of available anode materials.			
Anode	Radiation	Photon Energy (eV)	Line Width (eV)
Mg	K α	1253.6	0.7
Al	K α	1486.6	0.85
Zr	L α	2042.4	1.6
Ag	L α	2984.3	2.6
Ti	K α	4510.9	2.0
Cr	K α	5417	2.1

- X-rays can be generated by an X-ray tube, a vacuum tube that uses a high voltage to accelerate the electrons released by a hot cathode to a high velocity.
- The high velocity electrons collide with a metal target (the anode), creating the X-rays.

Instrument

Electron analyser



$$F = qE = \frac{mv^2}{r} = \frac{2KE}{r} = \frac{2e\Delta V}{\left(\frac{1}{r_i} - \frac{1}{r_o}\right)r^2}$$

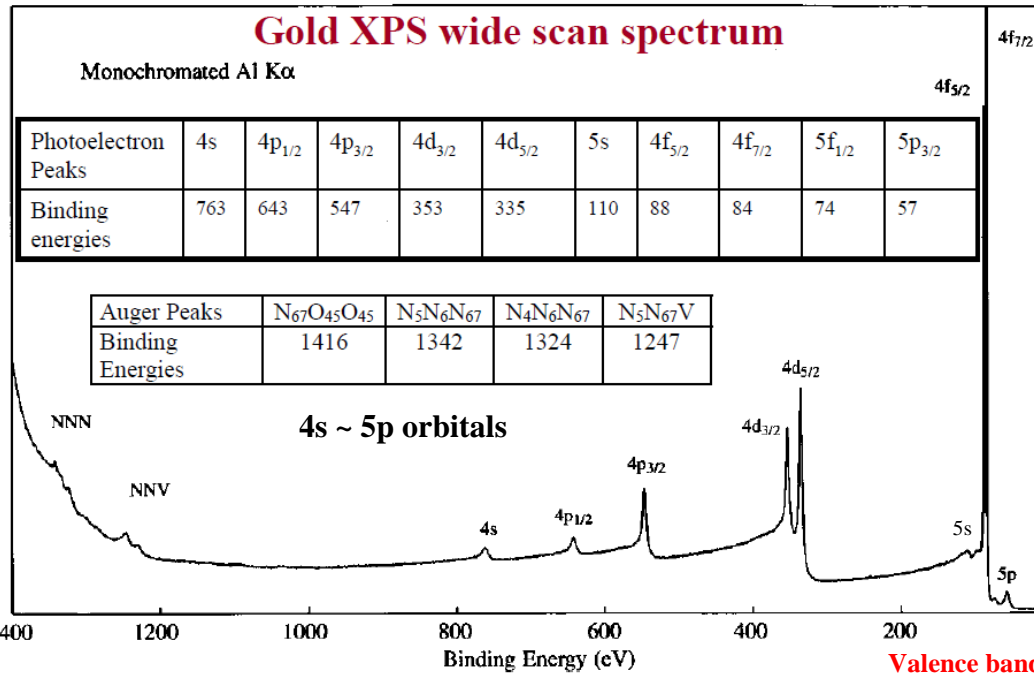
$$KE = \frac{e\Delta V}{\left(\frac{1}{r_i} - \frac{1}{r_o}\right)r}$$

F = force
 q = electron charge
 E = electrical fields
 m = electron mass
 v = electron velocity
 r = trajectory radius (i : inner, o : outer)
 V = voltage

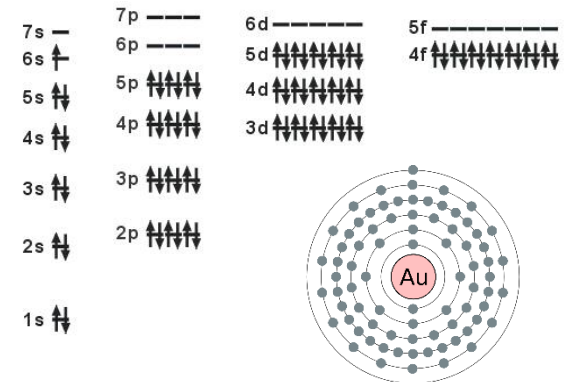
A typical XPS spectrum includes...

- 1. Wide scan spectrum provides the information of core level, valence band and auger electrons.**
- 2. Sharp peaks due to photoelectrons created within the first few atomic layers (elastic)**
 - e. g.) core level spectrum**
- 3. Multiplet splitting occurs when the unfilled shells contain unpaired electrons.**
- 4. A broad structure due to electrons from deeper in the solid which are inelastically scattered (reduced KE) forms the back ground.**
- 5. Auger peaks produced by X-rays**
 - e. g.) transitions from L to K shell: O KLL or C KLL**

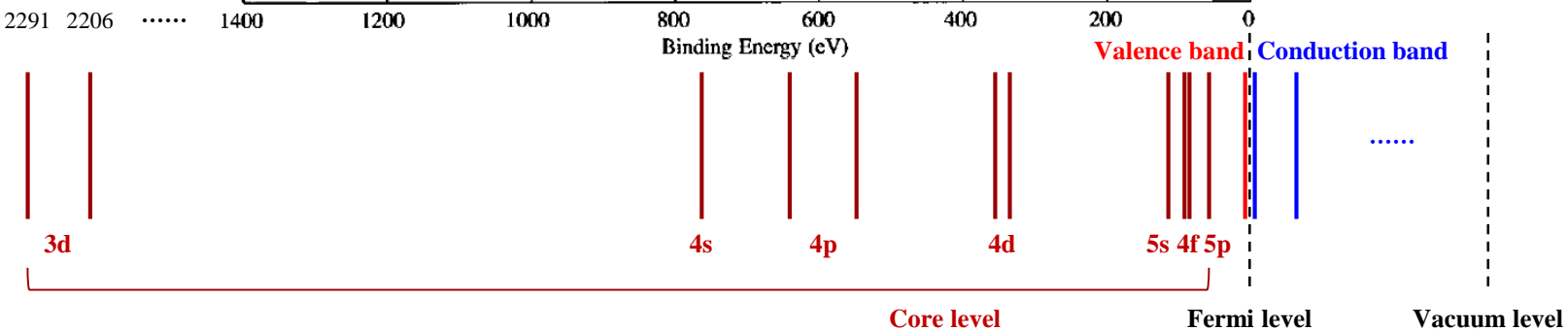
Au XPS spectrum: wide scan



Au: 79

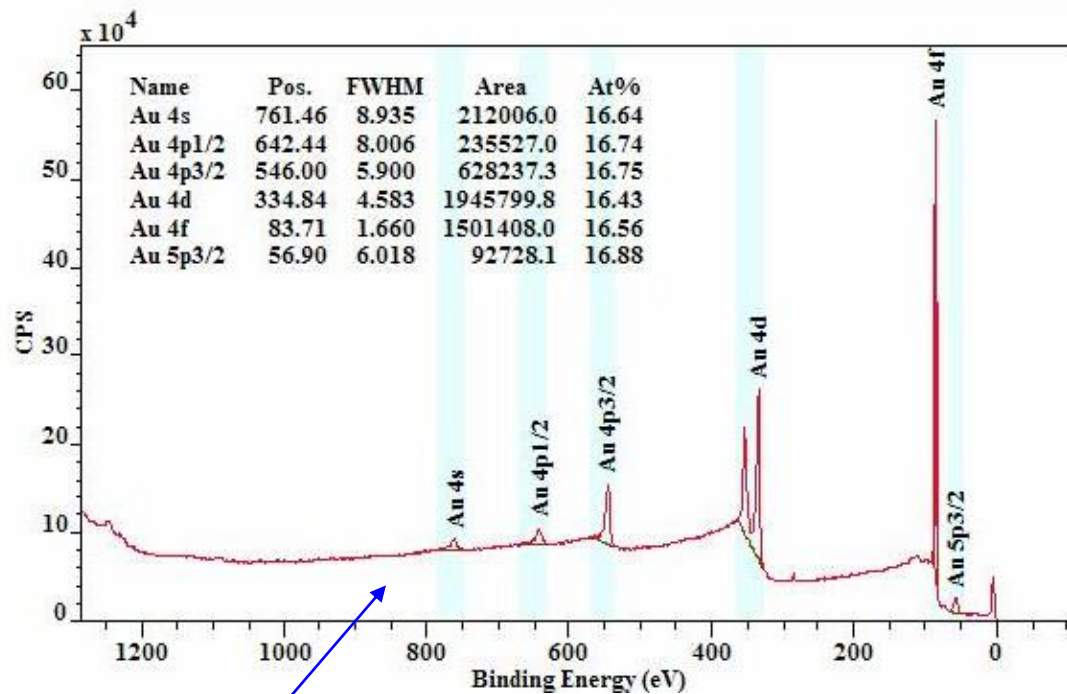


$1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6 4d^{10} 5s^2 5p^6 4f^{14} 5d^{10} 6s^1$

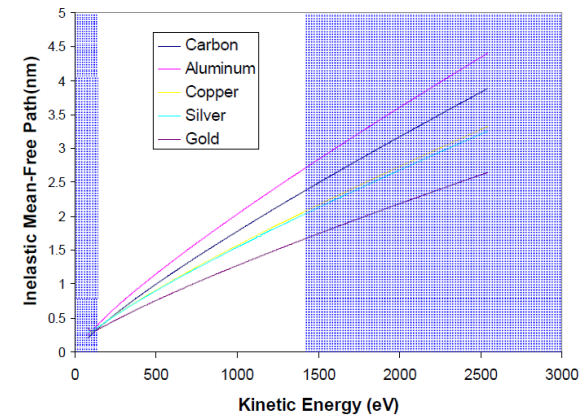
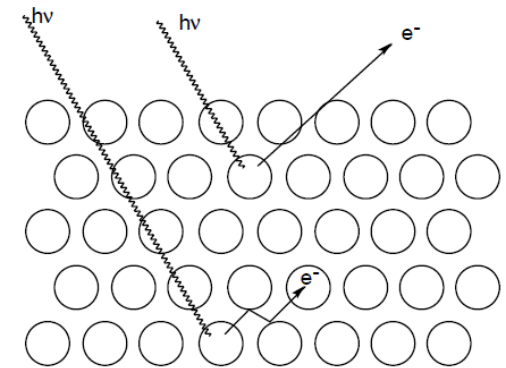


Au XPS spectrum: wide scan

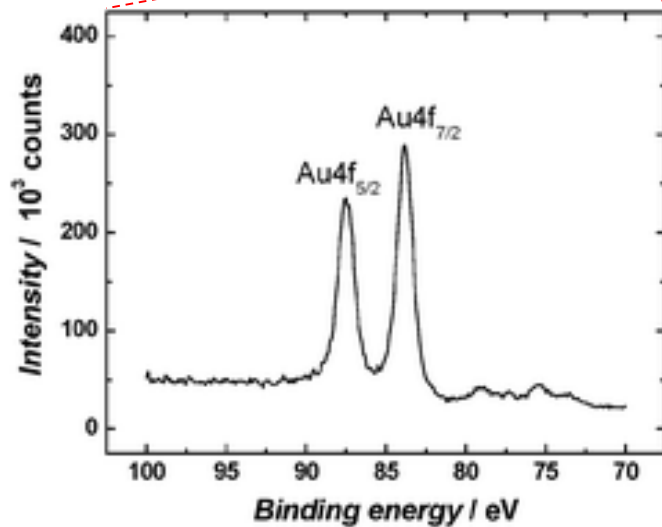
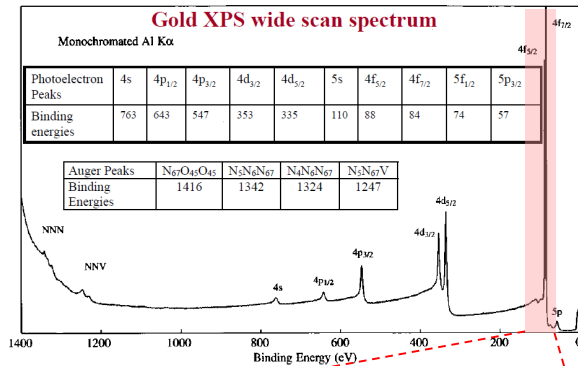
Background: emitted photoelectrons with energy loss



Inelastically scattered photoelectrons



Au XPS spectrum: core level (4f orbitals)



Spin-orbital splitting

n (quantum number)

$l = 0$ (s), 1 (p), 2 (d), 3 (f)

nl_j

$4f_{5/2}$

$j = l + S$
 $j = l - S$

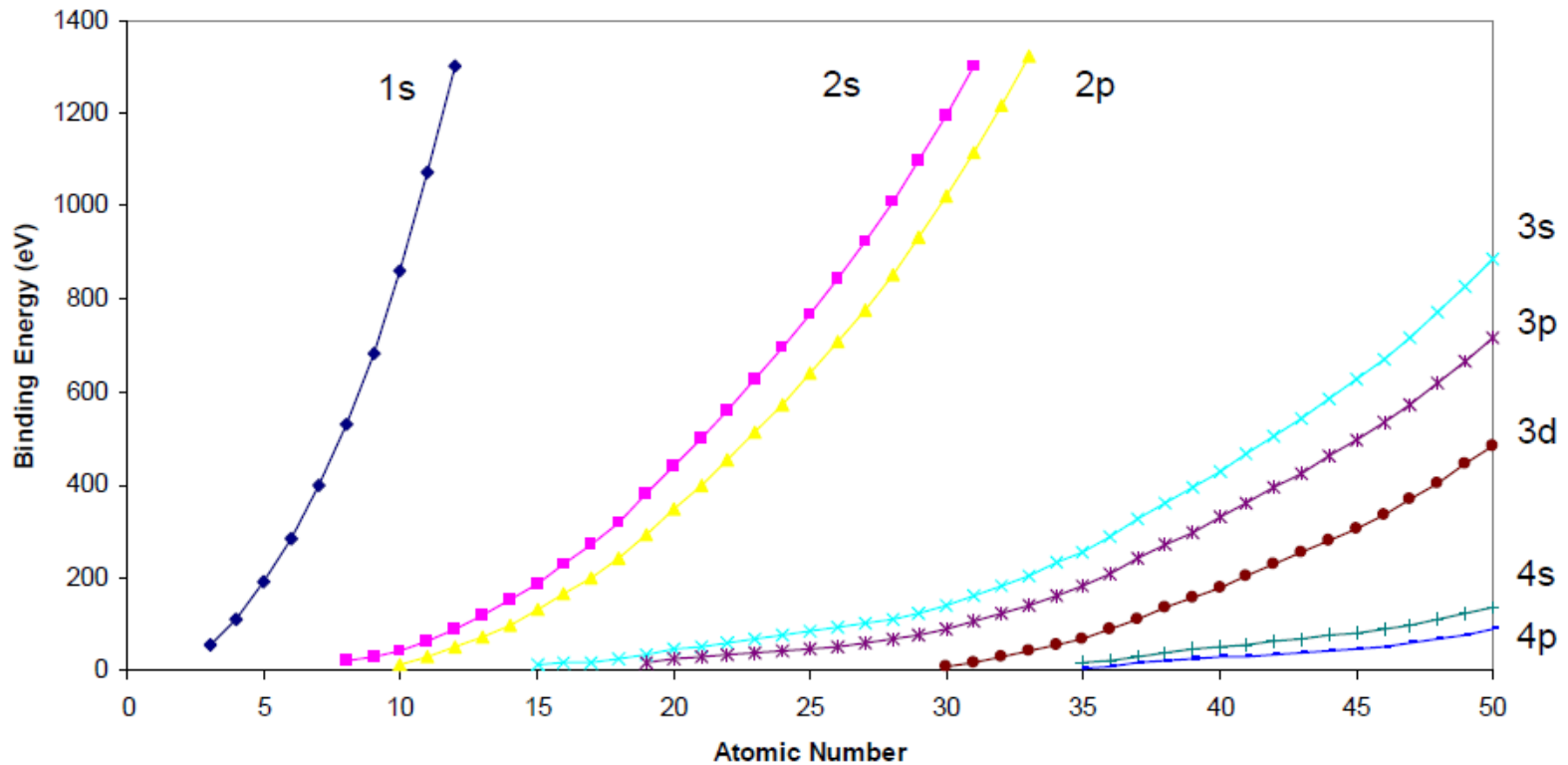
$S = 1/2$ $S = -1/2$
 $j = 3 + 1/2$ $j = 3 - 1/2$

$l = 1$ <p>p</p> <p>$p_{1/2}$ $p_{3/2}$</p> <p>$s = -1/2$ $s = +1/2$</p> <p>Area ratio 1 : 2</p>	$l = 2$ <p>d</p> <p>$d_{3/2}$ $d_{5/2}$</p> <p>$s = -1/2$ $s = +1/2$</p> <p>Area ratio 2 : 3</p>	$l = 3$ <p>f</p> <p>$f_{5/2}$ $f_{7/2}$</p> <p>$s = -1/2$ $s = +1/2$</p> <p>Area ratio 3 : 4</p>
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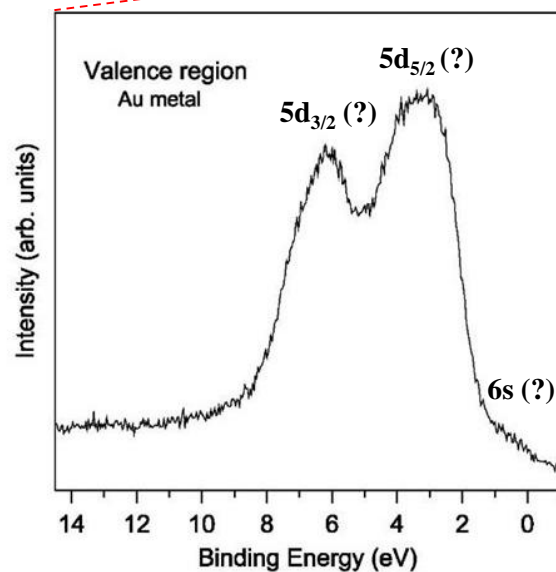
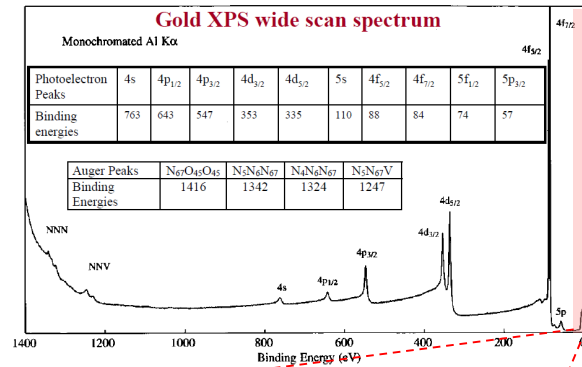
XPS: "soft" x-ray photon energies of 200-2000 eV for analysis of core levels.

Au XPS spectrum: core level

Core level binding energies depending on atomic number

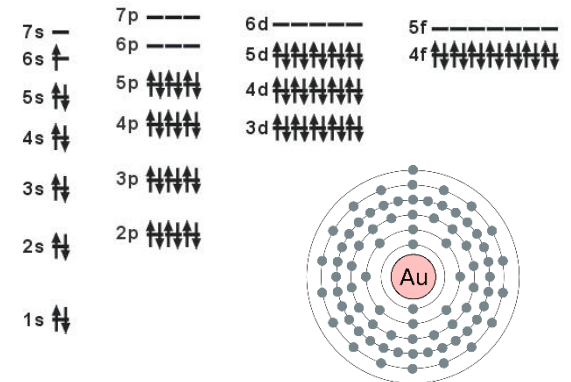


Au UPS spectrum: valence band



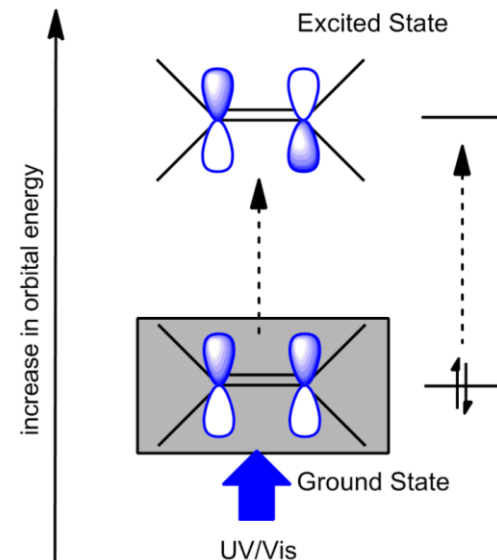
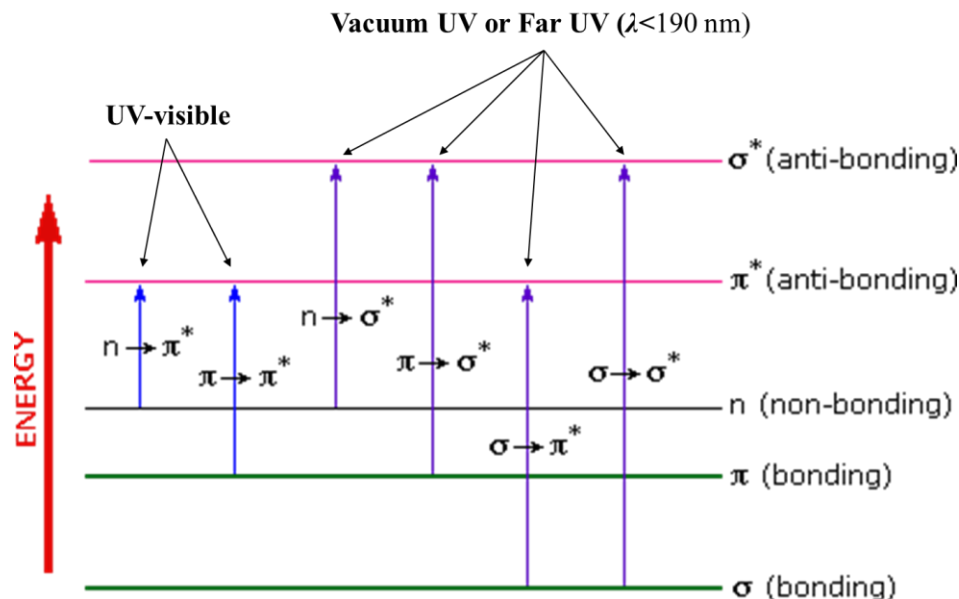
Gas	Emission Line	Energy (eV)	Wavelength (nm)
H	Lyman α	10.20	121.57
	Lyman β	12.09	102.57
He	1 α	21.22	58.43
	1 β	23.09	53.70
	1 γ	23.74	52.22
	2 α	40.81	30.38
	2 β	48.37	25.63
	2 γ	51.02	24.30
	1 α	16.67	74.37
	1 β	16.85	73.62
Ne	1 β	19.69	62.97
	1 β	19.78	62.68
	2 α	26.81	46.24
	2 α	26.91	46.07
	2 β	27.69	44.79
	2 β	27.76	44.66
	2 β	27.78	44.63
	2 β	27.86	44.51
	2 γ	30.45	40.71
	2 γ	30.55	40.58
Ar	1	11.62	106.70
	1	11.83	104.80
	2	13.30	93.22
	2	13.48	91.84

Au: 79



UPS: vacuum UV energies of 10-45 eV for analysis of valence electrons

Au UPS spectrum: valence band



Wavelength
 Visible: 400 ~ 750 nm
 Ultraviolet (UV): 200 ~ 400 nm
 Vacuum UV or Far UV: ~ 200 nm

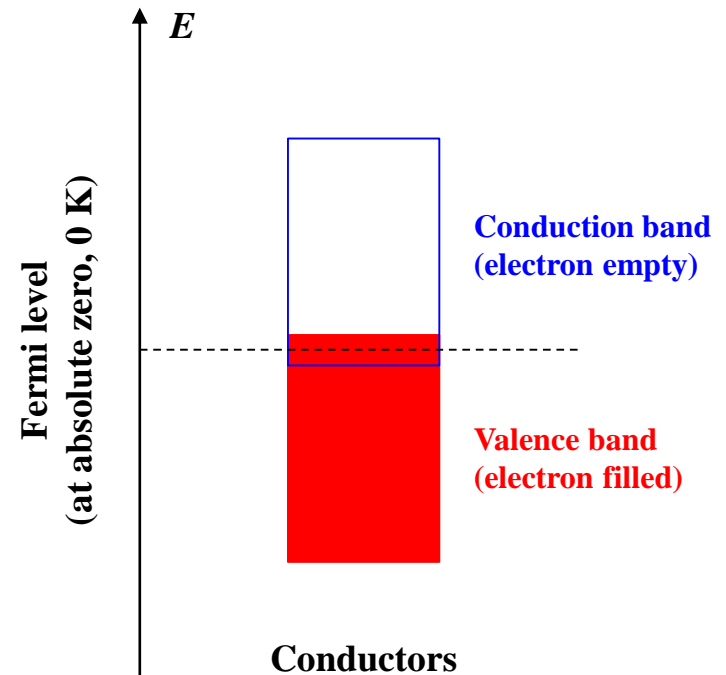
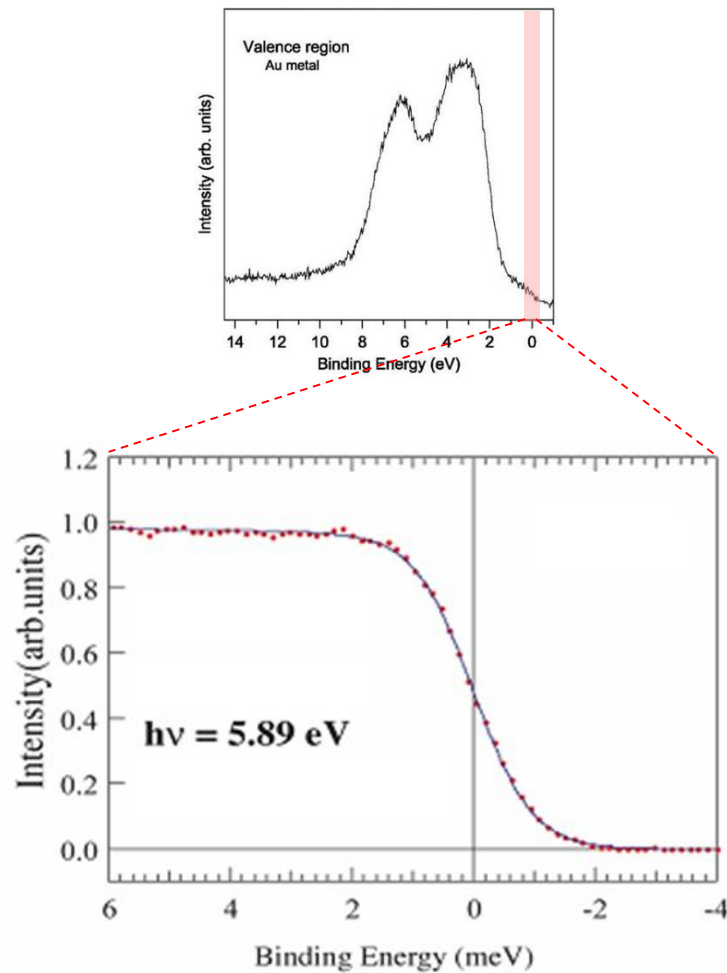
$\sigma \rightarrow \sigma^*$ transitions

1. An electron in a bonding s orbital is excited to the corresponding antibonding.
2. The required energies to these transitions are very large.
3. Methane shows an absorbance maximum at 125 nm which is not seen in typical UV-visible spectra.

$n \rightarrow \sigma^*$ transitions

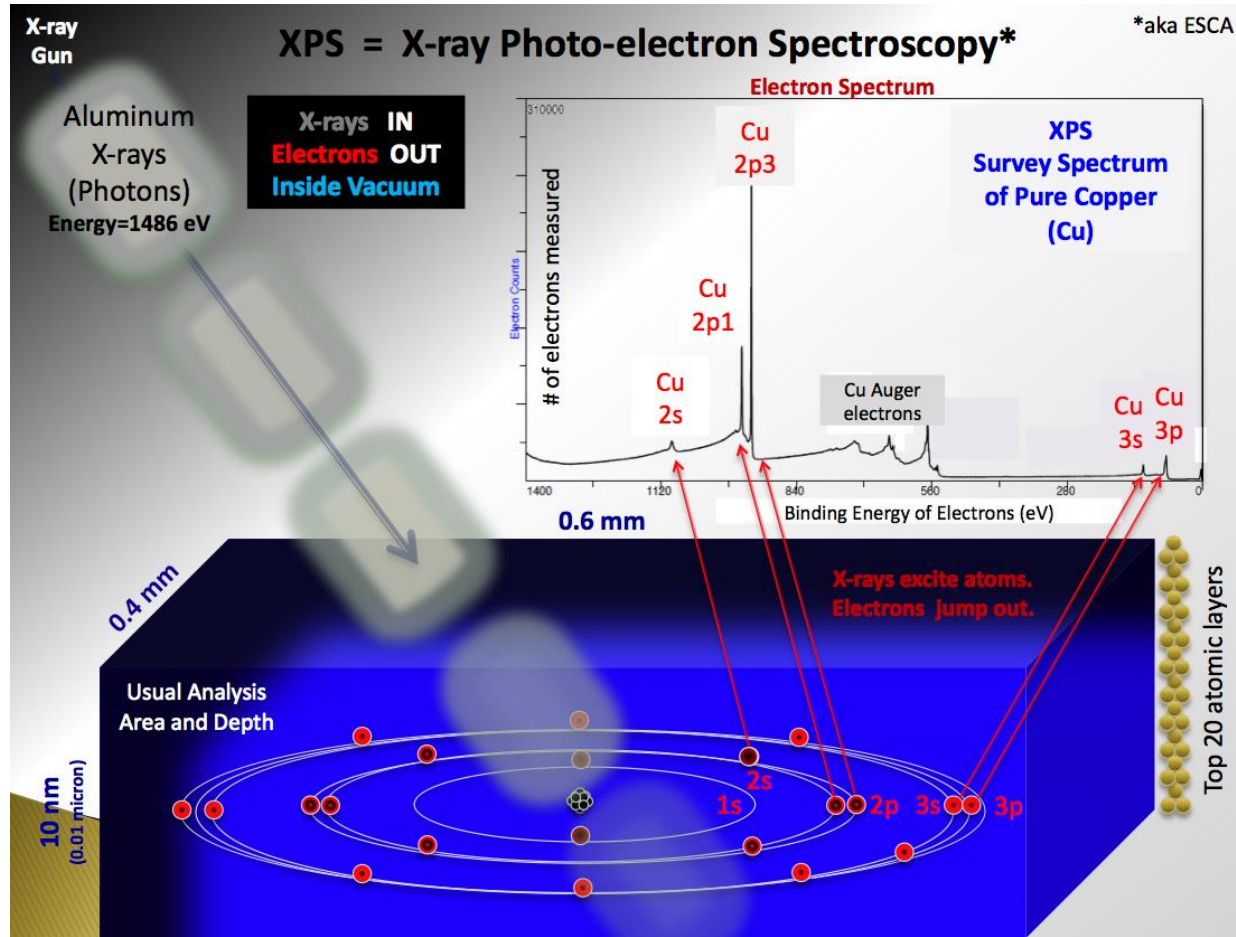
1. Saturated compounds containing atoms with lone pairs (nonbonding) are capable for these transitions.
2. These transitions usually need less energy than $\sigma \rightarrow \sigma^*$ transitions.
3. They can be initiated by light whose wavelength is in the range of 150 ~ 250 nm.

Au UPS spectrum: Fermi edge



Short summary

*electron spectroscopy for
chemical analysis (ESCA)



Data processing

Step 1: Binding energy referencing

Step 2: Background subtracting

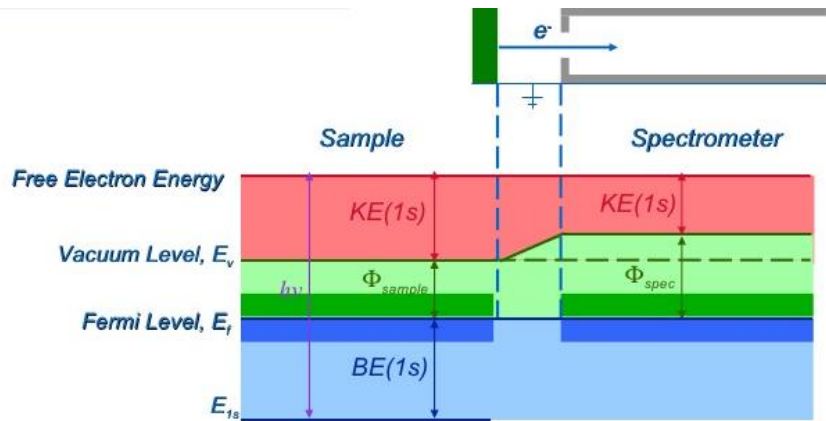
Step 3: Peak fitting

Step 4: Peak identifying

Data processing step 1

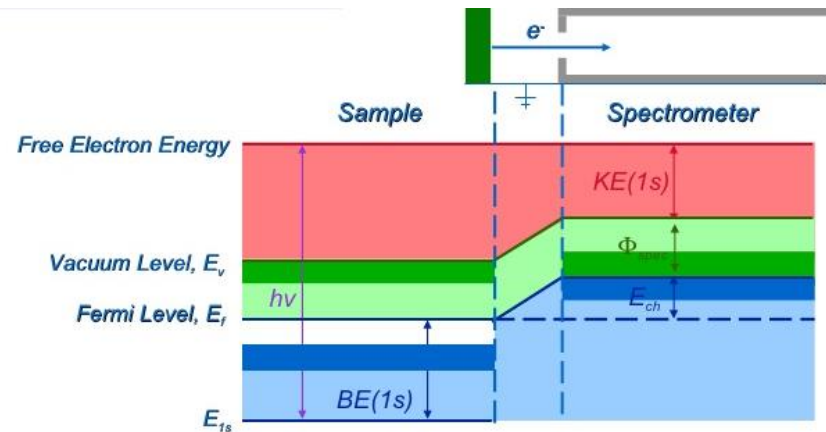
Binding energy referencing (calibration)

Sample/spectrometer energy level diagram (conductor)



Because the Fermi levels of the sample and spectrometer are aligned, we only need to know the spectrometer work function, Φ_{spec} to calculate BE (1s).

Sample/spectrometer energy level diagram (insulator)



A relative build-up of electrons at the spectrometer raises the Fermi level of the spectrometer relative to the sample. A potential E_{ch} (surface charge energy) will develop.

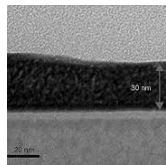
$$BE = h\nu - KE - \Phi_{\text{spec}} - E_{\text{ch}}$$

Data processing step 1

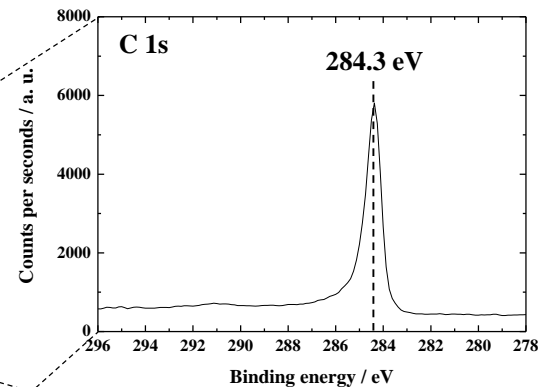
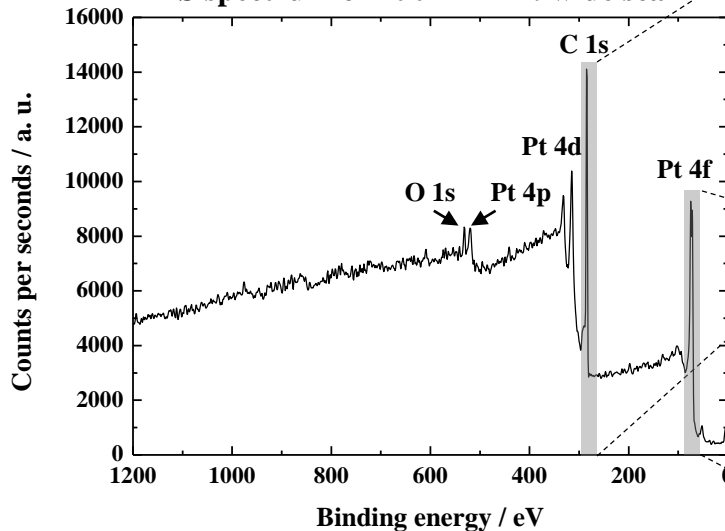
Binding energy referencing (calibration)

$$BE = h\nu - KE - \Phi_{\text{spec}} - E_{ch}$$

E_{ch} can be determined by electrically calibrating the instrument to a spectral feature.

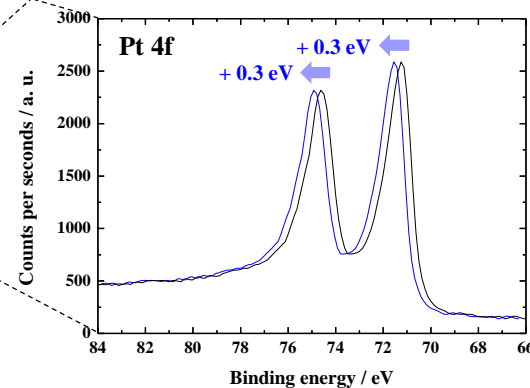


XPS spectrum of Pt thin film: wide scan

[illegible]

**C 1s reference
: 284.6 eV**

[<http://srdata.nist.gov/xps/Default.aspx>]



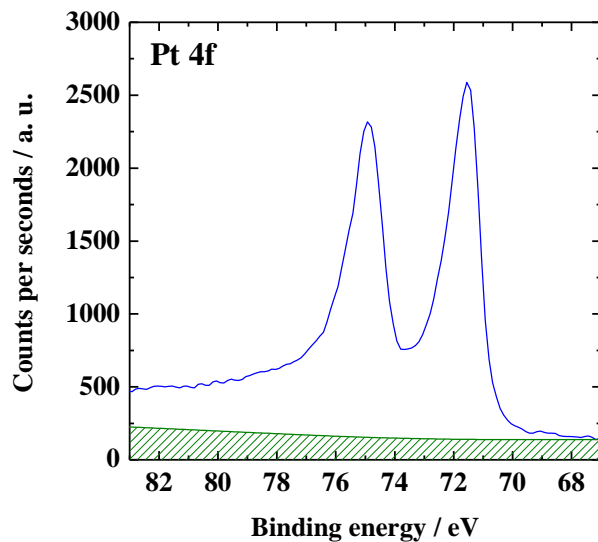
Black: raw data

Blue: calibrated data (+ 0.3 eV)

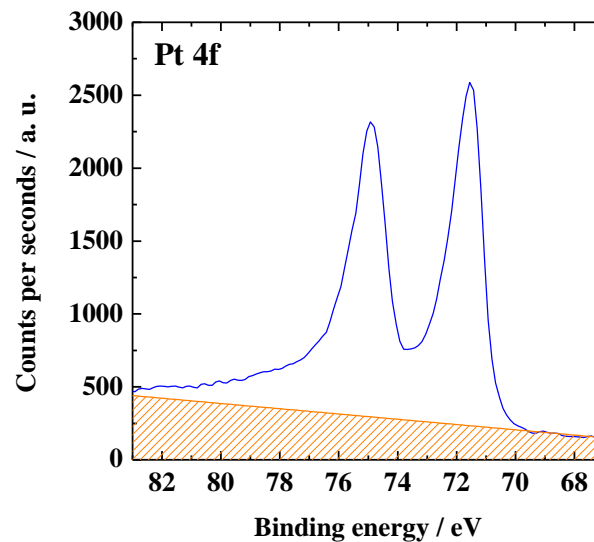
Data processing step 2

Back ground subtracting

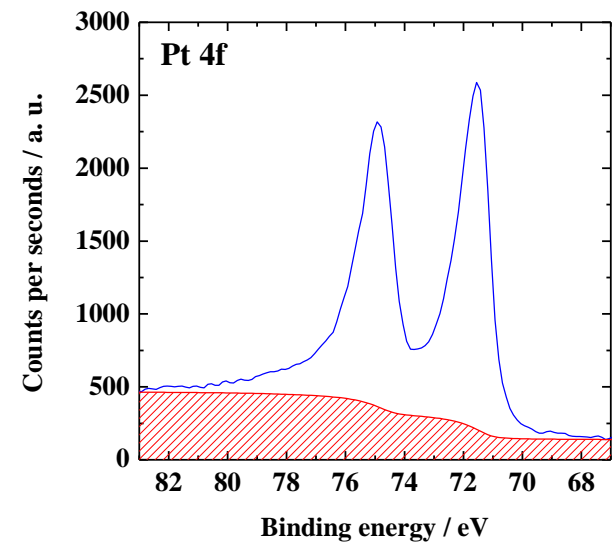
**Tougaard method
(worst)**



**Linear method
(moderate)**



**Shirley method
(best)**



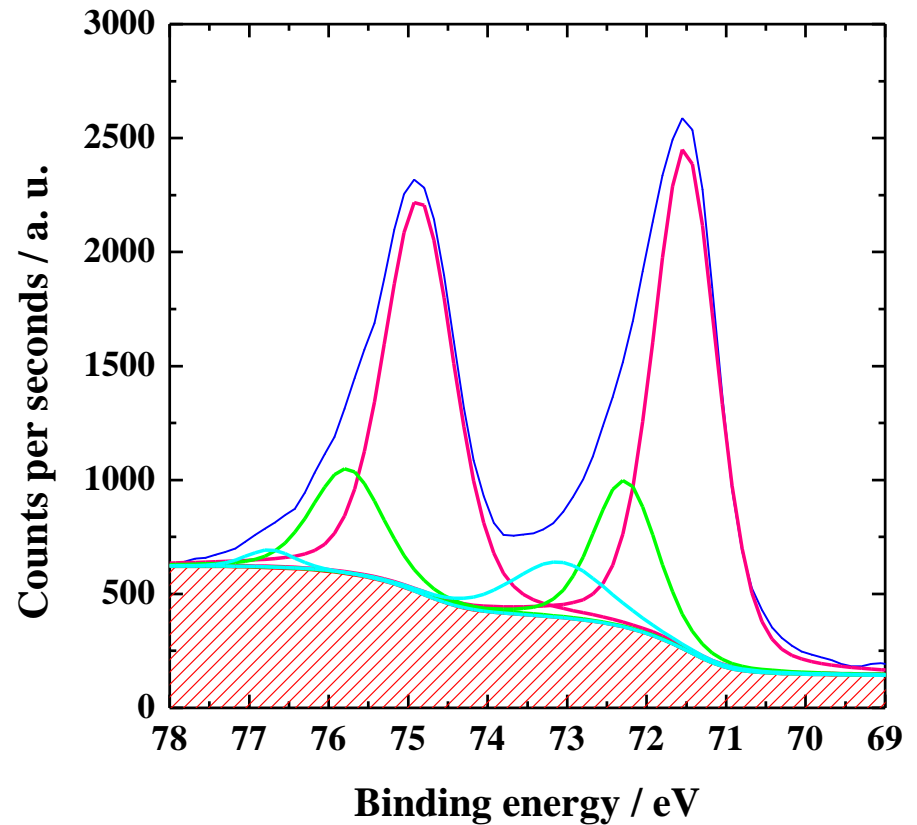
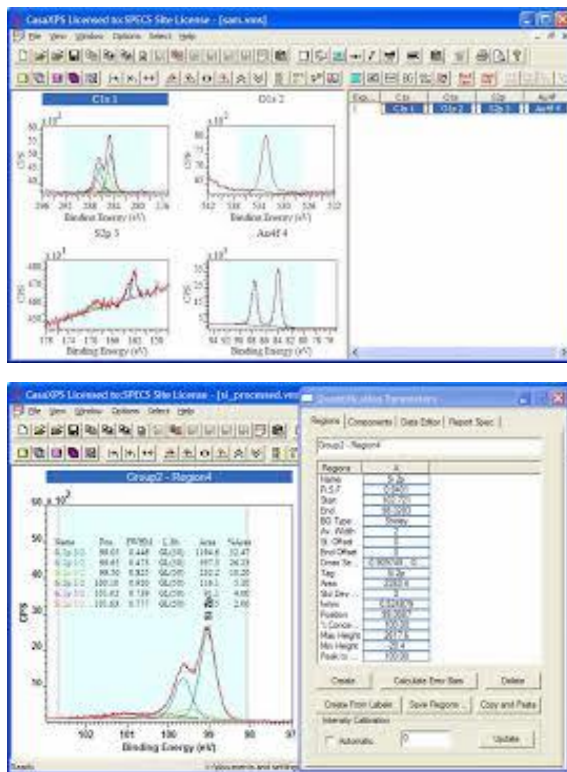
Peak: photoelectrons without energy loss (elastic)

Background: photoelectrons with energy loss (inelastic)

Data processing step 3

Peak fitting (separation)

Using software: CasaXPS, XPSpeak41...



Data processing step 4

Peak identifying from database

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[Introduction](#)
[Search Menu](#)
[Data Field](#)
[Definitions](#)

[Version History](#)

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Available photoelectron line(s) for Pt:
 Click on checkbox(s) and then click on Search button to retrieve data for desired line(s).

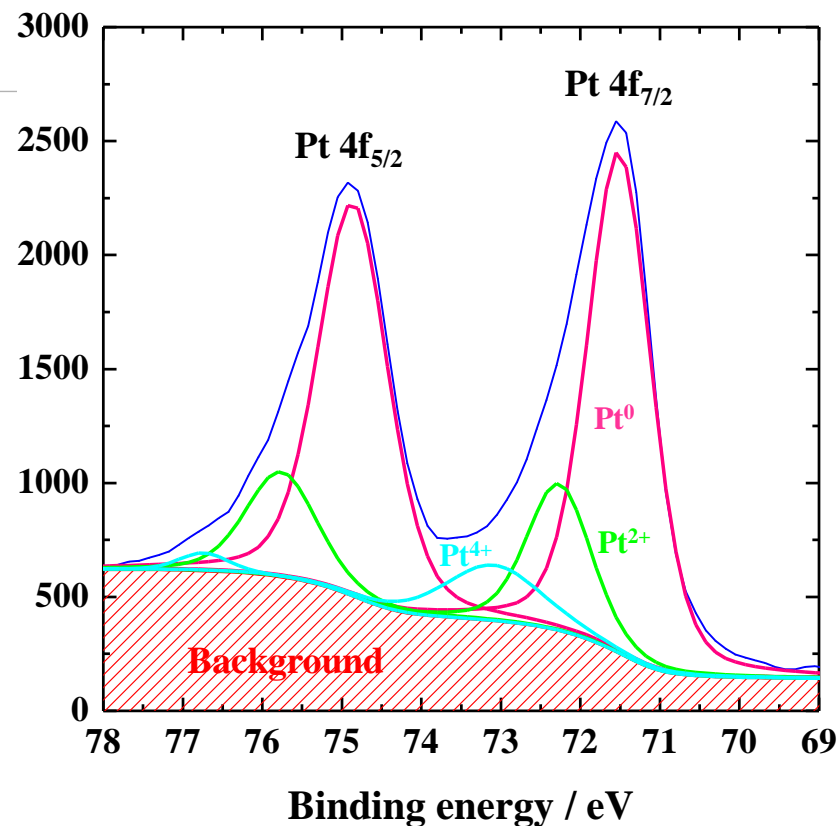
☐ 2p3/2 ☐ 3d3/2 ☐ 3d5/2 ☐ 3p1/2 ☐ 3p3/2 ☐ 3s ☐ 4d ☐ 4d3/2 ☐ 4d5/2 ☒ 4f5/2 ☒ 4f7/2 ☐ 4p3/2 ☐ 4s ☐ 5p3/2

Search

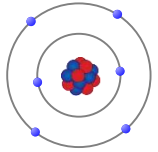
Matches from selected element and spectral line(s) search:

Element	Spectral Line	Formula	Energy (eV)	Details ?
Pt	4f5/2	cis-[PtCl2(P(C6H5)3)2]	76.50	Click
Pt	4f5/2	Pt	74.40	Click
Pt	4f5/2	Pt3Ti	74.65	Click
Pt	4f5/2	Pt	74.50	Click
Pt	4f5/2	[PtCl2(P(C6H5)3)2]	76.50	Click
Pt	4f5/2	Pt	74.23	Click
Pt	4f5/2	(C6H4S4)2[Pt(S2C2O2)2]	75.25	Click
Pt	4f5/2	(C6H4S4)2(C6H4S4)[Pt(S2C2O2)2]	75.20	Click
Pt	4f5/2	O2/Pt3Ti	74.60	Click
Pt	4f5/2	O2/Pt3Ti	74.65	Click
Pt	4f5/2	O2/Pt3Ti	74.70	Click
Pt	4f5/2	Pt(C32H16N8)(ClO4)0.5	76.60	Click
Pt	4f5/2	N(C2H5)4[Pt(S2C2O2)2]	75.35	Click
Pt	4f5/2	Pt(C32H16N8)	76.60	Click
Pt	4f5/2	Pt-Ni	74.50	Click
Pt	4f5/2	Pt-Ni	74.55	Click
Pt	4f5/2	Pt-Ni	74.45	Click
Pt	4f5/2	Pt-Ni	74.40	Click
Pt	4f5/2	Pt-Ni	74.50	Click
Pt	4f5/2	Pt-Ni	74.55	Click
Pt	4f5/2	Pt-Ni	74.55	Click
Pt	4f5/2	[Pt(NH2(CH2)2NH(CH2)2NH2)I]I	78.20	Click
Pt	4f5/2	[Pt(NH2(CH2)2NH(CH2)2NH2)Cl]Cl	76.60	Click
Pt	4f5/2	[Pt(NH2(CH2)2NH(CH2)2NH2)CN]I	77.80	Click
Pt	4f5/2	[Pt(NH2(CH2)2NH(CH2)2NH2)NO3]NO3	76.30	Click
Pt	4f5/2	[Pt(NH2(CH2)2NH(CH2)2NH2)NO2]I	77.90	Click
Pt	4f5/2	[Pt2(P(C6H5)3)4SSCHCl2]PF6	76.00	Click
Pt	4f5/2	Pt4H7Na4I(AIO2)56(SiO2)136	75.20	Click
Pt	4f5/2	[Pt2(P(C6H5)3)4SSCH3]I	76.00	Click
Pt	4f5/2	[(Pt2(P(C6H5)3)4S2Cu)2(mu-dppf)][PF6]2	76.00	Click
Pt	4f5/2	[(Pt(P(C6H5)3)2S)2Hg(C6H5)2PCH2CH2P(C6H5)2][PF6]2	76.10	Click
Pt	4f5/2	[(Pt(P(C6H5)3)2S)2Ni(C6H5)2PCH2CH2P(C6H5)2][PF6]2	76.30	Click
Pt	4f5/2	PtS2	77.50	Click
Pt	4f5/2	[(Pt(P(C6H5)3)2S)2]	75.50	Click

[<http://srdata.nist.gov/xps/Default.aspx>]

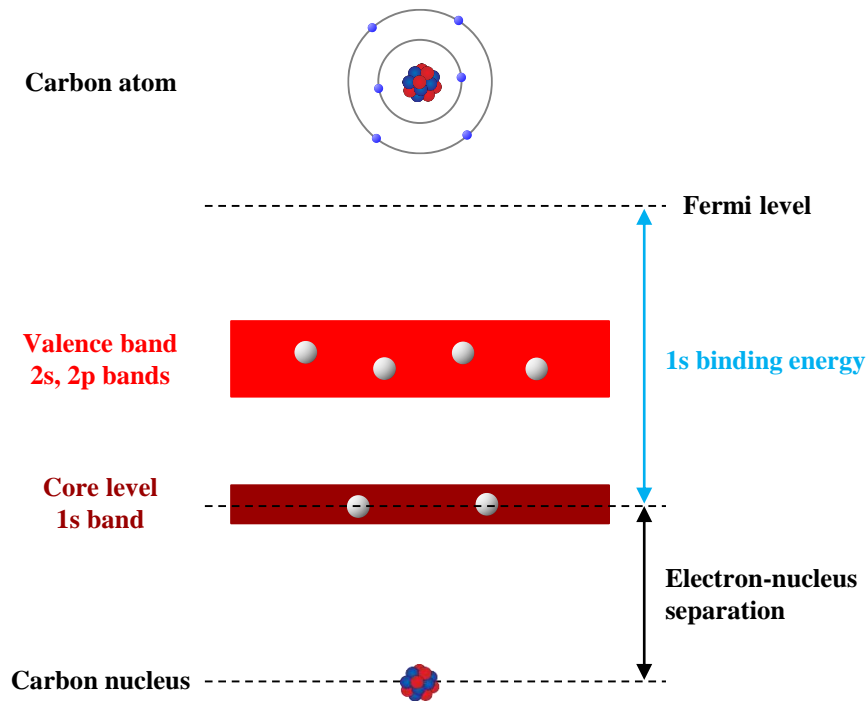


Chemical shift

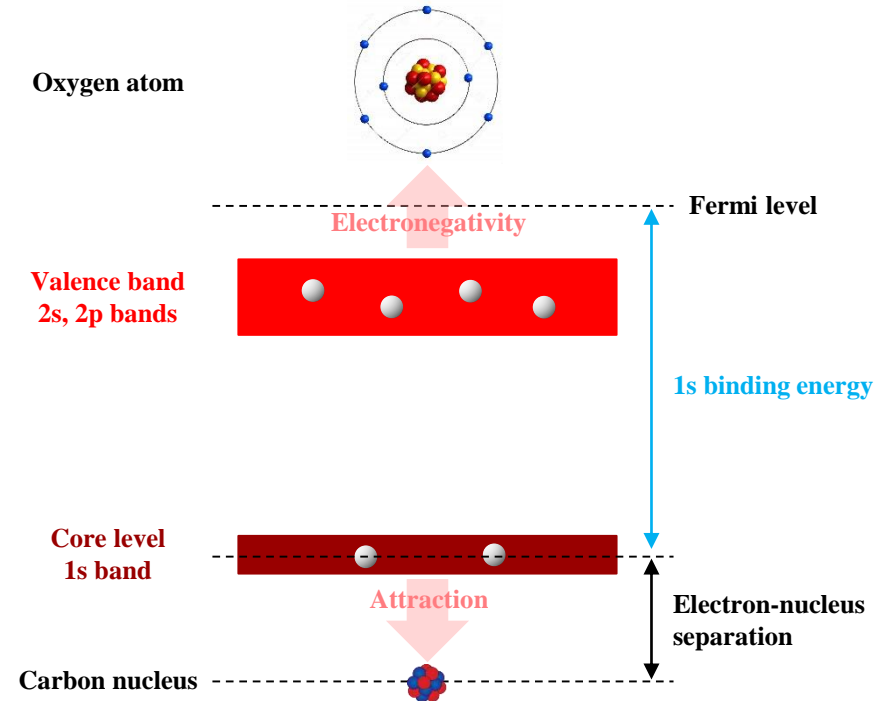


Electronegativity effect

carbon-carbon bond



carbon-oxygen bond



Chemical shift

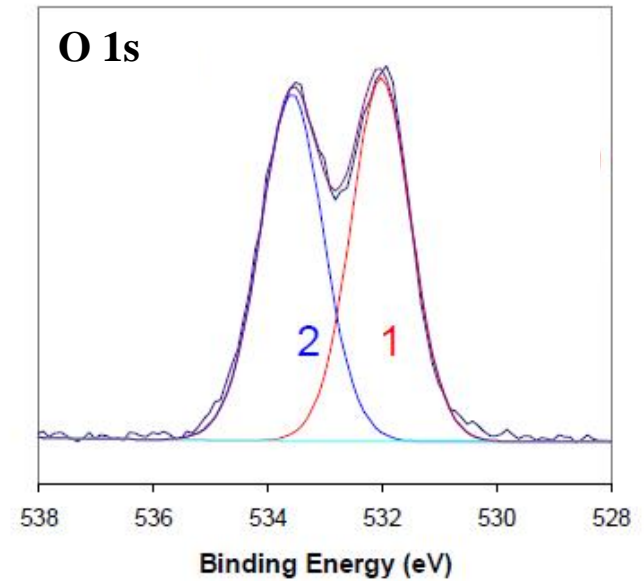
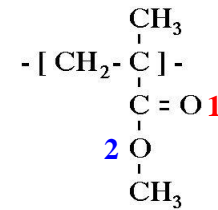
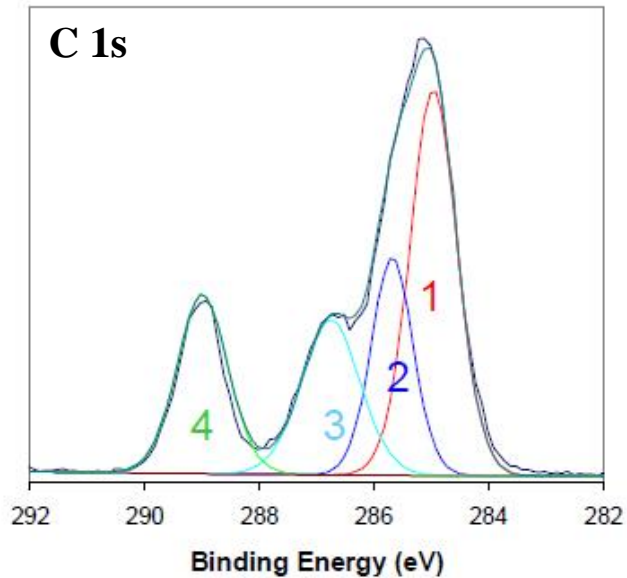
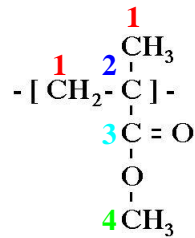
Electronegativity effect: example

<i>Functional Group</i>		<i>C 1s Binding Energy (eV)</i>
<i>hydrocarbon</i>	<u>C</u> -H, <u>C</u> -C	285.0
<i>amine</i>	<u>C</u> -N	286.0
<i>alcohol, ether</i>	<u>C</u> -O-H, <u>C</u> -O-C	286.5
<i>Cl bound to C</i>	<u>C</u> -Cl	286.5
<i>F bound to C</i>	<u>C</u> -F	287.8
<i>carbonyl</i>	<u>C</u> =O	288.0

H 2.20	Electronegativity Values for Some Elements					
Li 0.98	Be 1.57	B 2.04	C 2.55	N 3.04	O 3.44	F 3.98
Na 0.90	Mg 1.31	Al 1.61	Si 1.90	P 2.19	S 2.58	Cl 3.16
K 0.82	Ca 1.00	Ga 1.81	Ge 2.01	As 2.18	Se 2.55	Br 2.96

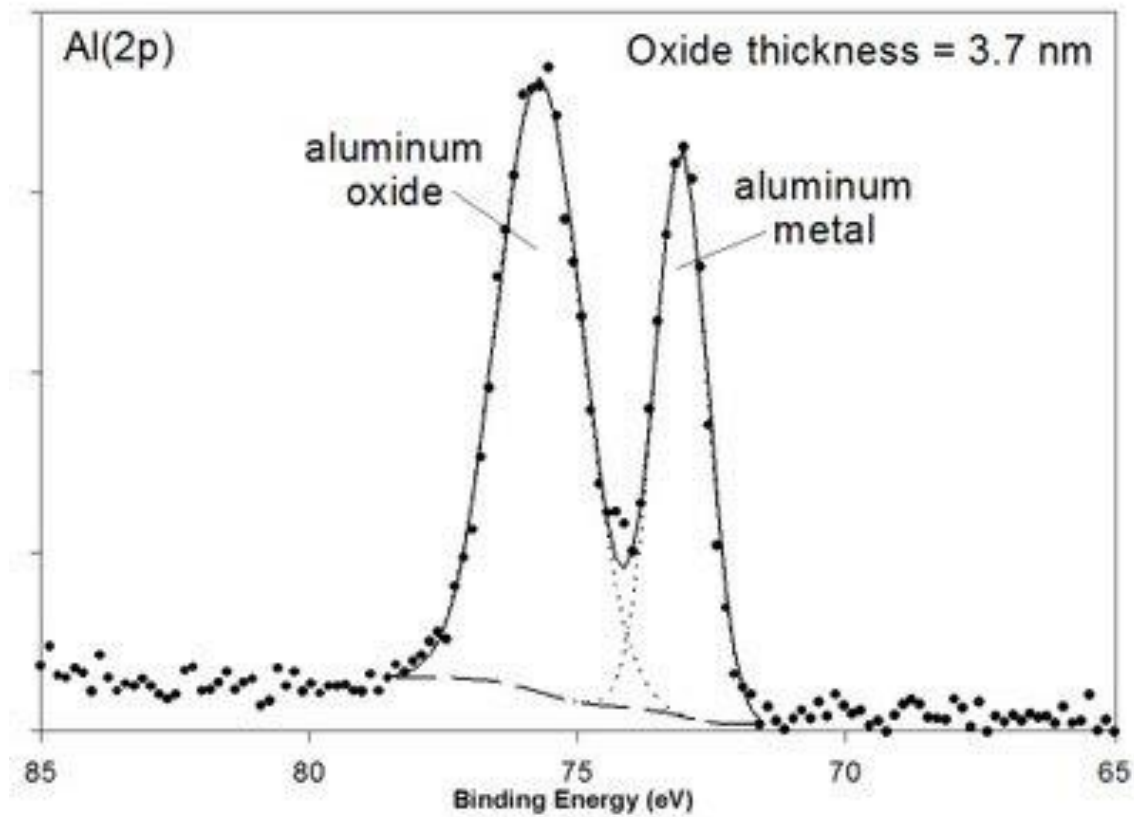
Chemical shift

Electronegativity effect: example (polymethylmethacrylate)



Chemical shift

Electronegativity effect: example (Al oxide)

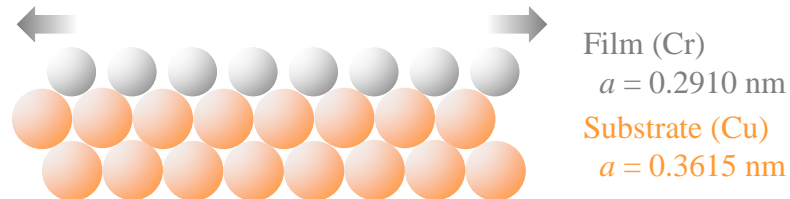


Chemical shift

Lattice strain effect

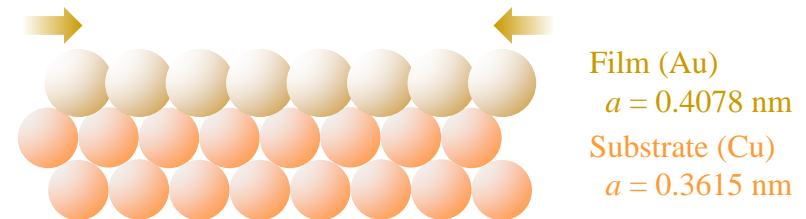
Expansion

Film (Cr) becomes more electron poor.

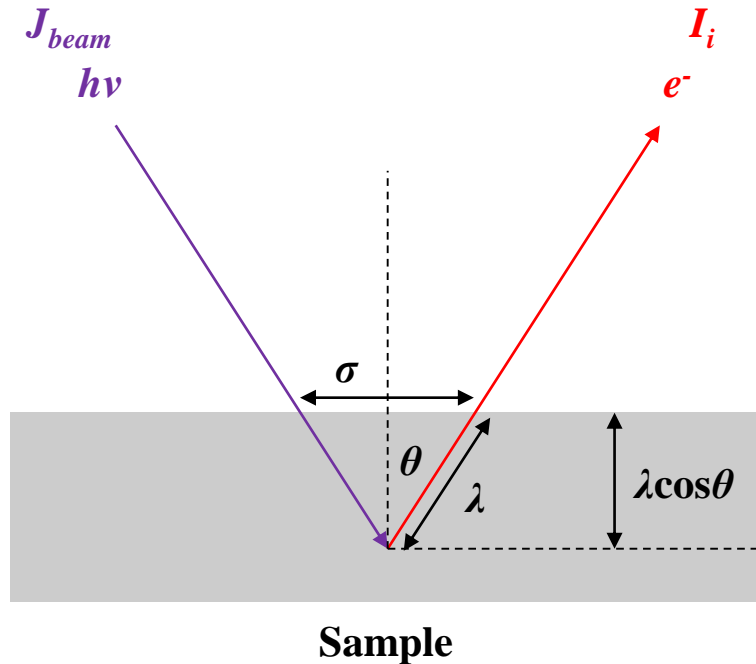


Compression

Film (Au) becomes more electron rich.



Quantification



I_i : intensity of i element = (electron/volume)(volume)

$$I_i = (N_i \sigma_i J T) (a \lambda_i \cos \theta)$$

Sample dependent terms

N_i : number of atoms (#/cm³)
 σ_i : photoelectric cross-section (cm²)
 λ_i : inelastic mean free path (cm)

Instrument dependent terms

J : X-ray flux (#/cm²·s)
 T : analyzer transmission function
 a : analysis area (cm²)
 θ : photoelectron emission angle

By assuming the concentration to be a relative ratio of atoms, instrument dependent term can be neglected.

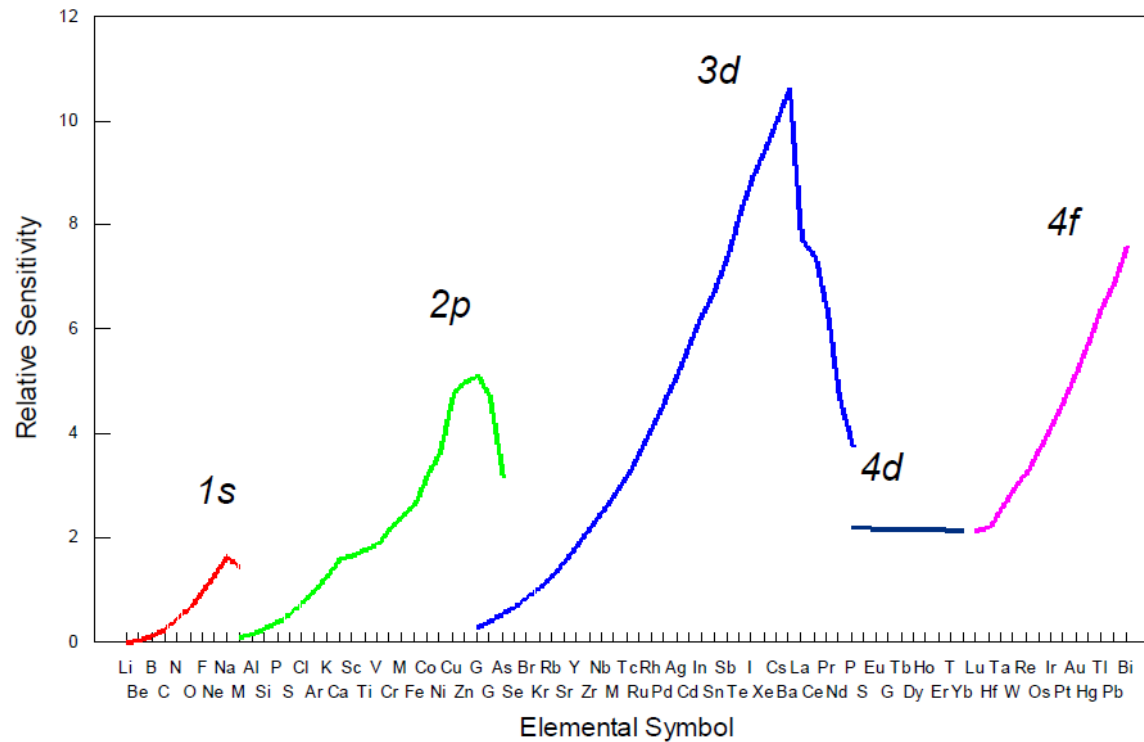
$$N_i = I_i / \sigma_i T \lambda_i = I_i / S_i$$

Relative sensitivity factor $S_i := f(\sigma_i, T, \lambda_i)$

Quantification

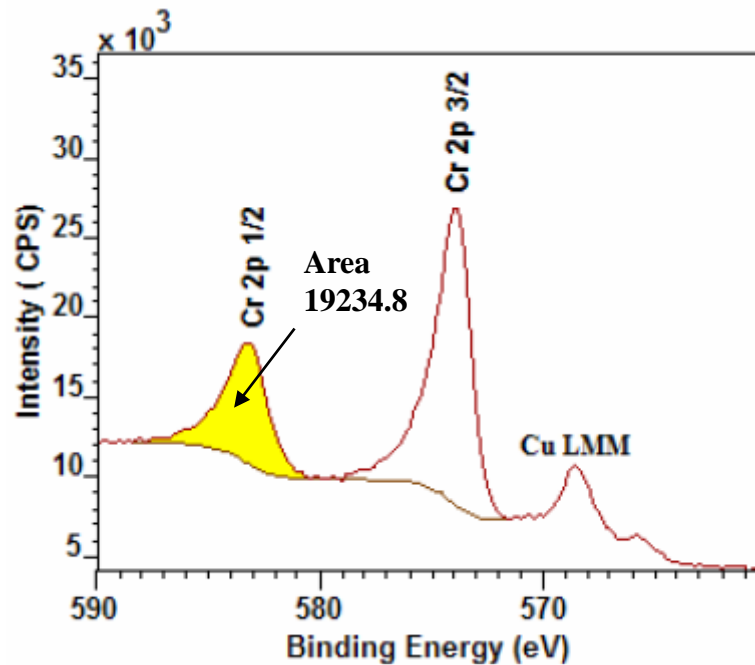
Relative sensitivity factor (RSF)

$$N_i = I_i / \sigma_i T \lambda_i = I_i / S_i \quad \text{Relative sensitivity factor } S_i := f(\sigma_i, T, \lambda_i)$$

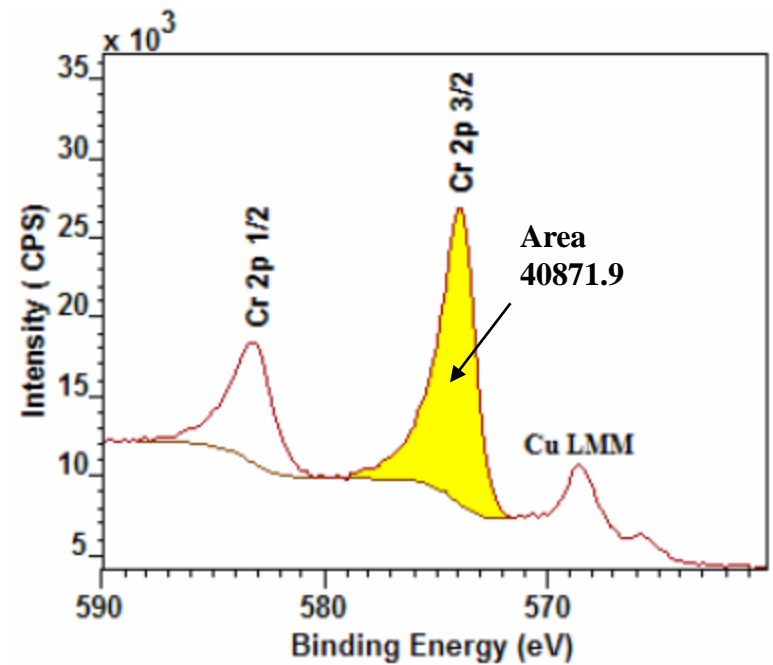


Quantification

Example: Cr 2p spectrum



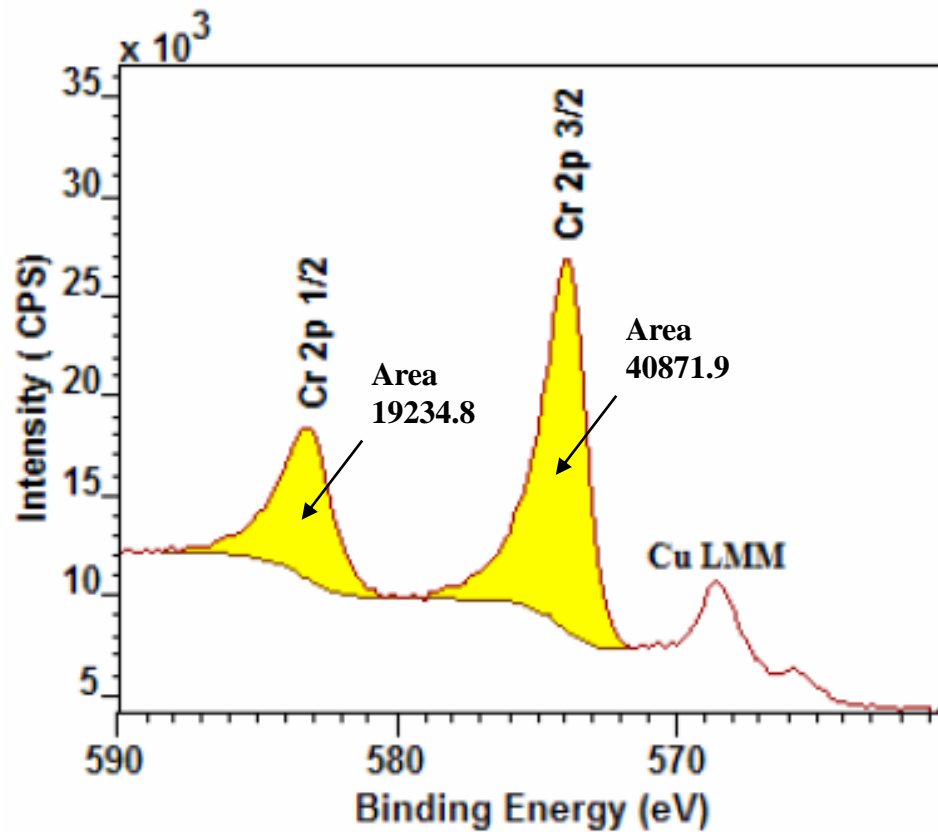
Cr 2p_{1/2} RSF: 3.60721



Cr 2p_{3/2} RSF: 6.9697

Quantification

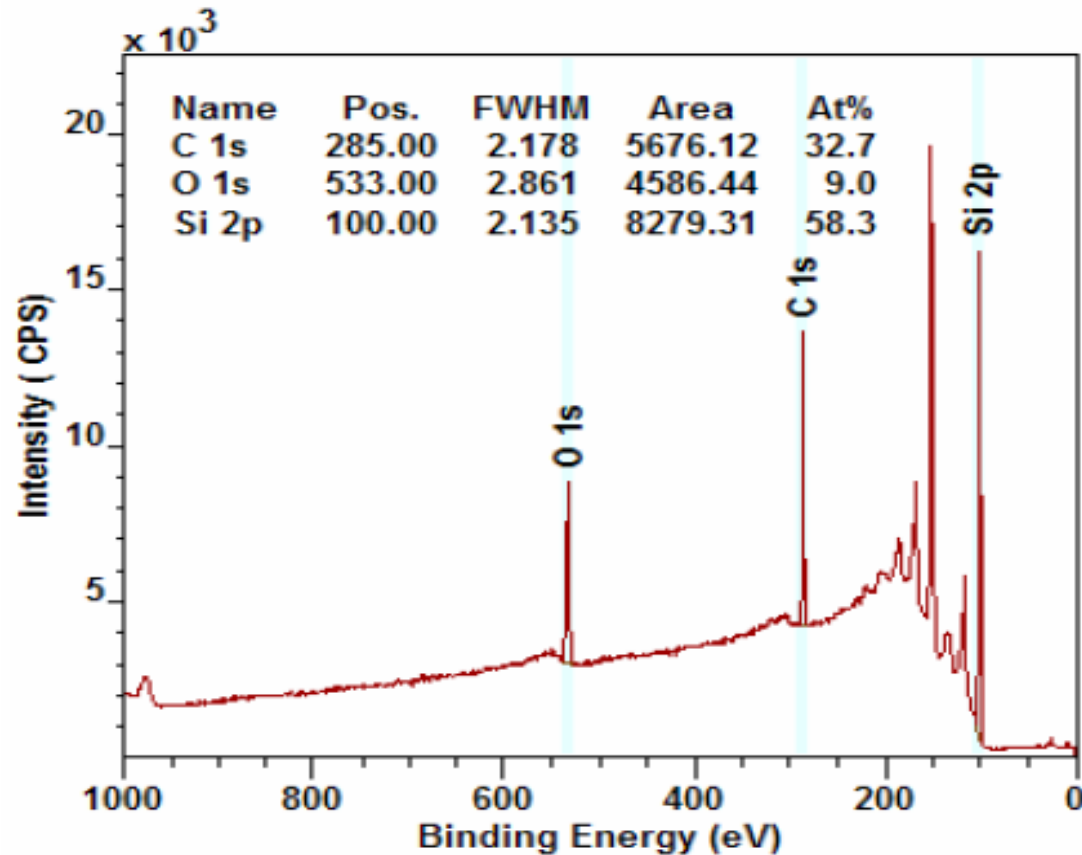
Example: Cr 2p spectrum



Total area: 60098.5
Cr 2p RSF: 10.6041

Quantification

Example: Si XPS wide scan spectra



RSF

C 1s: 1.01548

O 1s: 2.97535

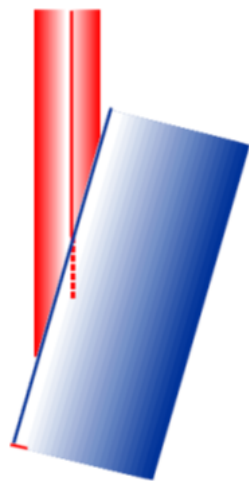
Si 2p: 0.82965

Quantification

Angle-resolved XPS: overlayer film vs. alloy

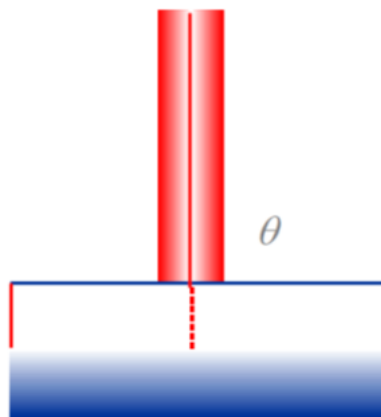
More Surface Sensitive

$$\theta = 75^\circ$$

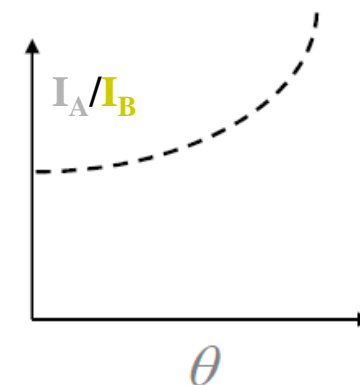
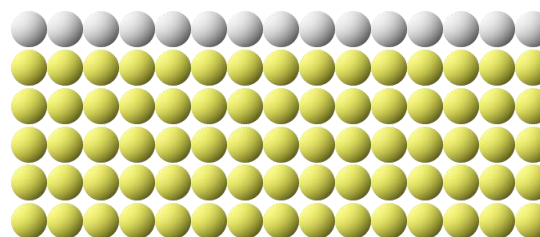


Less Surface Sensitive

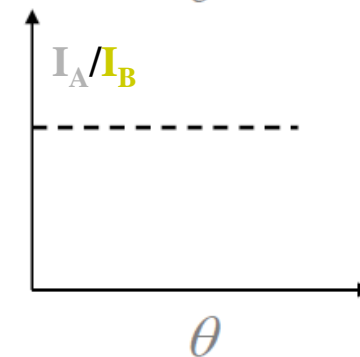
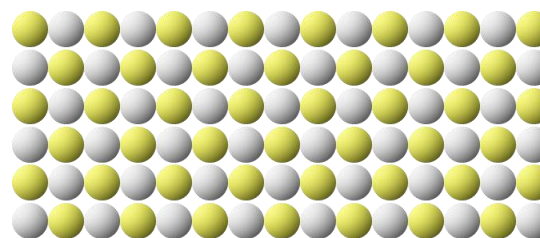
$$\theta = 0^\circ$$



A thin film on B

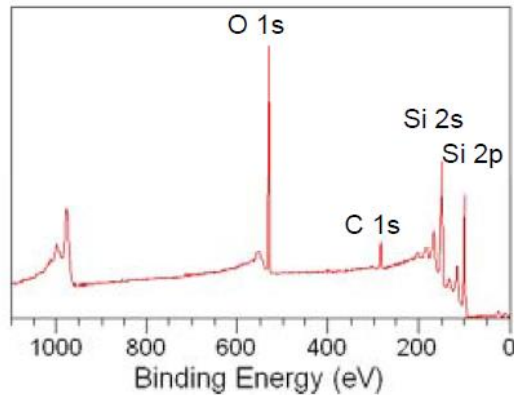


AB alloy

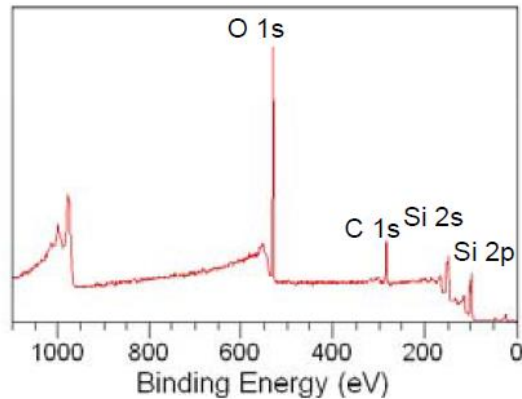
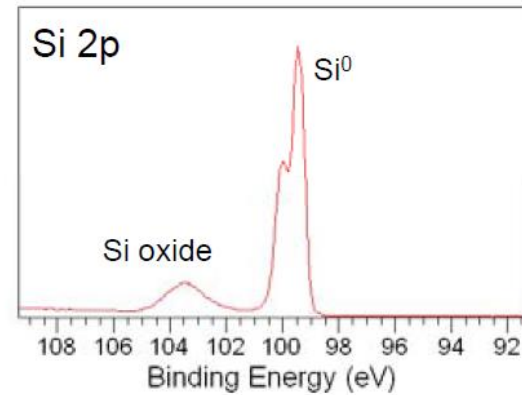


Quantification

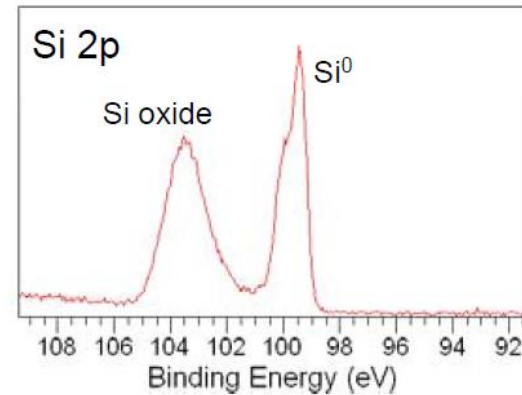
Angle-resolved XPS: Si with native oxide



$\theta = 0^\circ$

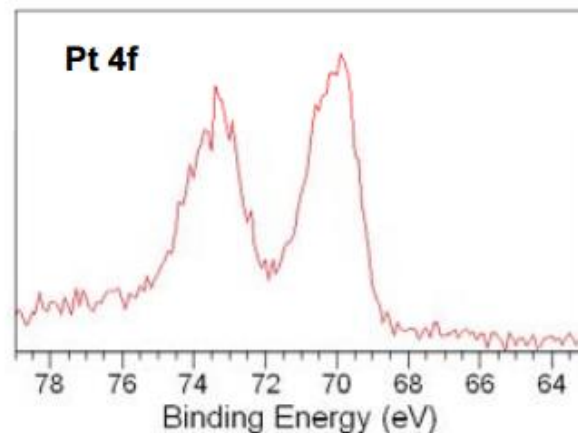
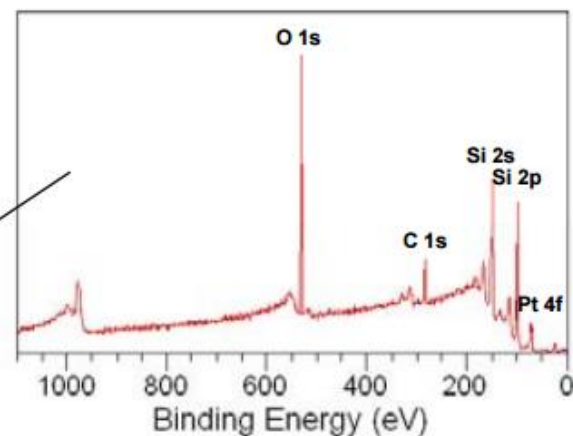
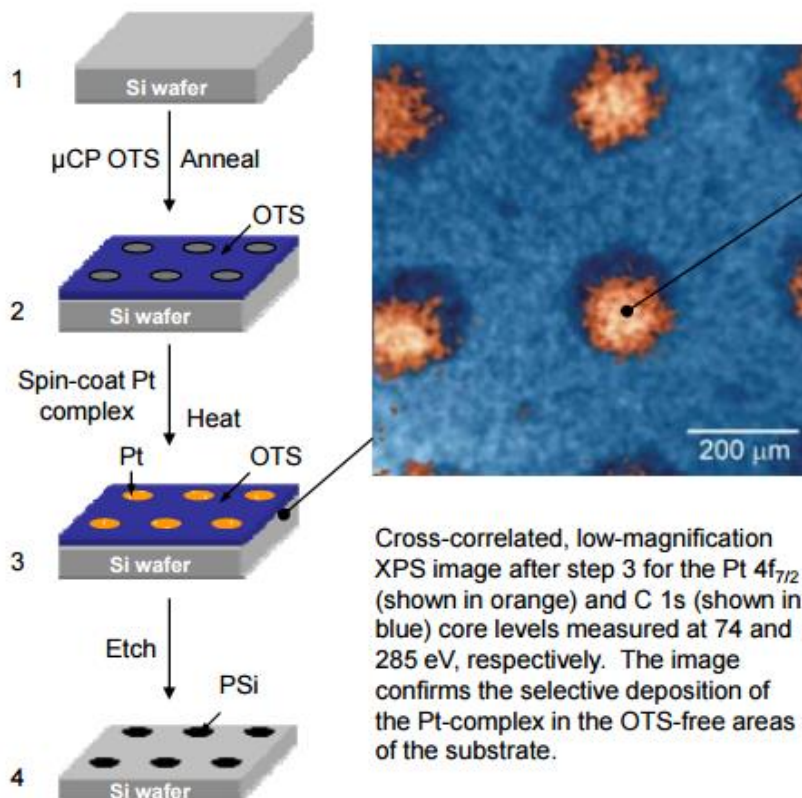


$\theta = 75^\circ$



Imaging

Pt catalyzed etching of patterned porous silicon

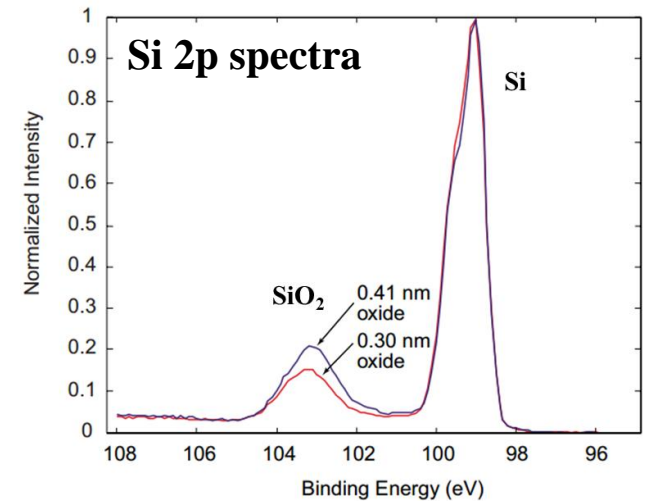
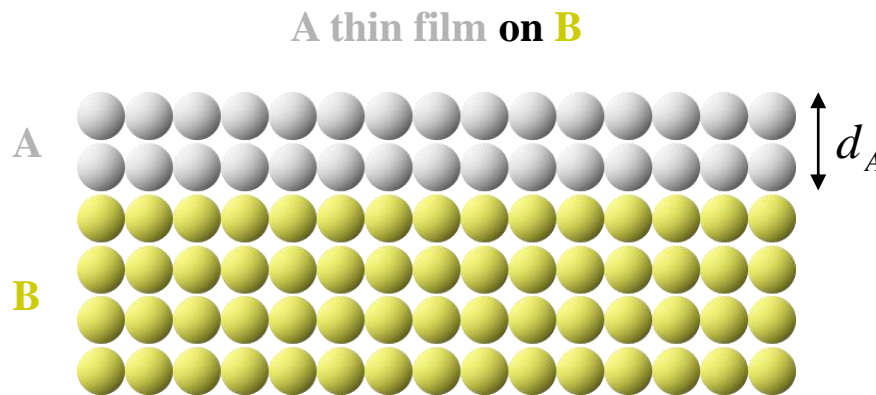


Cross-correlated, low-magnification XPS image after step 3 for the Pt 4f_{7/2} (shown in orange) and C 1s (shown in blue) core levels measured at 74 and 285 eV, respectively. The image confirms the selective deposition of the Pt-complex in the OTS-free areas of the substrate.

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

Thickness

Thin overlayer film thickness calculation

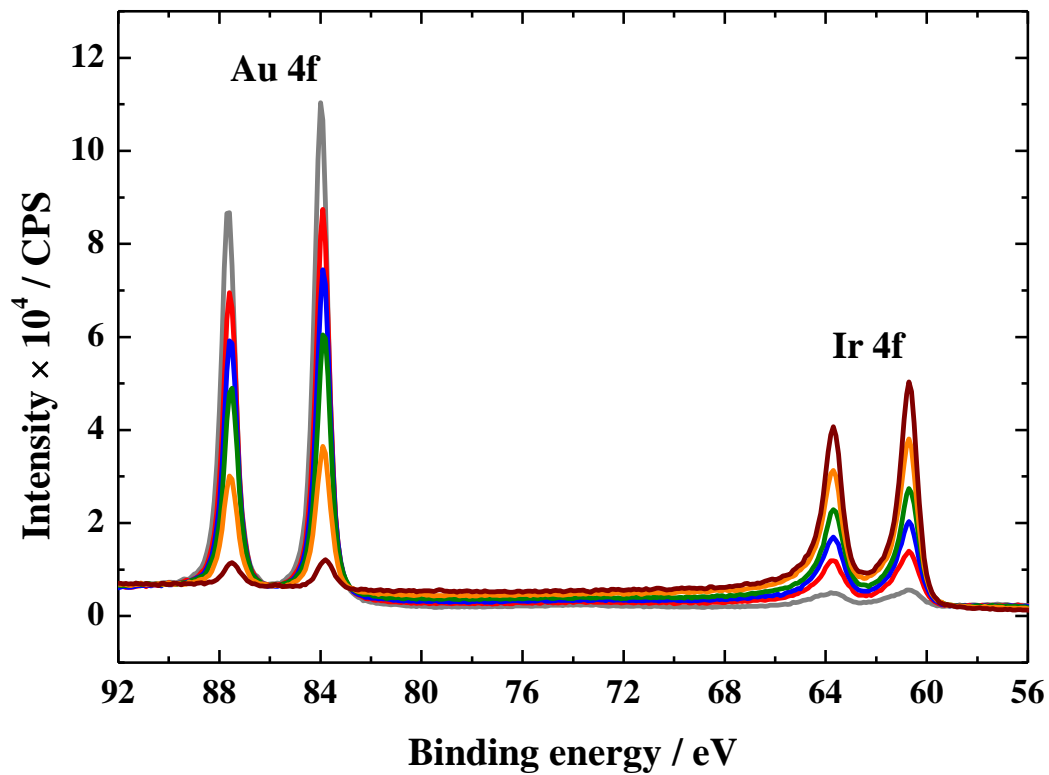


Beer-Lambert relationship

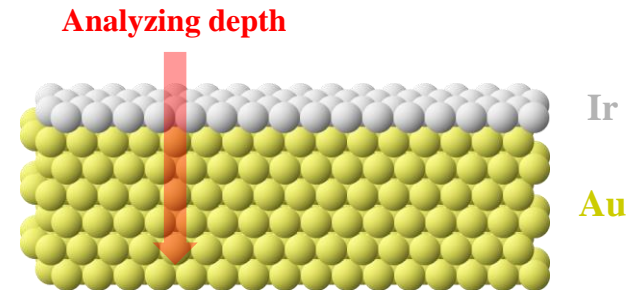
$$I = I_0 \exp\left(-\frac{d}{\lambda \cos \theta}\right) \longrightarrow d_A = \lambda_A \cos \theta \ln \left[1 + \frac{(I_A / S_A)}{(I_B / S_B)} \right]$$

Thickness

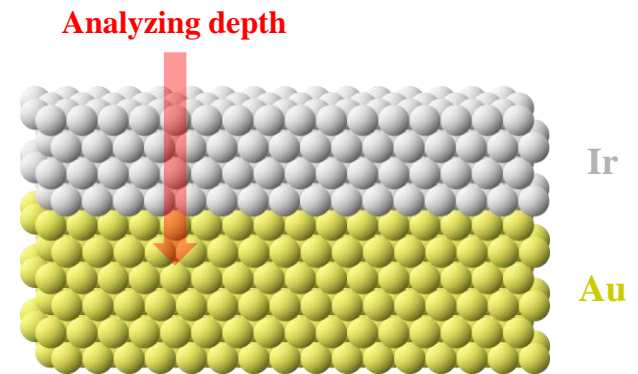
Ir thin overlayer film on Au substrate



Thin overlayer film

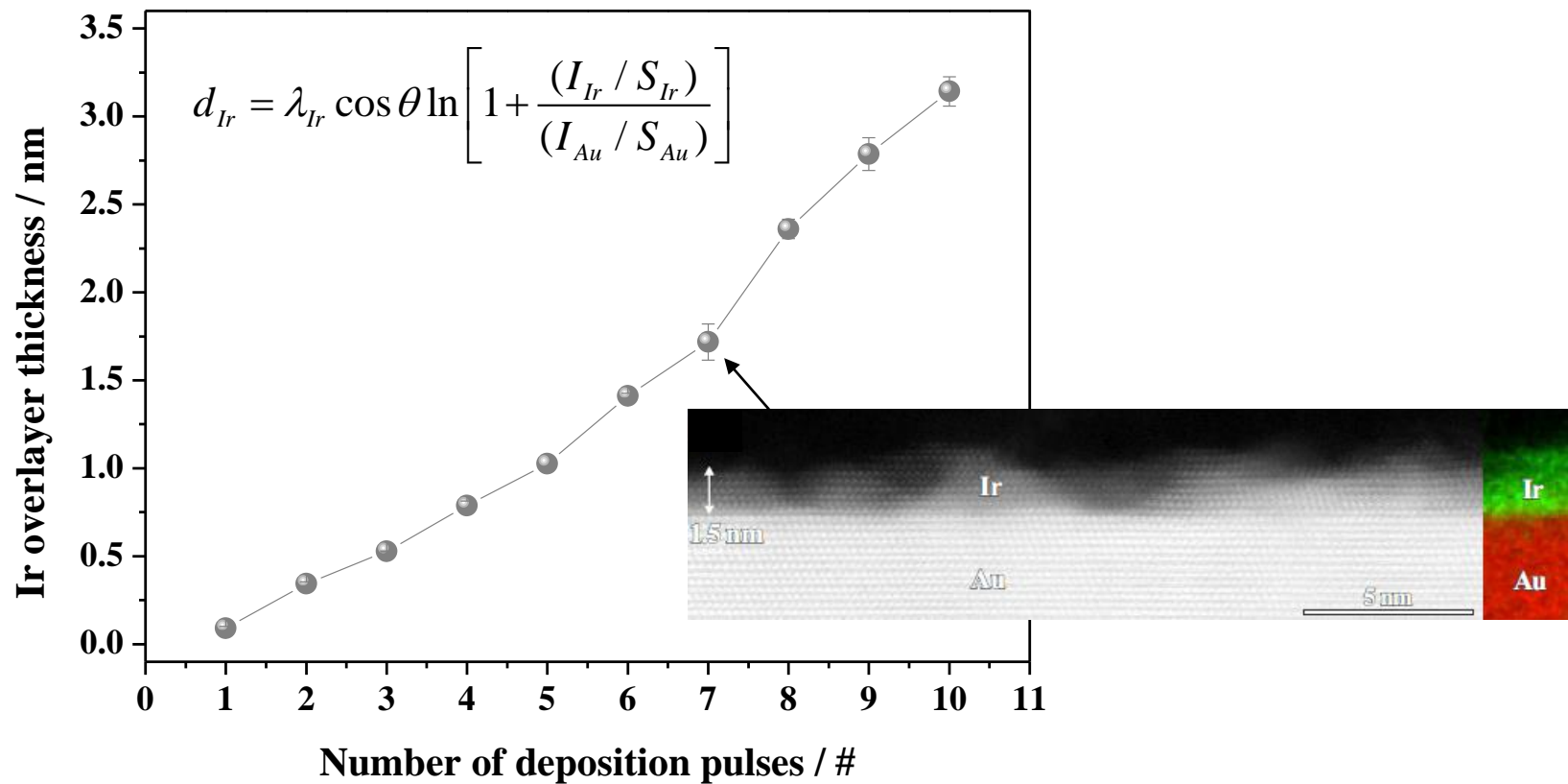


Thick overlayer film



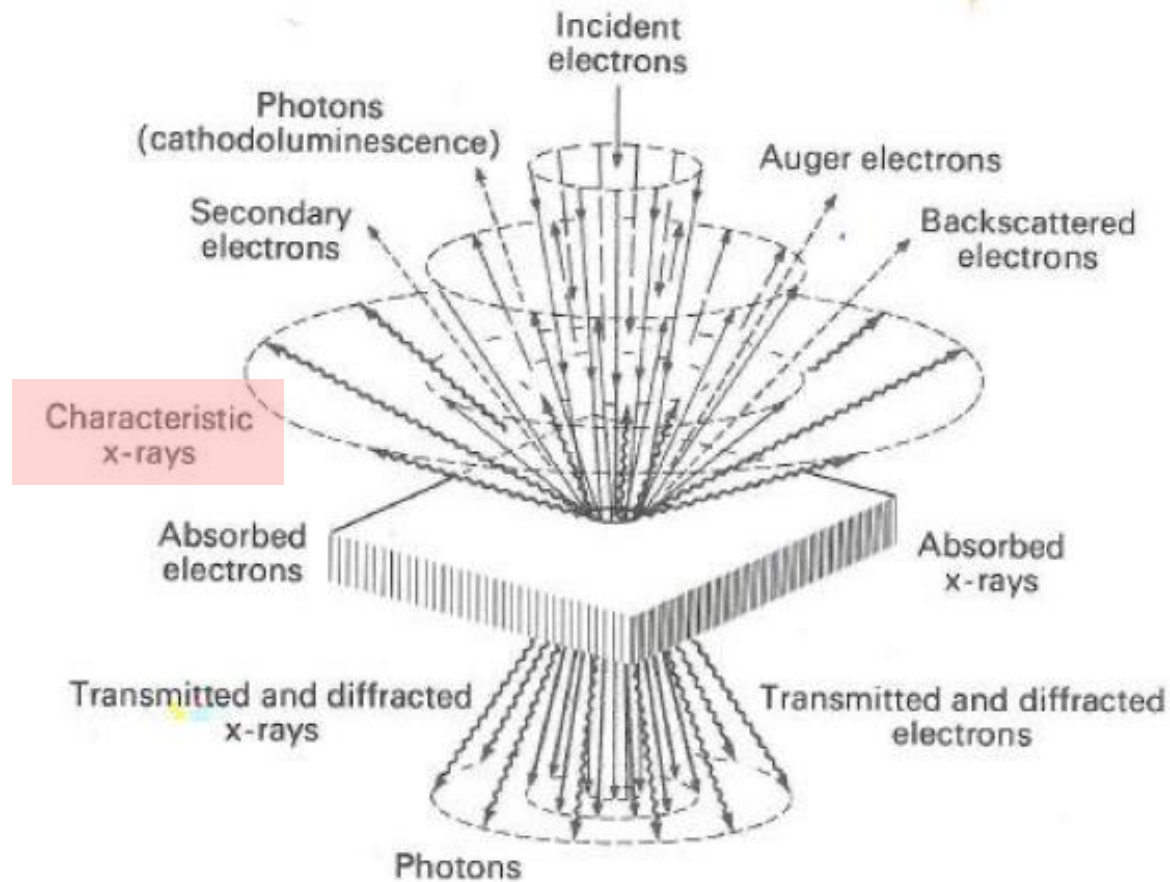
Thickness

Ir thin overlayer film on Au substrate

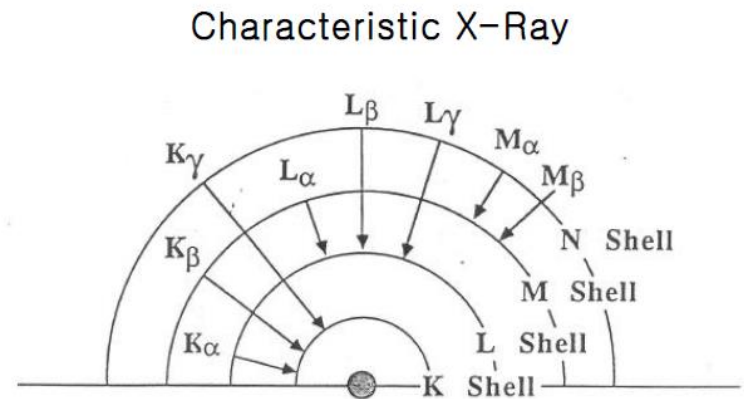
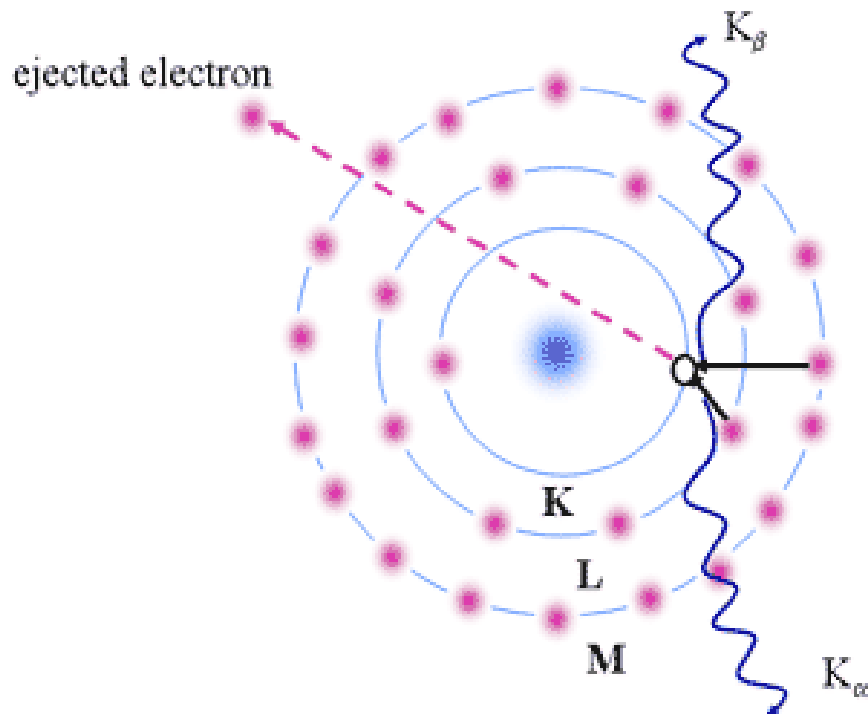


Energy dispersive spectroscopy

Incident electron beam interaction with sample

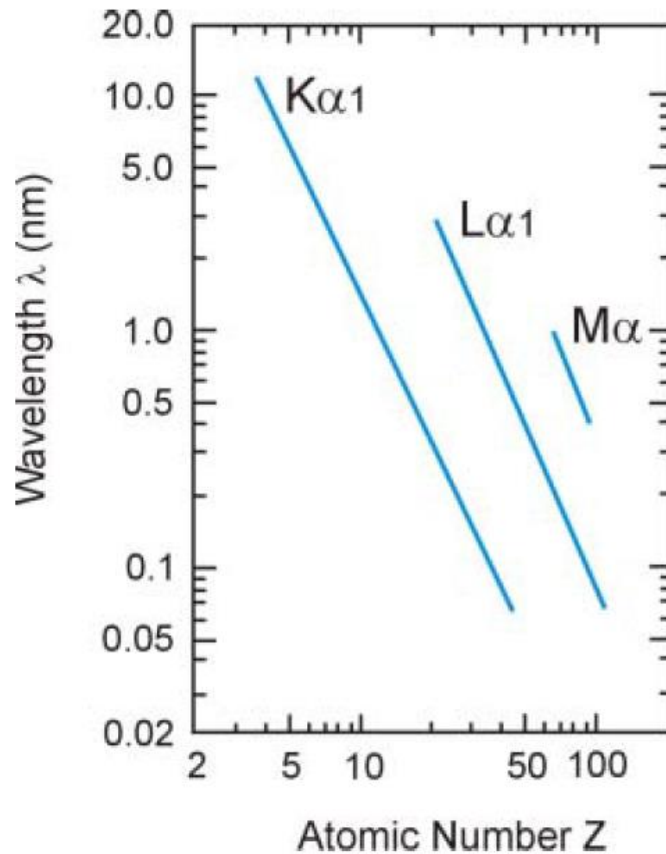


Characteristic X-ray



Energy of characteristic X-ray line
 $= E_{\text{final}} - E_{\text{initial}}$

Moseley's law



$$\lambda = \frac{B}{(Z - C)^2}$$

$$\Rightarrow \lambda \propto \frac{1}{Z^2}$$

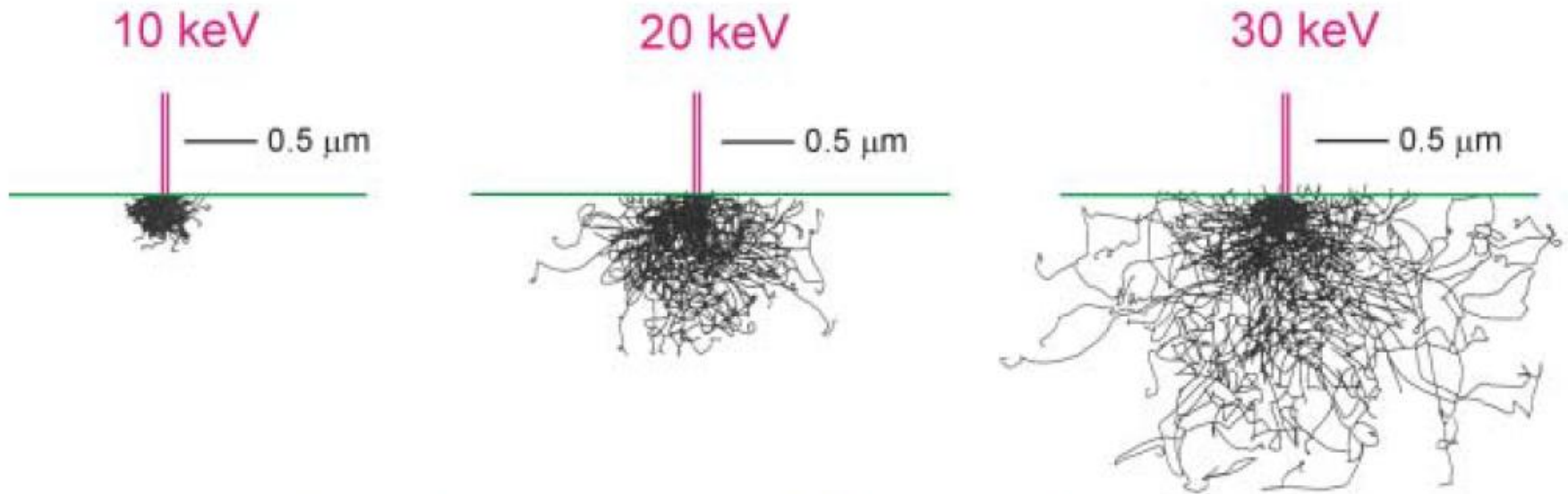
λ : wavelength of characteristic X-ray

B, C : constant

Z : atomic number

Interaction volume

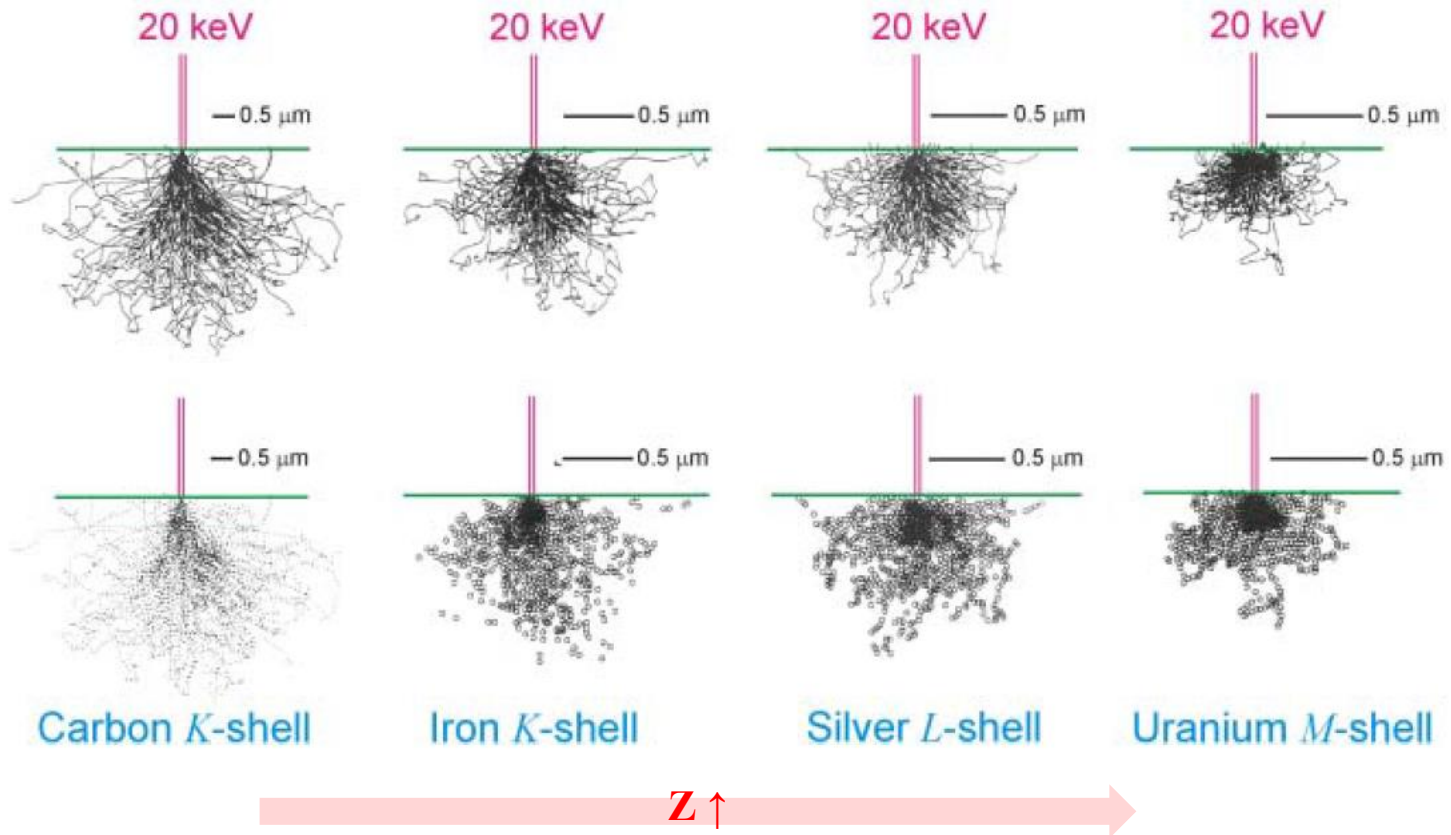
Electron beam energy effect



Interaction volume in iron (Fe) as a function of electron beam energy.

Interaction volume

Atomic number (Z) effect

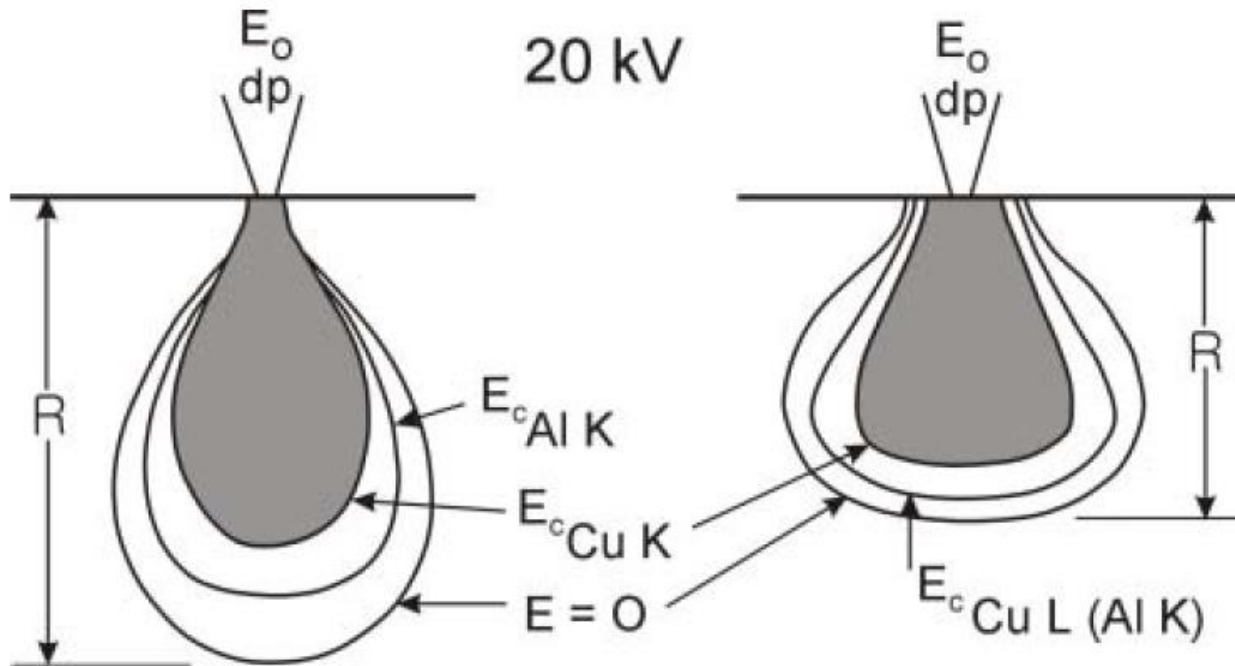


Interaction volume

Atomic number (Z) effect

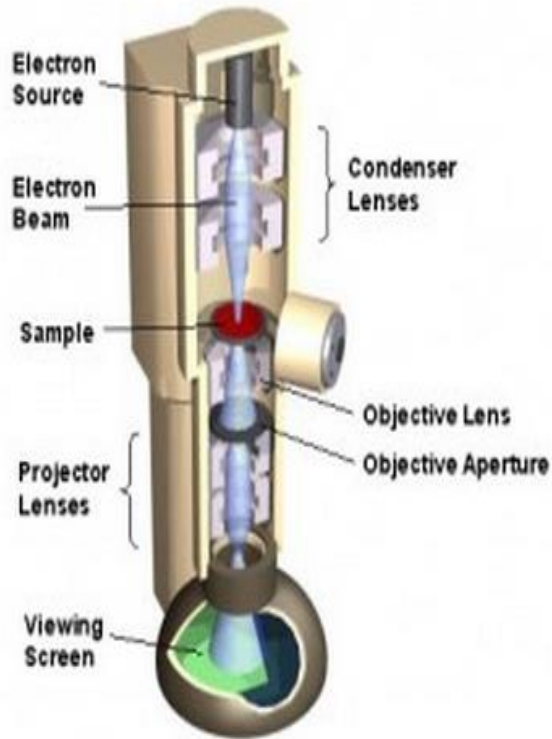
Small atomic number
: pear shape

Large atomic number
: sphere shape

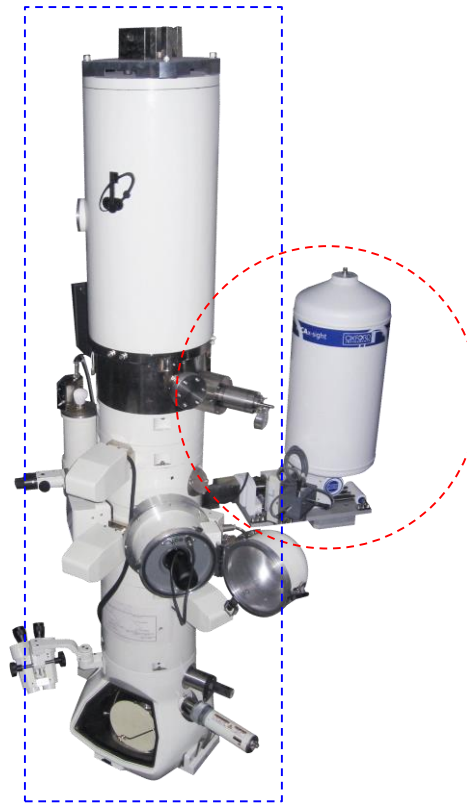


Instrumental image and schematic diagram

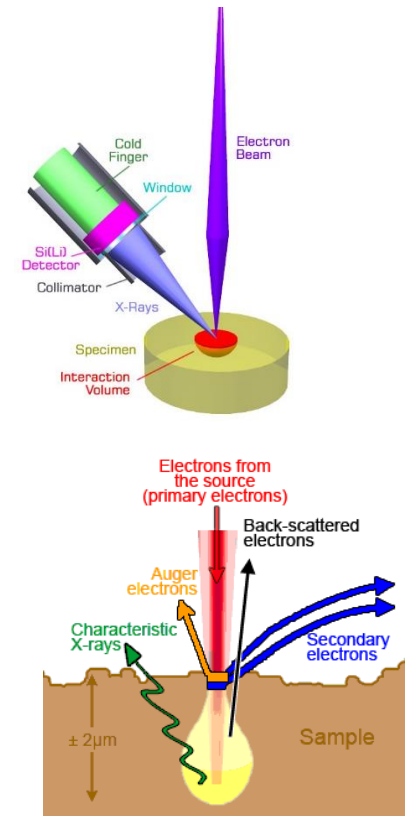
TEM schematic diagram



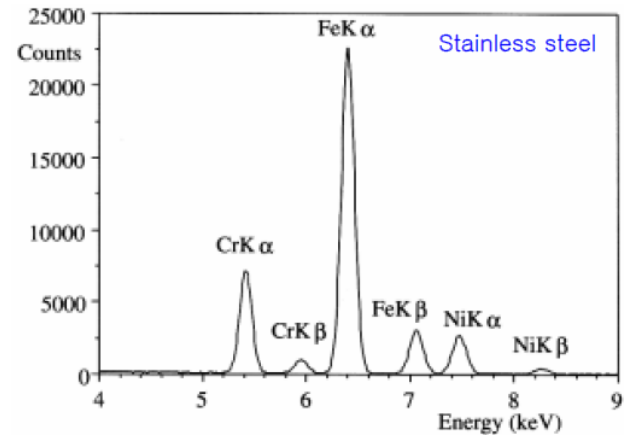
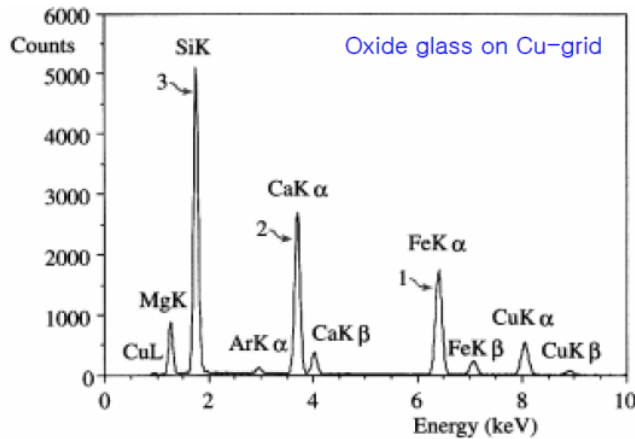
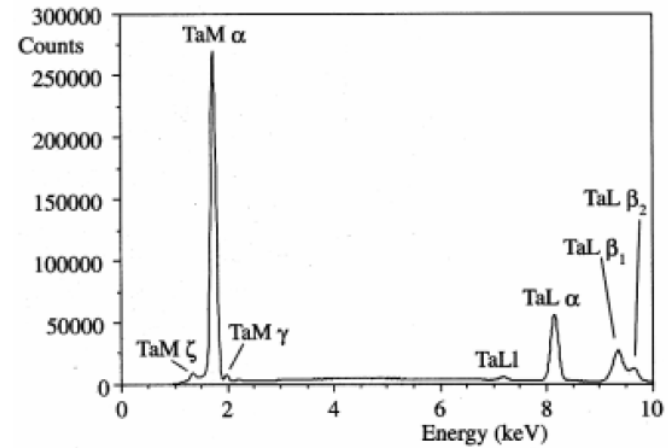
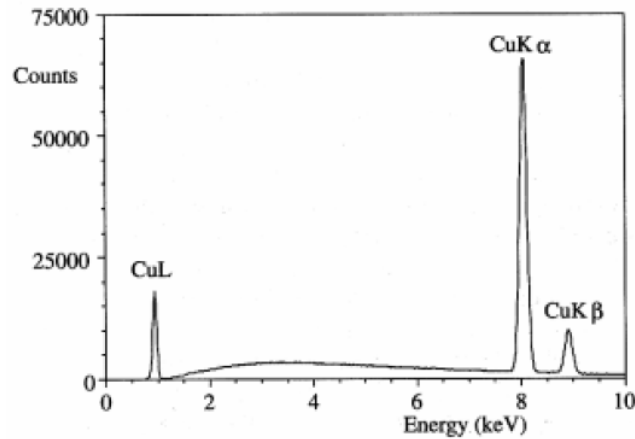
TEM image



EDS schematic diagram



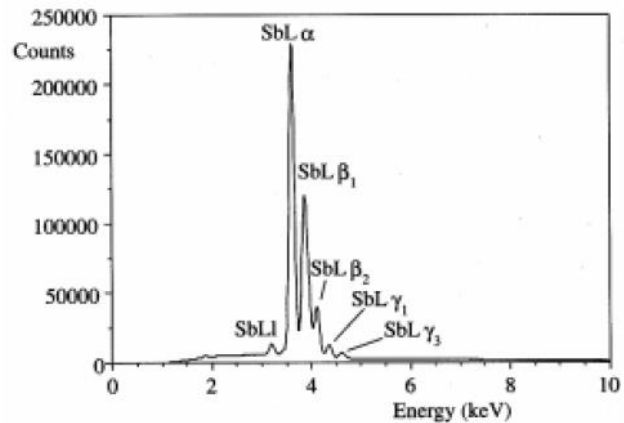
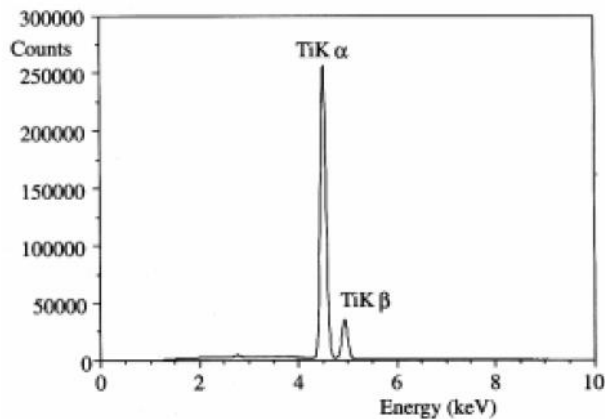
Qualitative analysis



Quantitative analysis

Relative intensity of X-ray line family

Family	Approximate intrafamily weights
K	$K\alpha = 1$ $K\beta = 0.1$
L	$L\alpha = 1$ $L\beta_1 = 0.7$ $L\beta_2 = 0.2$ $L\gamma_1 = 0.08$ $L\gamma_2 = 0.03$ $L\gamma_3 = 0.03$ $L\eta = 0.01$
M	$M\alpha = 1$ $M\beta = 0.6$ $M\zeta = 0.06$ $M\gamma = 0.05$ $M_{II}N_{IV} = 0.01$



Quantitative analysis

Overlapping problem

Element	Interfering x-ray line	Interferes with	X-ray line interfered with
Ti	$K\beta$	V	$K\alpha$
V	$K\beta$	Cr	$K\alpha$
Cr	$K\beta$	Mn	$K\alpha$
Mn	$K\beta$	Fe	$K\alpha$
Fe	$K\beta$	Co	$K\alpha$
Pb	$M\alpha$	S	$K\alpha$
		Mo	$L\alpha$
Si	$K\alpha$	Ta	$M\alpha$
Ba	$L\alpha$	Ti	$K\alpha$

Quantitative analysis

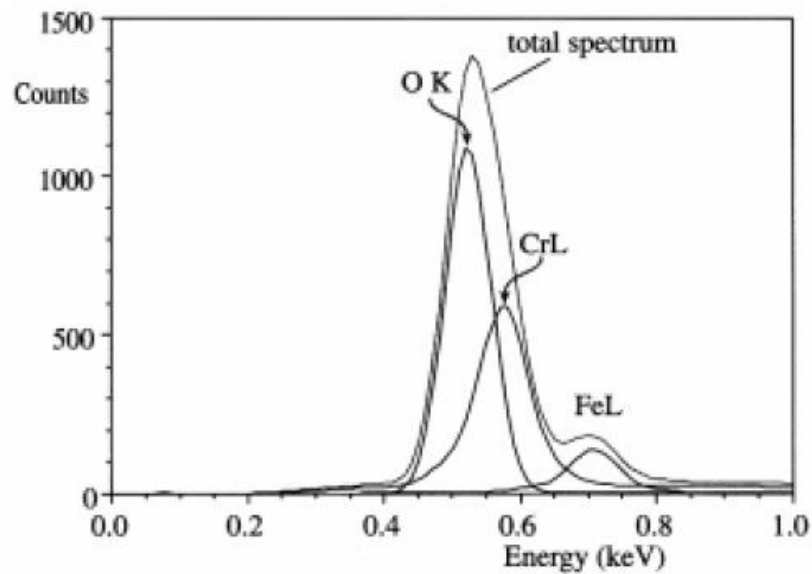
Overlapping problem

Element in stain or fixative	Interfering x-ray line	Interferes with	X-ray line interfered with
U	<i>M</i>	K, Cu, Ti	<i>Kα</i>
		Cd, In, Sn, Sb, Ba	<i>Lα</i>
Os	<i>M</i>	Al, P, S, Cl	<i>Kα</i>
		Sr	<i>Lα</i>
Pb	<i>M</i>	S, Cl	<i>Kα</i>
		Mo	<i>Lα</i>
	<i>L</i>	As, Se	<i>Kα</i>
Ru	<i>L</i>	S, Cl, K	<i>Kα</i>
Ag	<i>L</i>	Cl, K	<i>Kα</i>
As	<i>L</i>	Na, Mg, Al	<i>Kα</i>
Cu (grid)	<i>L</i>	Na	<i>Kα</i>
Biological elements			
K	<i>Kβ</i>	Ca	<i>Kα</i>
Zn	<i>Lα</i>	Na	<i>Kα</i>

Quantitative analysis

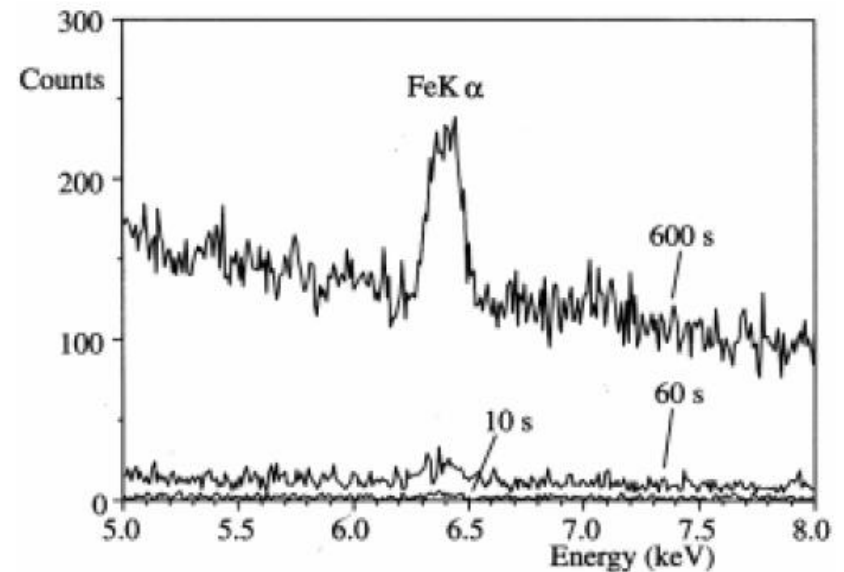
Solutions

Peak overlapping



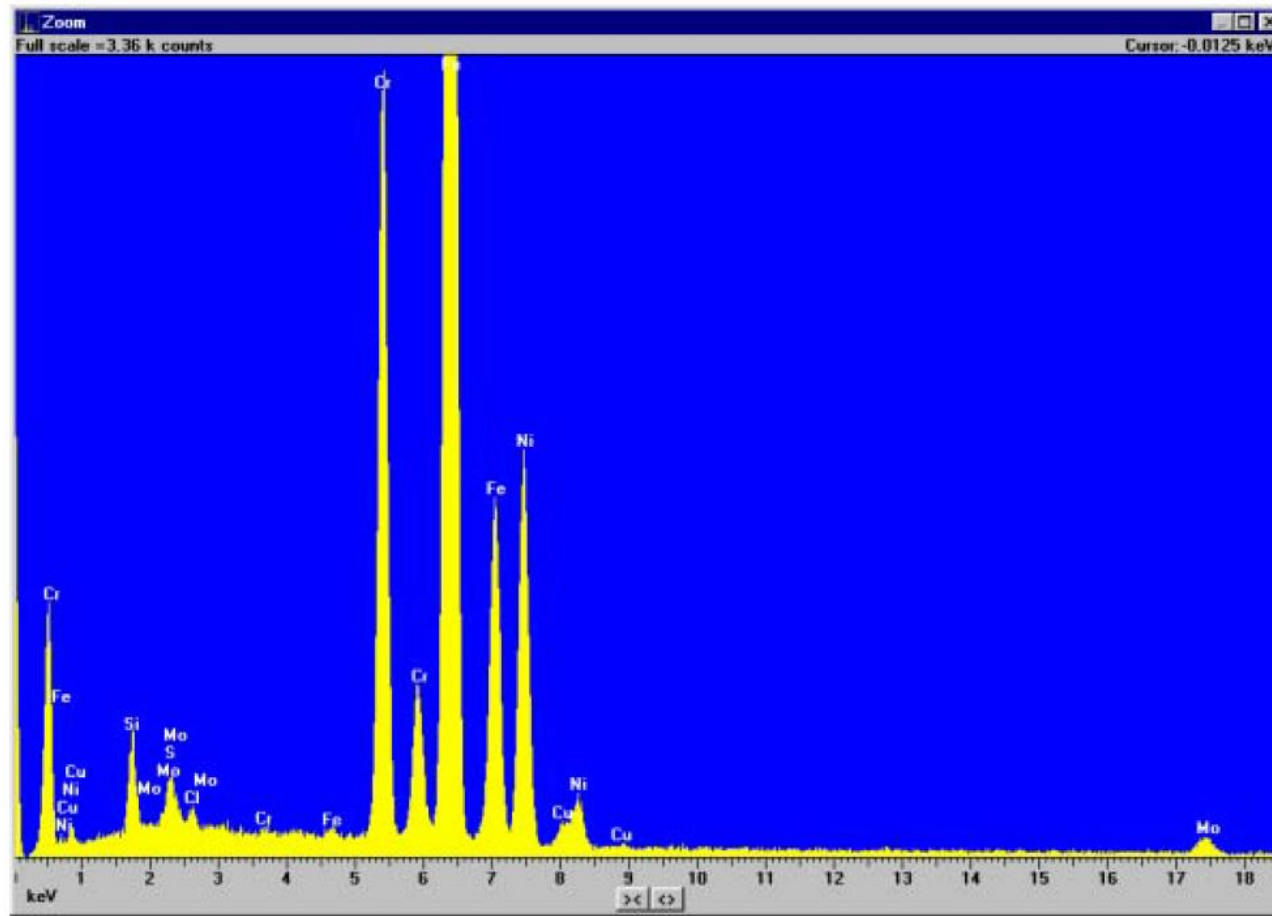
Peak deconvolution

Weak peak intensity



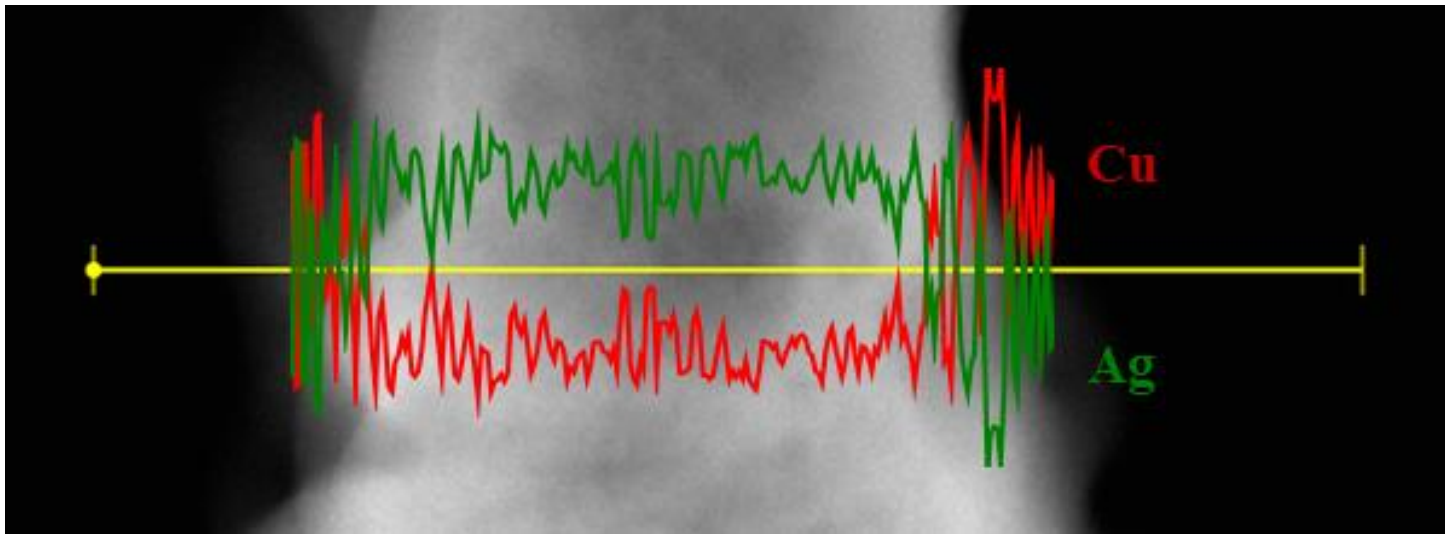
Increase analysis time

Examples



Examples

Line scanning



Examples

Mapping

