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X-ray photoelectron spectroscopy: how does it work and what can we learn from it?

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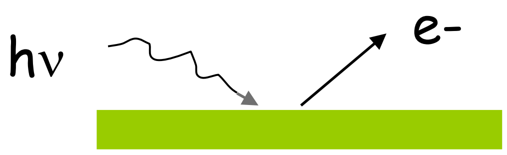
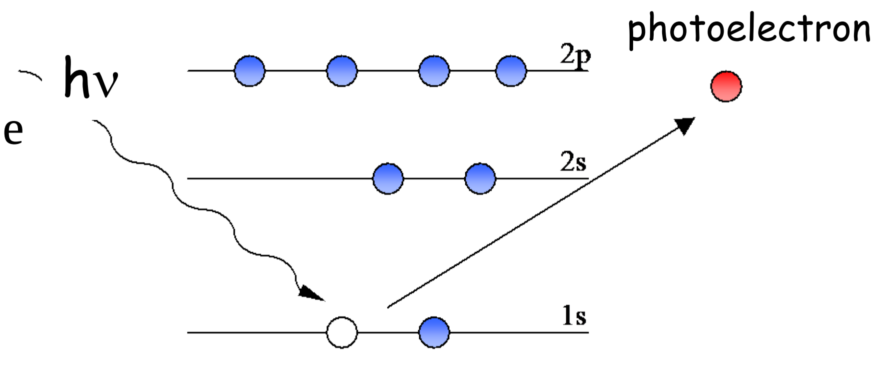
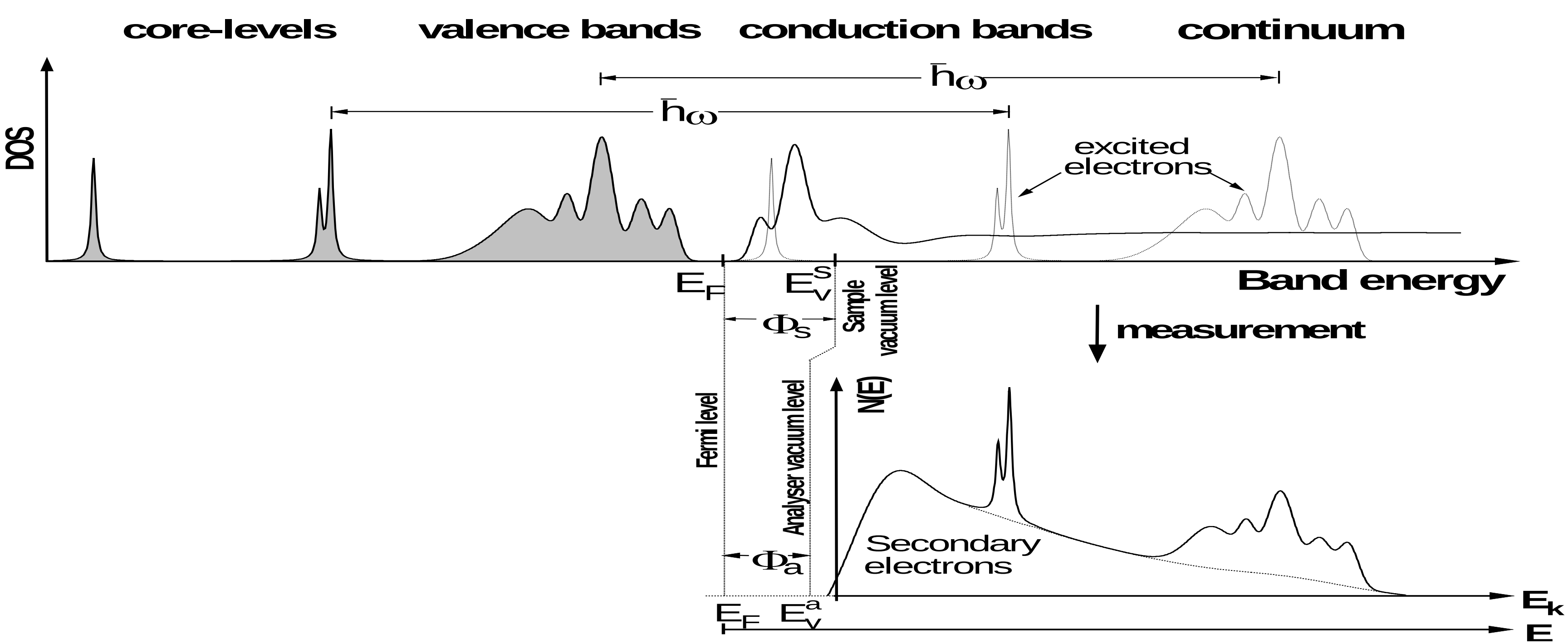
How does it work?

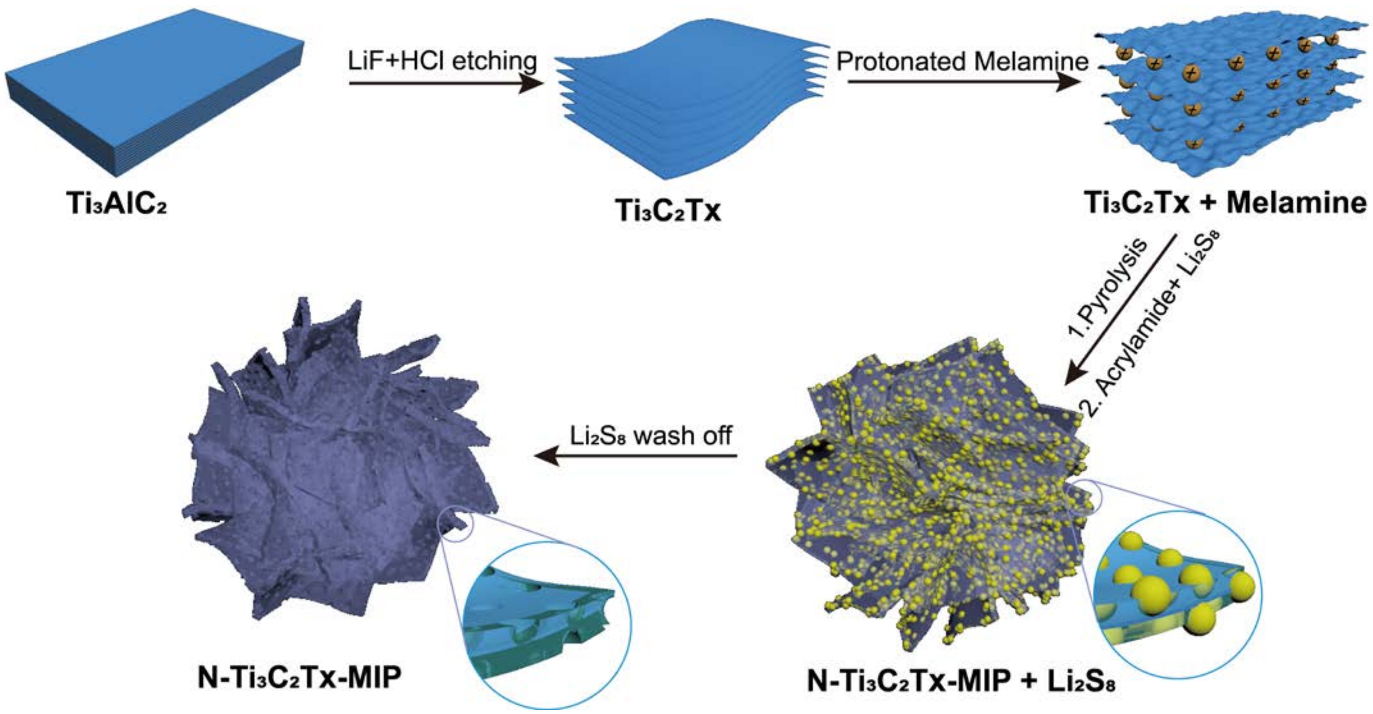
- monochromatic X-rays, UV light
- measure kinetic energy of emitted electrons
- deduce binding energy from electronic structure







Molecularly imprinted polymer (MIP) in conjunction with 2D material, MXene, developed for cathodes of Li-S batteries



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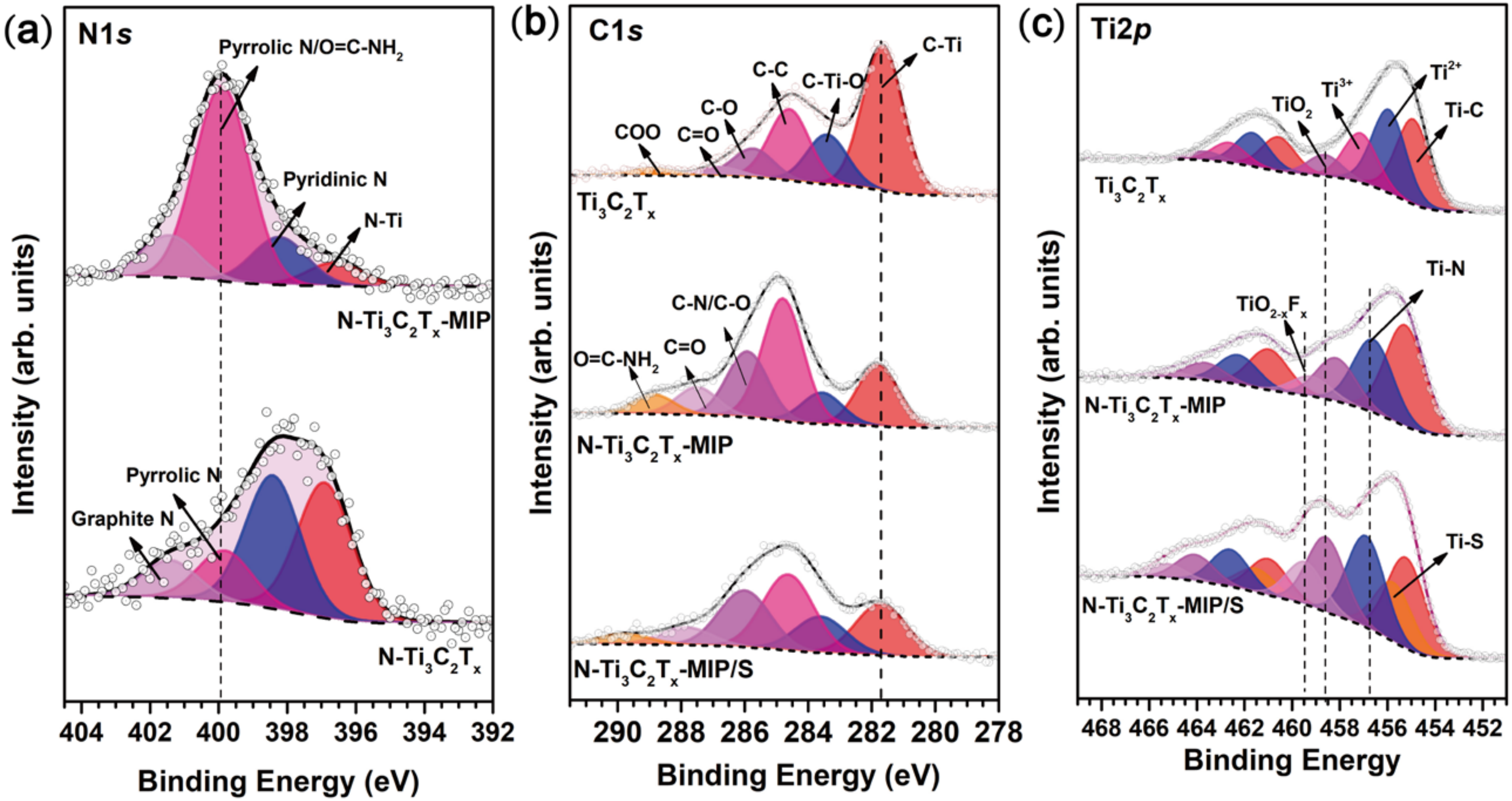
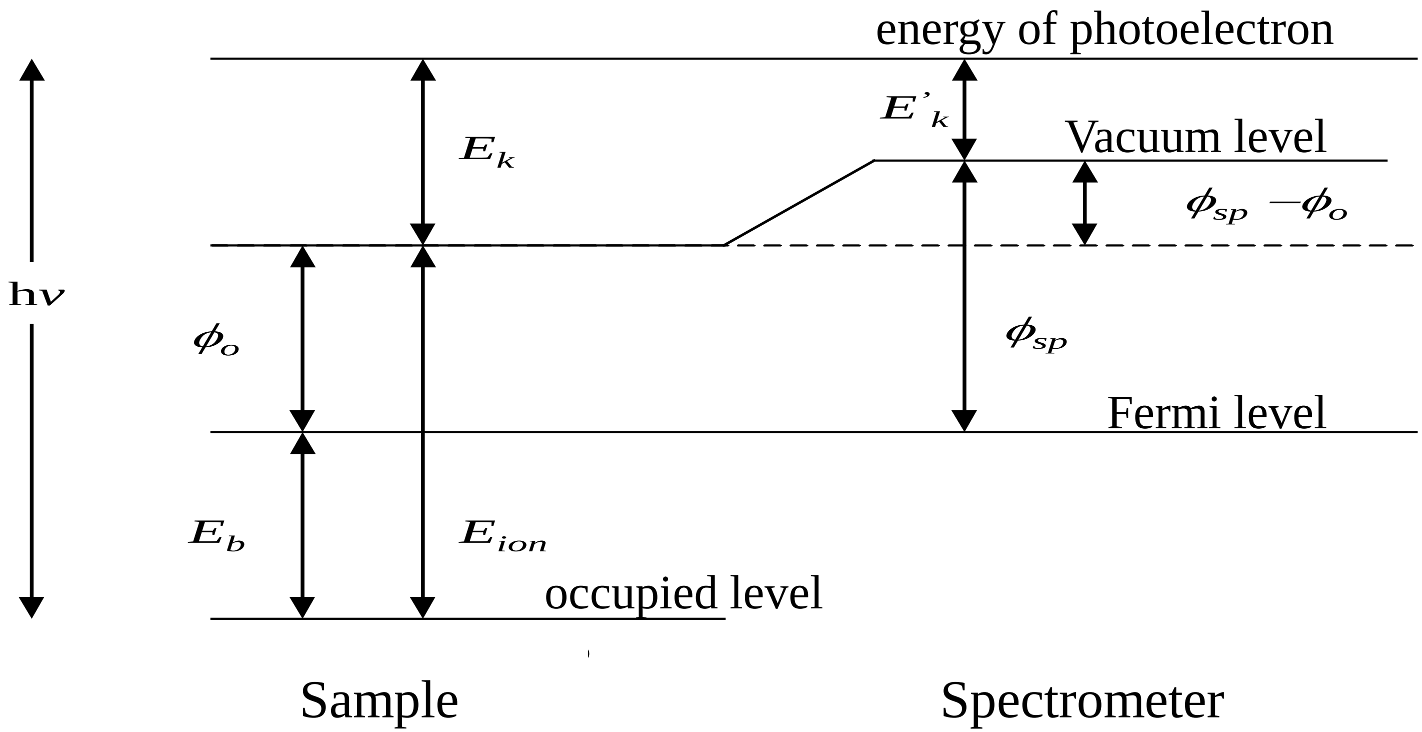


What is the binding energy in XPS ?



$h\nu = E_b + E_k + \phi_0$

$E_b = E_f - E_i = h\nu - E'_k + \phi_{sp}$

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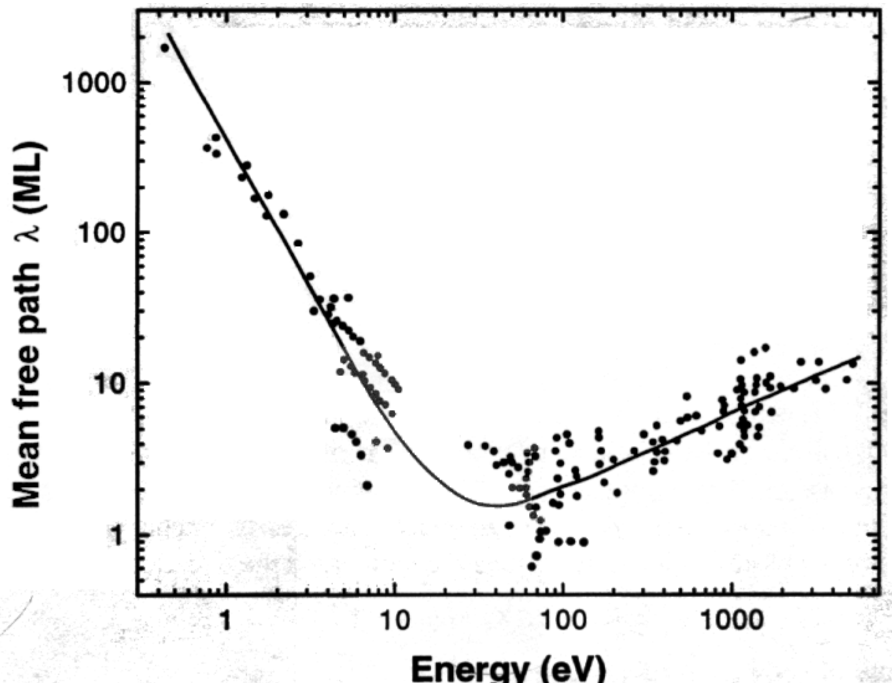
Photoemission can be seen as 3 step process

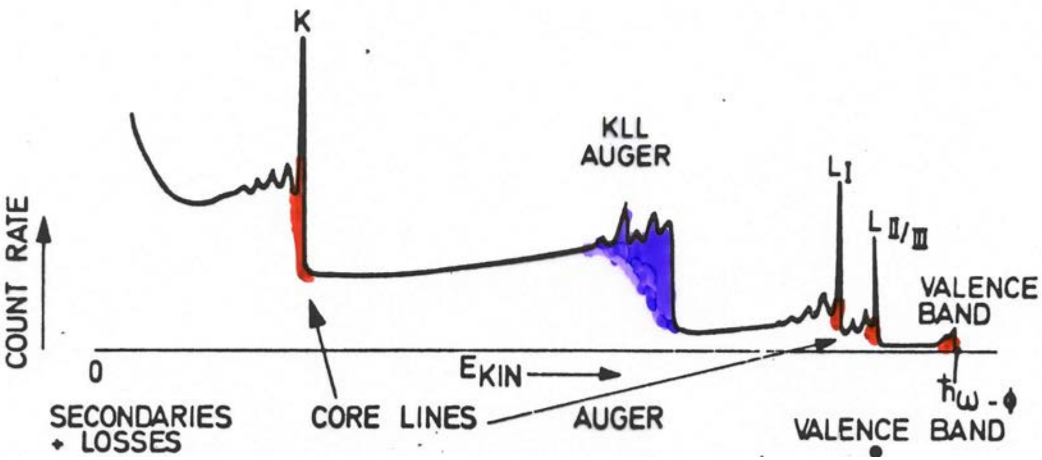
1) photoionisation - optical absorption machinery, selection rules
2) transport of photoelectron through sample - inelastic mean free path
3) emission of photoelectron into vacuum - refractive effects at the surface, k-parallel vs. k-normal

Universal curve of electron mean free path (Zangwill ' 88)



E_k < 1500 eV : XPS gives information on surface layer (typically <10 nm)

The photoionisation of core level → Auger decay or fluorescent decay (X-ray emission)



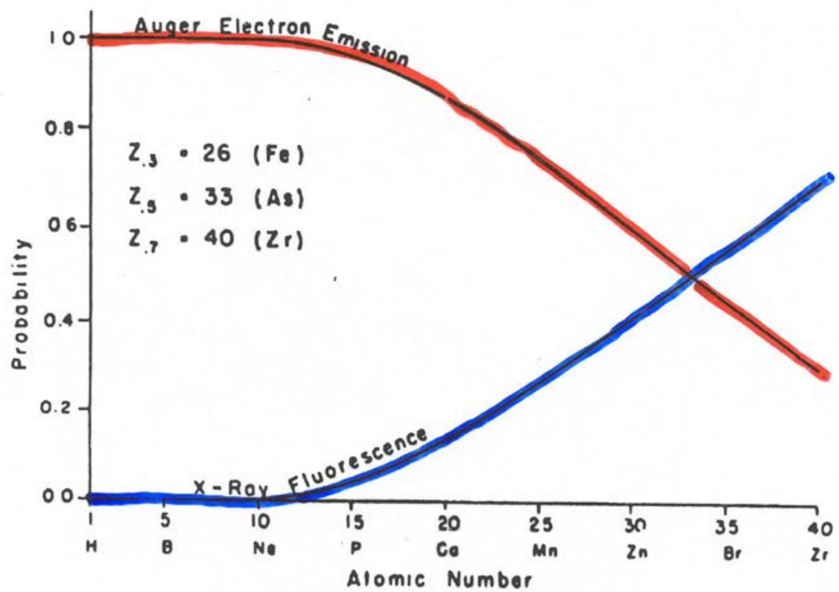
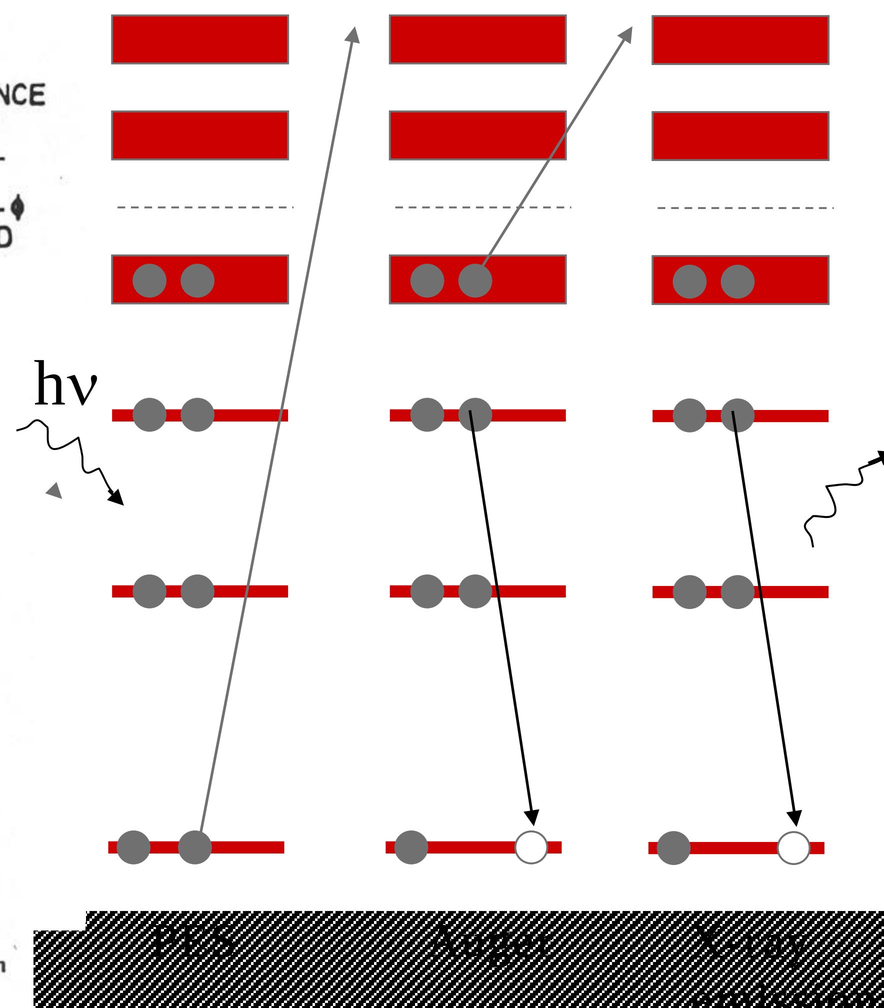
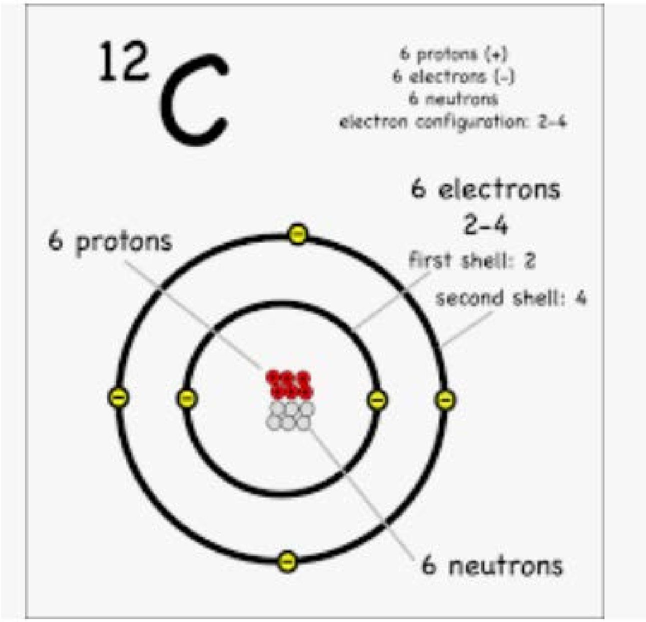


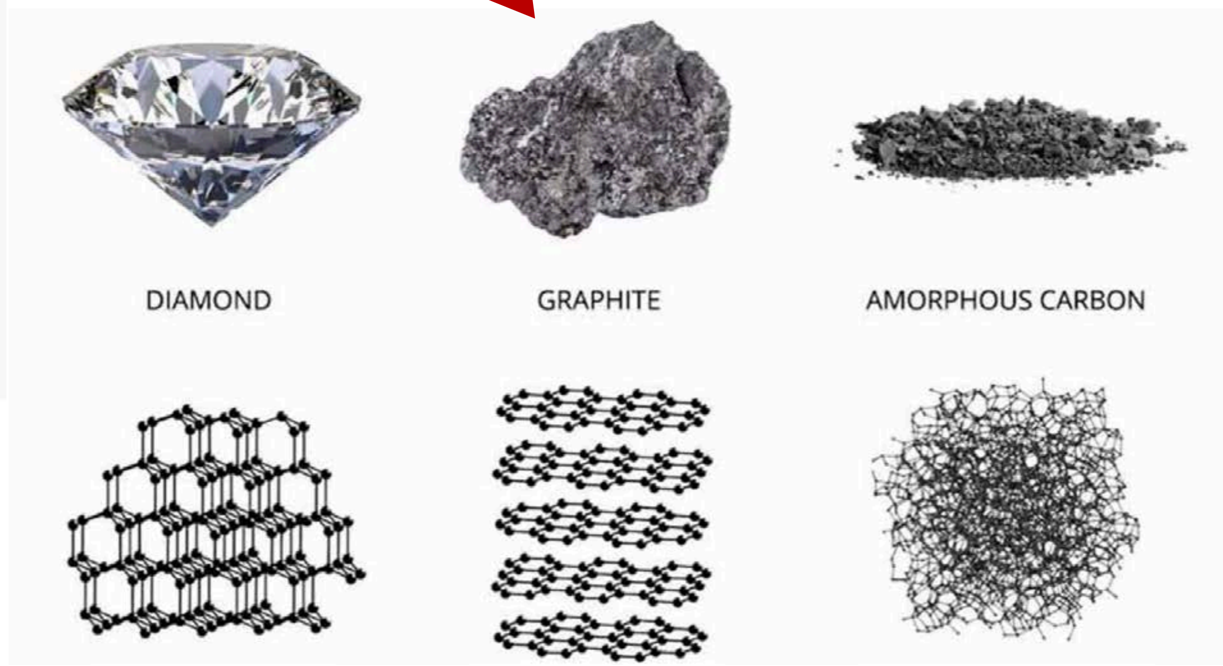
Figure 3.5 Relative probabilities of relaxation by emission of an Auger electron and by emission of an X-ray photon of characteristic energy, following creation of a core hole in the K shell



Let’s start simple: Carbon



C: $1s^2\ 2s^2\ 2p^2$



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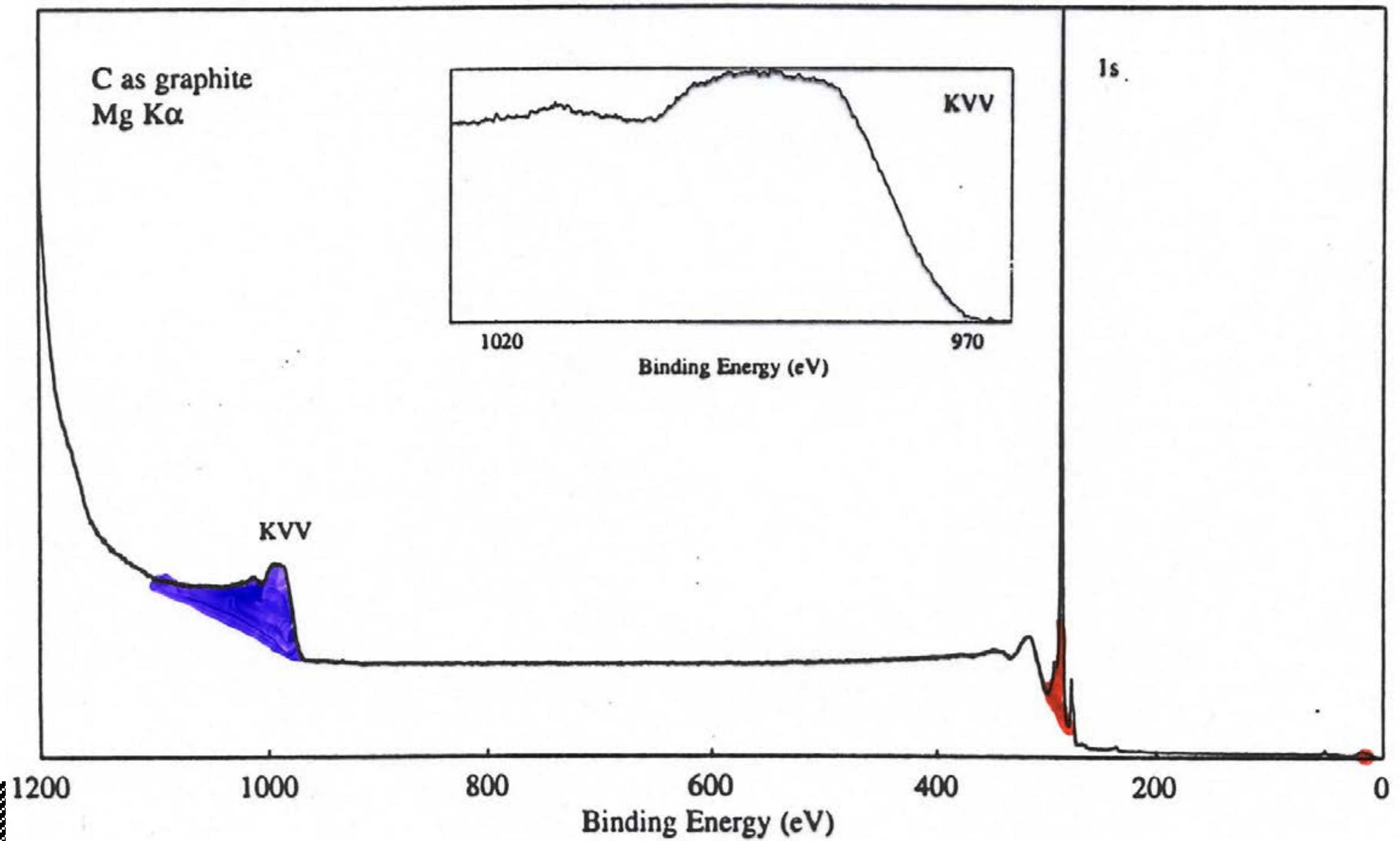
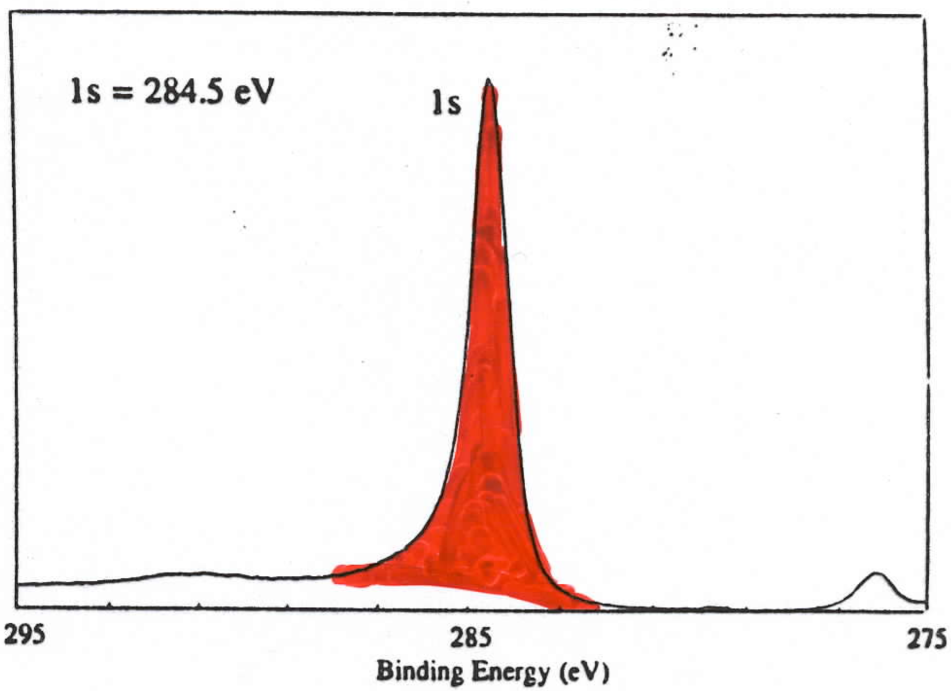
Wide XPS spectrum of graphite (C)



The singlet **C 1*s*** line is characterized by:

Core level XPS spectrum of graphite (C)

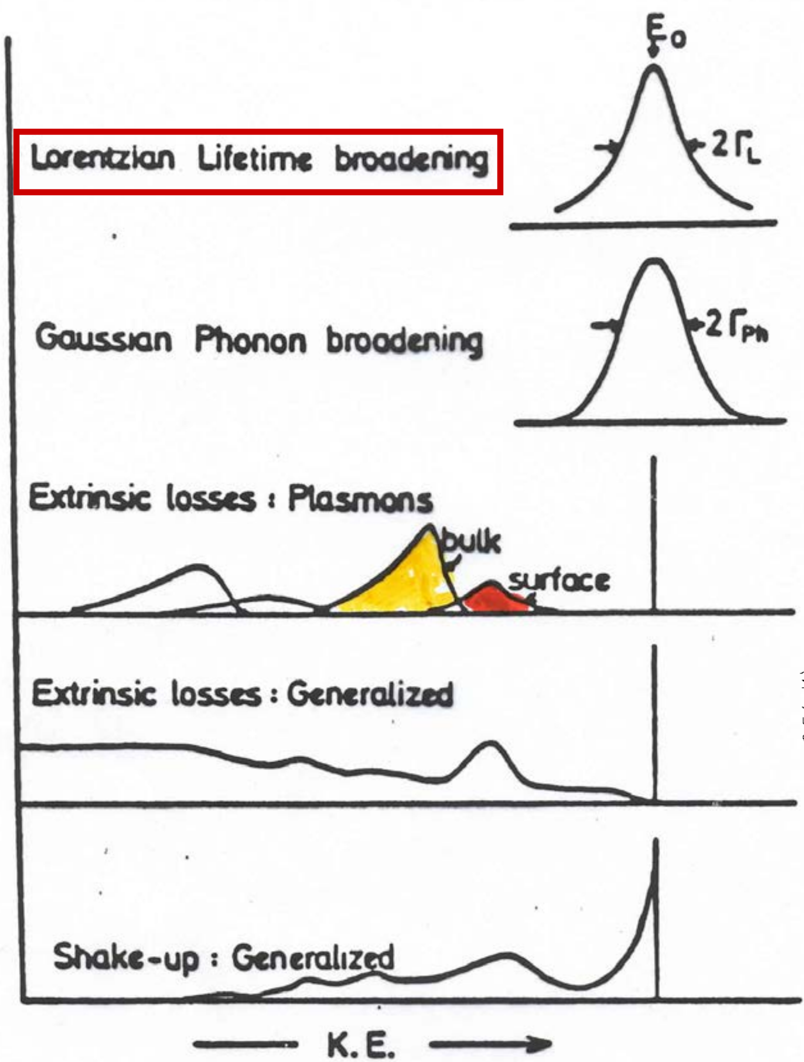


1) A specific binding energy which reflects the specific atomic species (C) in a specific chemical environment

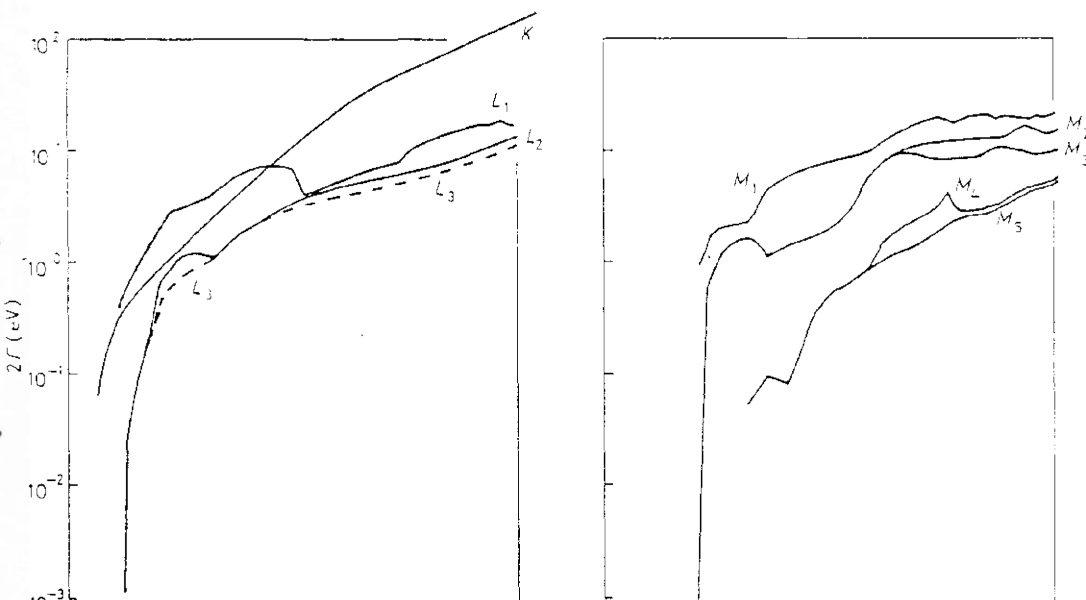
2) A finite width reflecting the instrumental resolution, lifetime broadening and other many-body effects

What determines the line shape ?

photoionisation process takes 10^{-17}sec – core hole of light element decays in 10^{-15} sec – indetermination in energy



(4) $$\frac{1}{2}\mathrm{FWHM} = \Gamma_L = h/\tau = 6.58 \cdot 10^{-16}/\tau \ \mathrm{eV},$$



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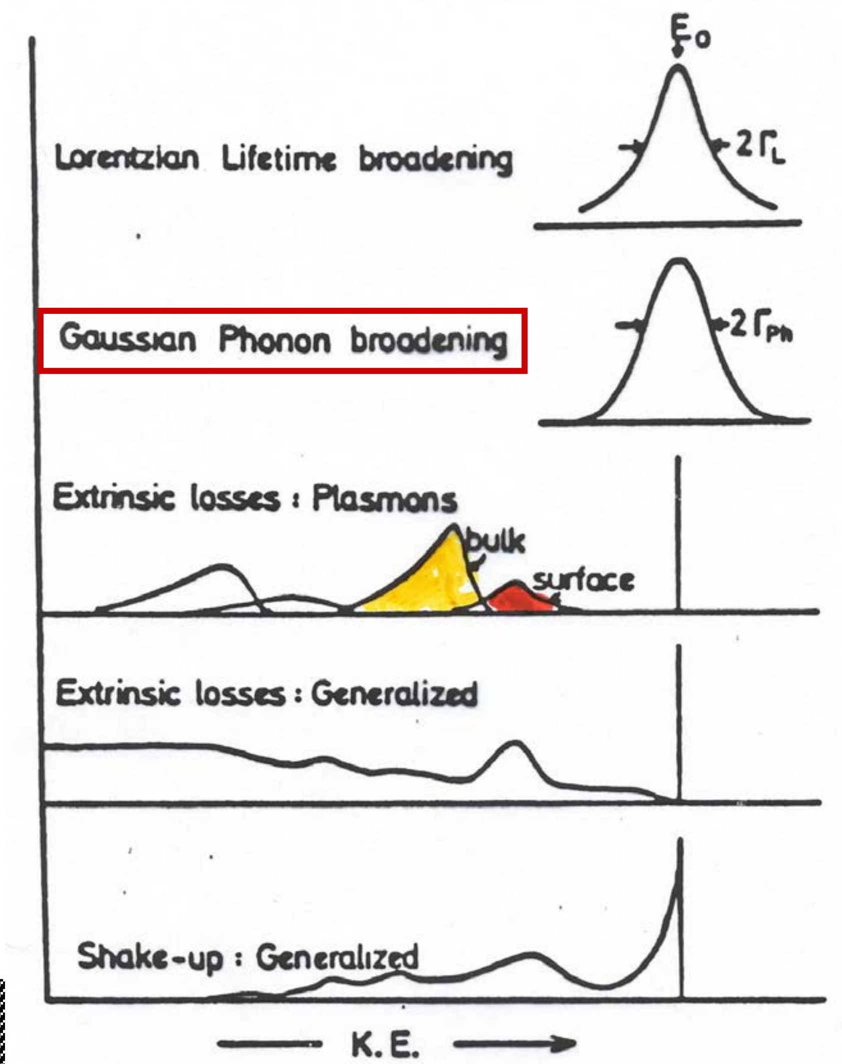

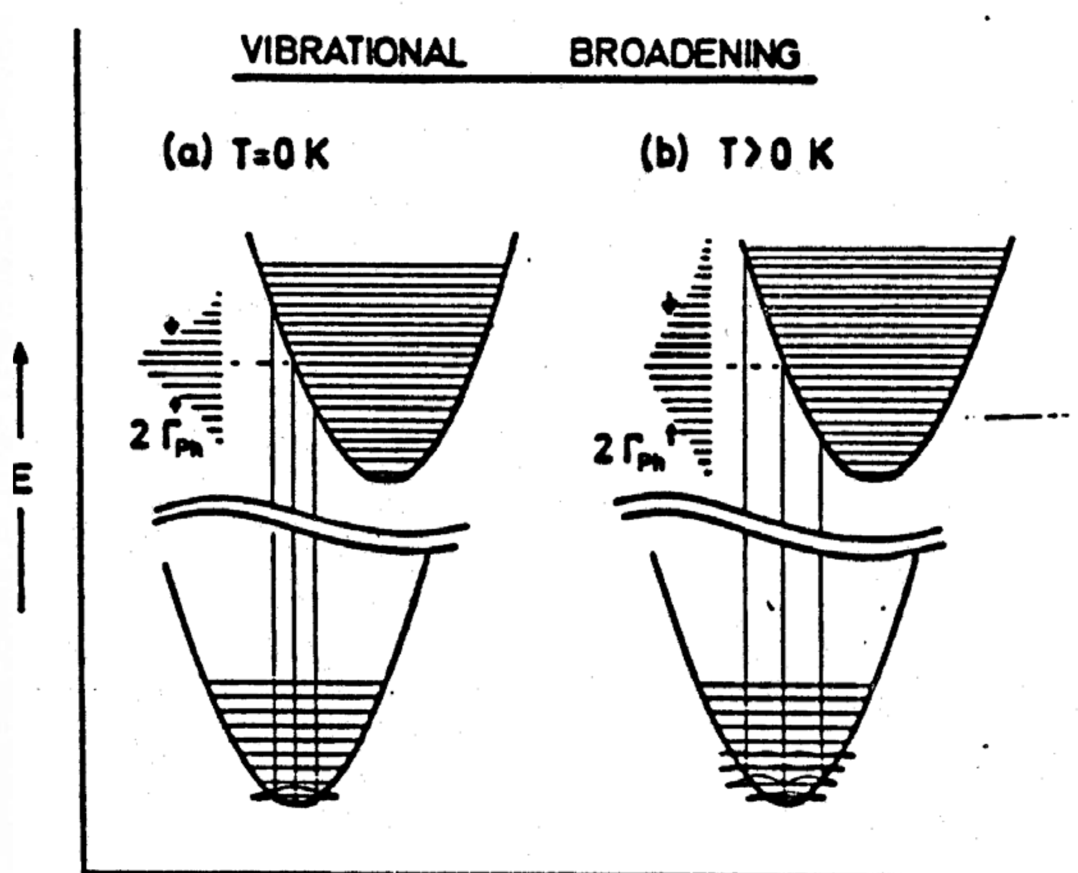

The origin of phonon broadening in XPS and Auger lines.

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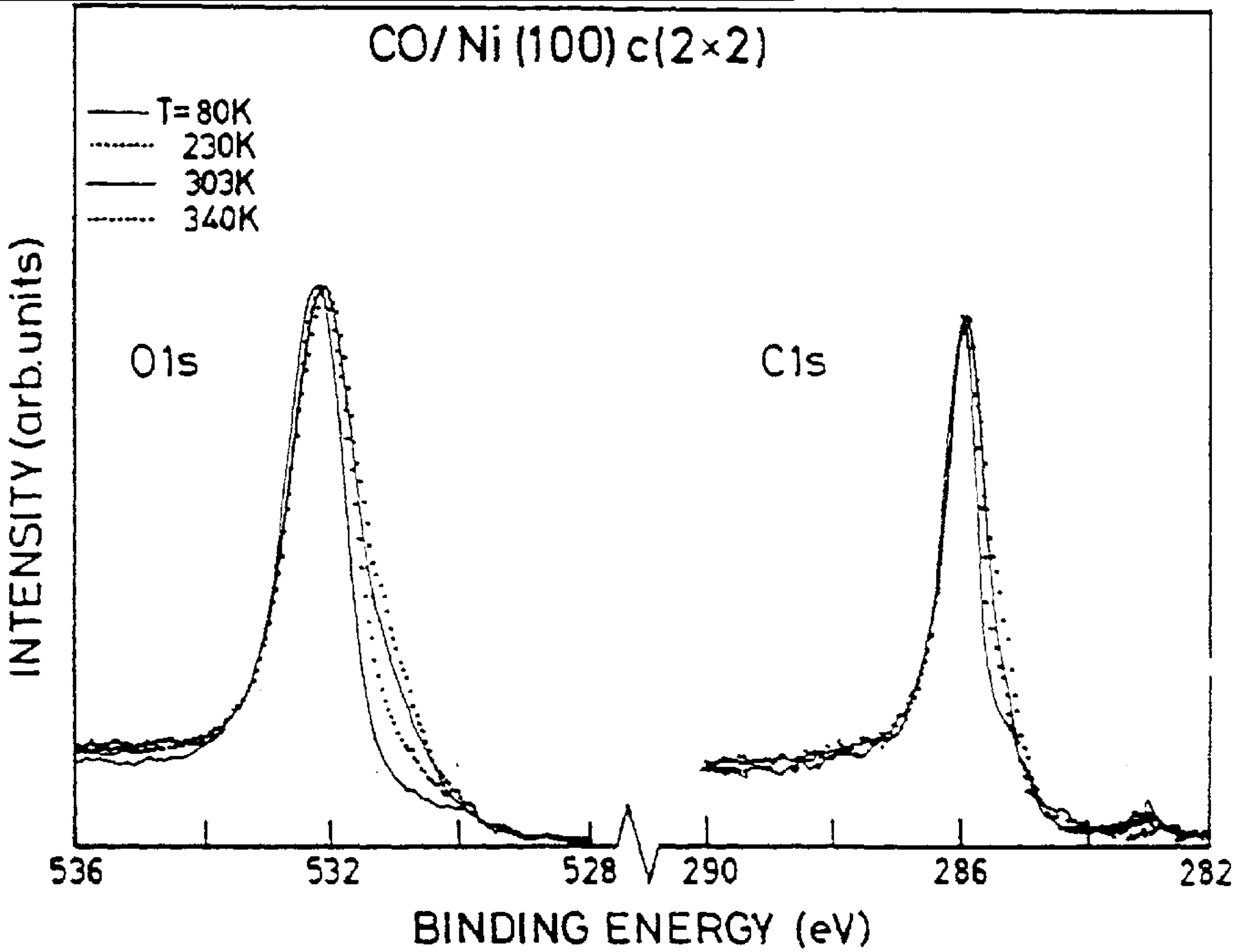
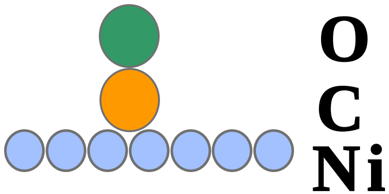
Vibrational Broadening





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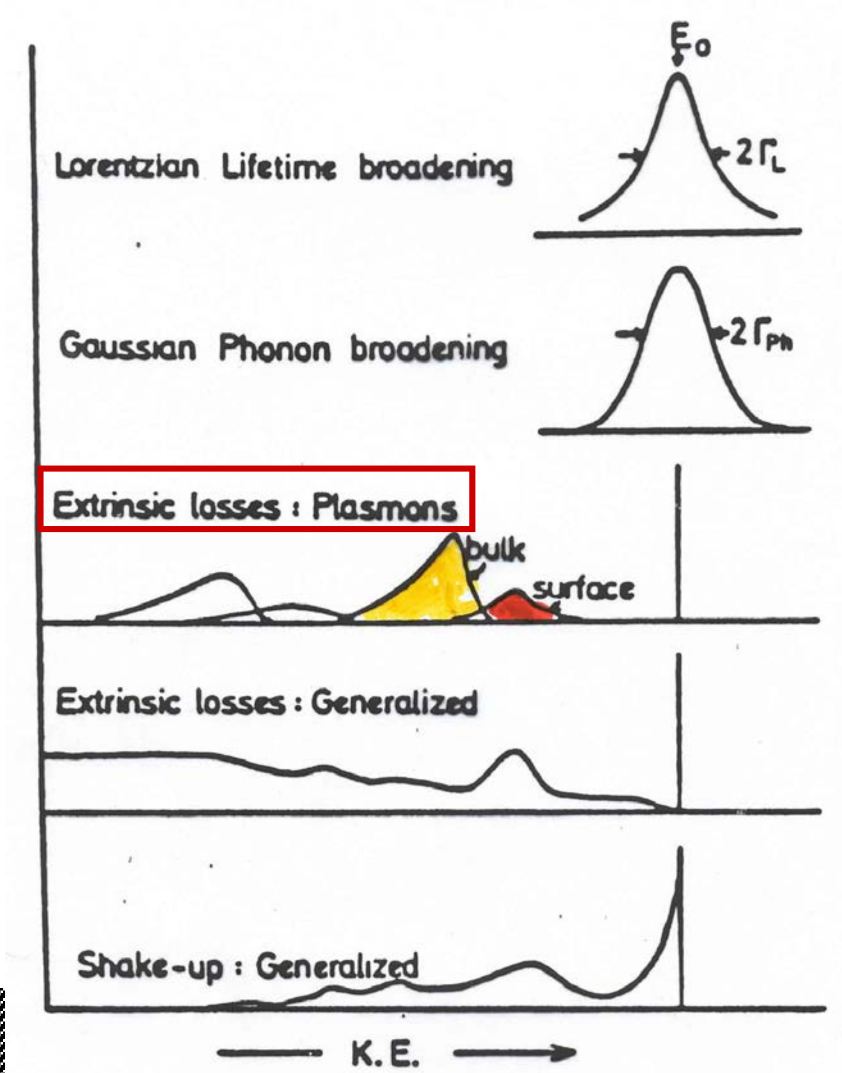
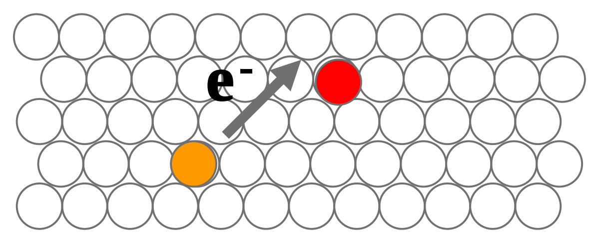
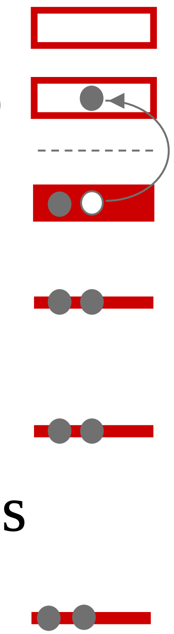


Extrinsic losses





- single electron transitions
- collective excitations = plasmons

photoelectron loses energy
spectral features appear at lower kinetic energy

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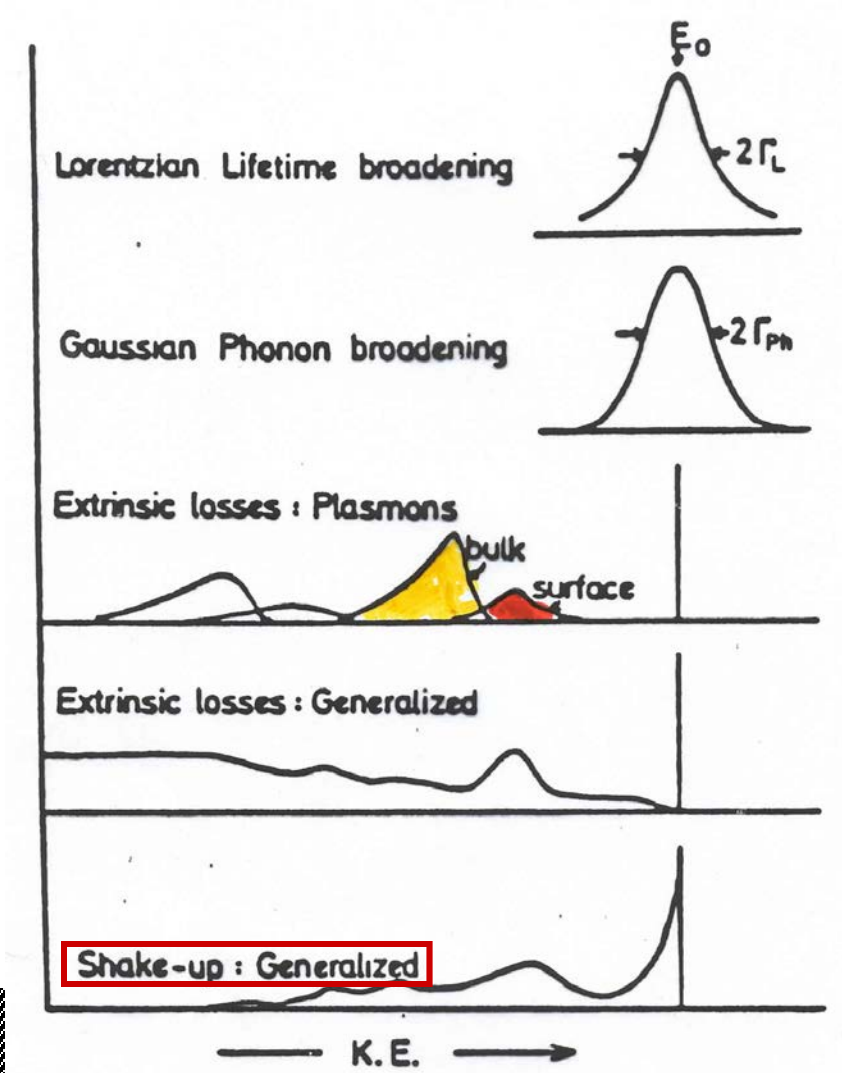
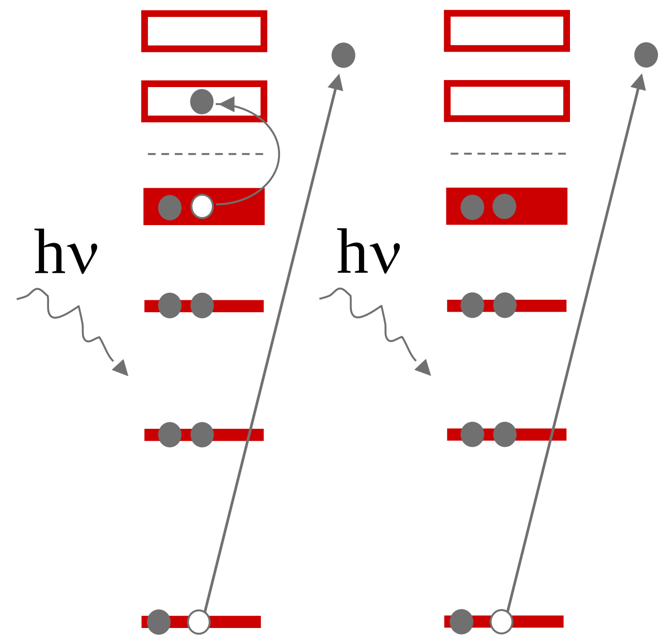
What determines the line shape ?



Shake-up: photoemission is not a single particle process - different final states possible



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Line-asymmetry in Core Level XPS

The line-asymmetry scales with the density of states at E_F

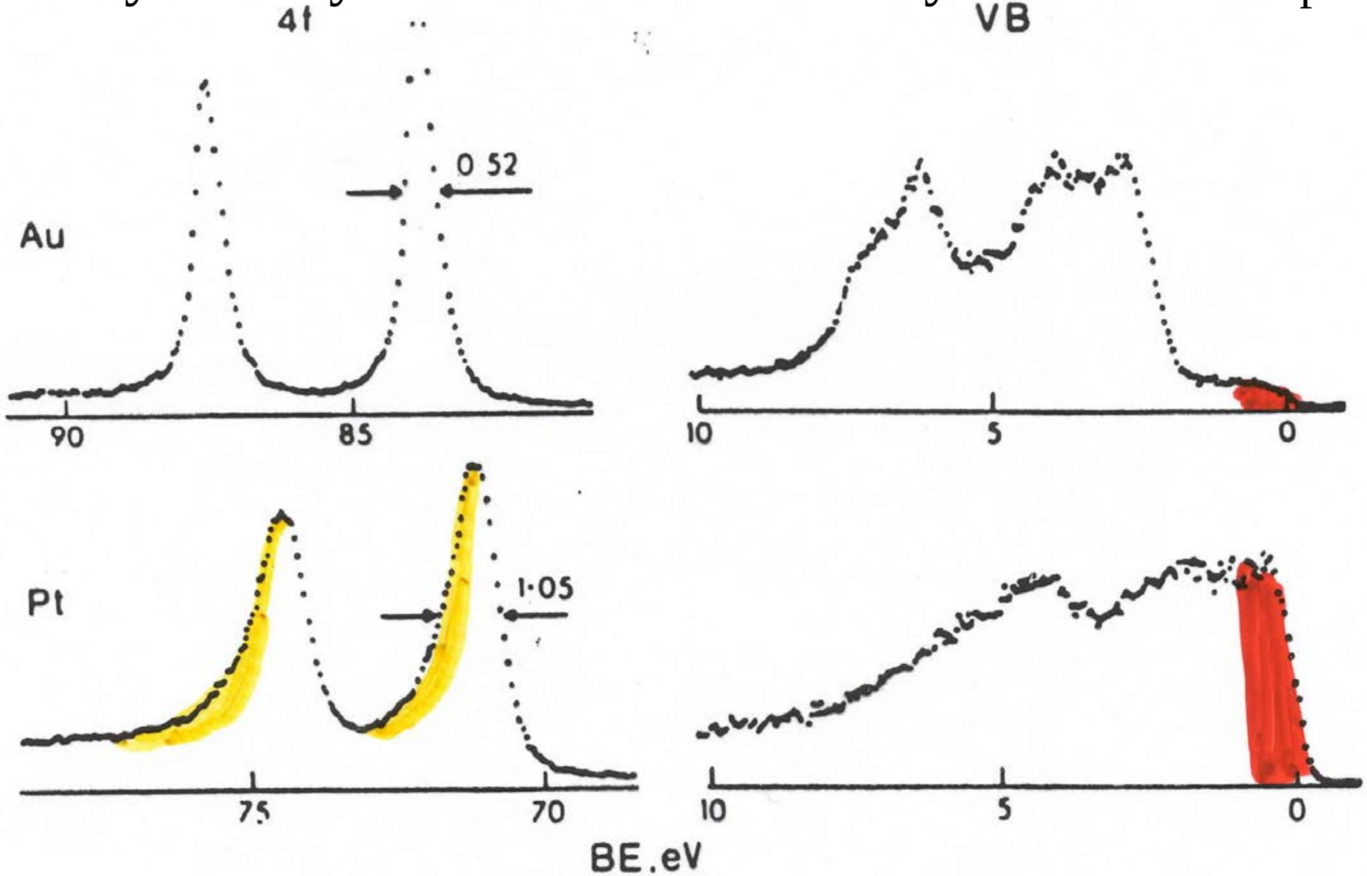
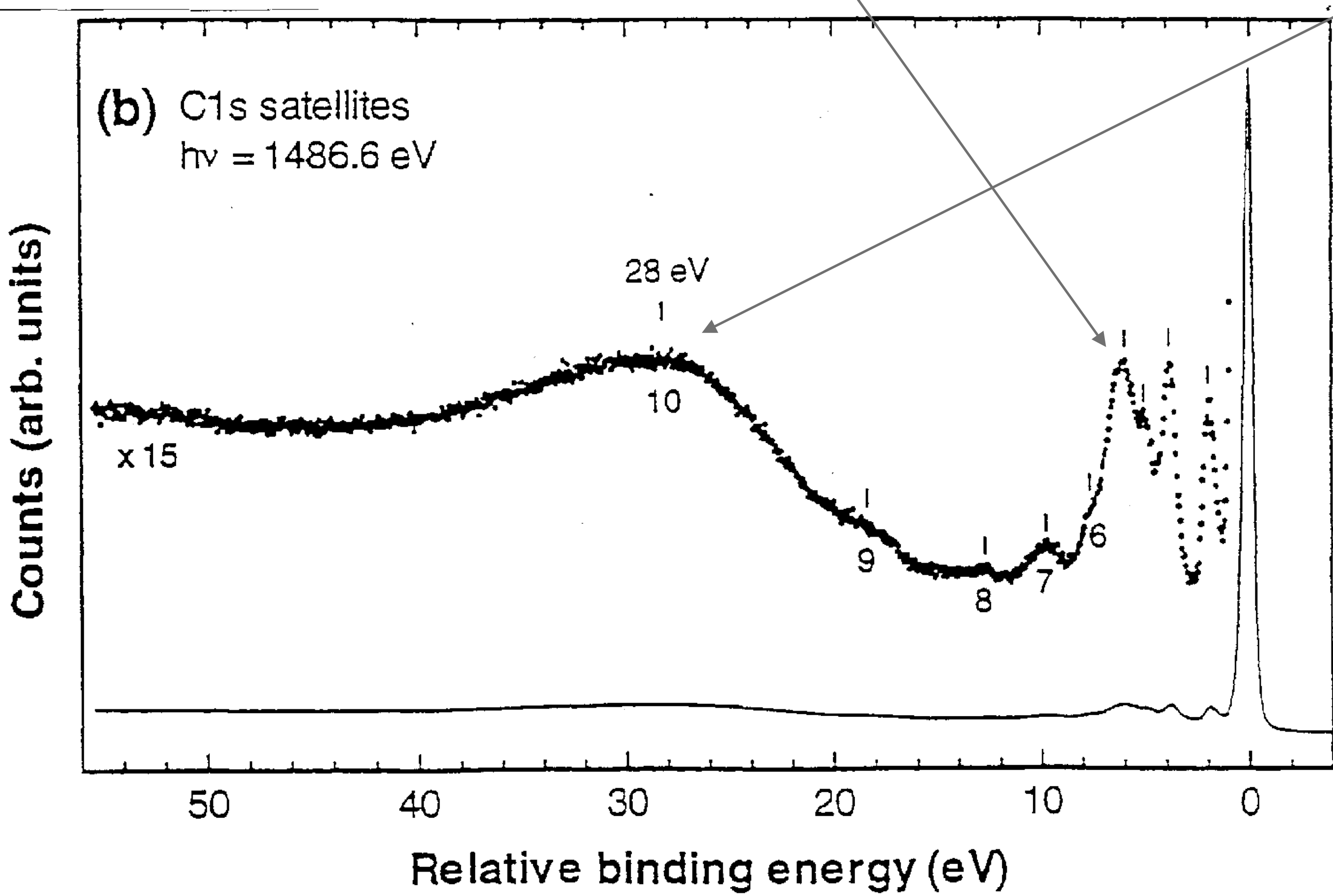


Figure 3.33 Core (4f) and valence (VB) photoelectron spectra of gold and platinum recorded using monochromatic Al Kα radiation. Note the relationship between the degree of core level asymmetry and the density of states at the Fermi level (BE = 0 eV). (After Barrie, Swift and Briggs[49])

Example: C_{60} : 3 valence electrons of carbon form s orbitals – cage structure,

1 valence electron in π orbitals.

single electron excitations; all π → π*: π plasmon; all π+ σ → π*+ σ*: σ + π plasmon



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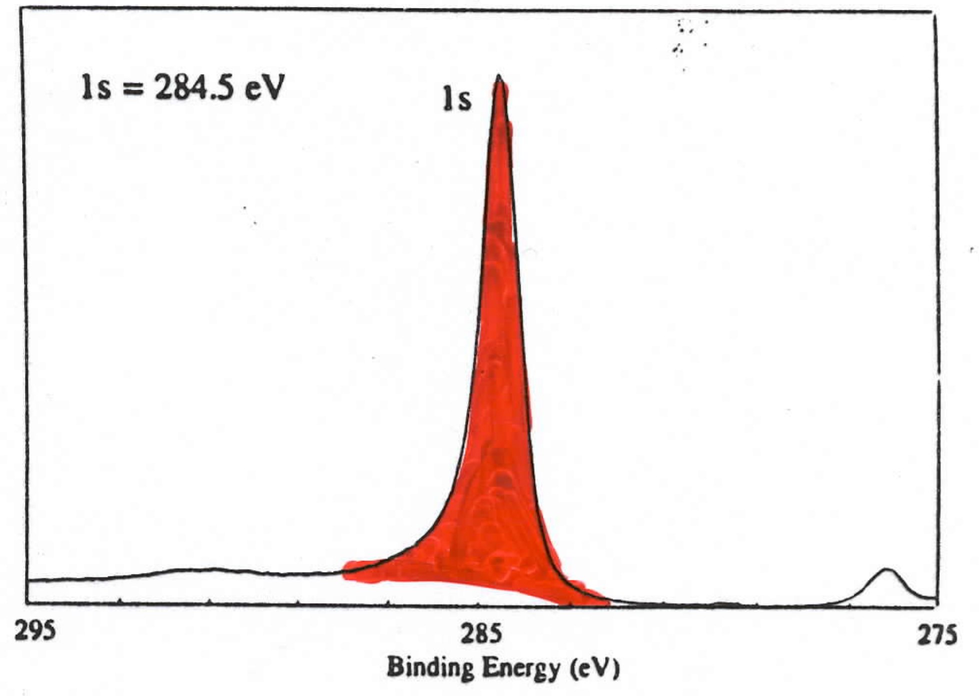
Core level XPS spectrum of graphite (C)



The singlet **C 1*s*** line is characterized by:

1) A specific binding energy which reflects the specific atomic species (C) in a specific chemical environment

2) A finite width reflecting the instrumental resolution, lifetime broadening and other many-body effects

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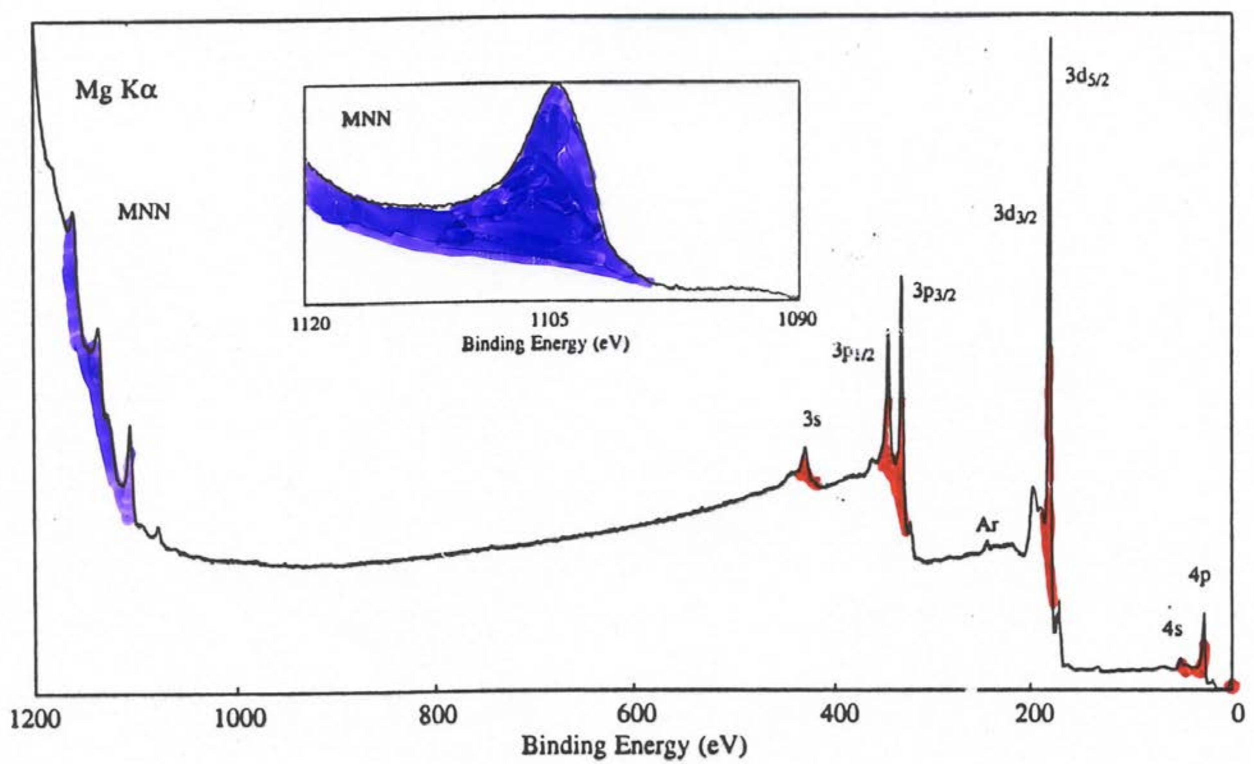
Wide XPS spectrum of zirconium (Zr)



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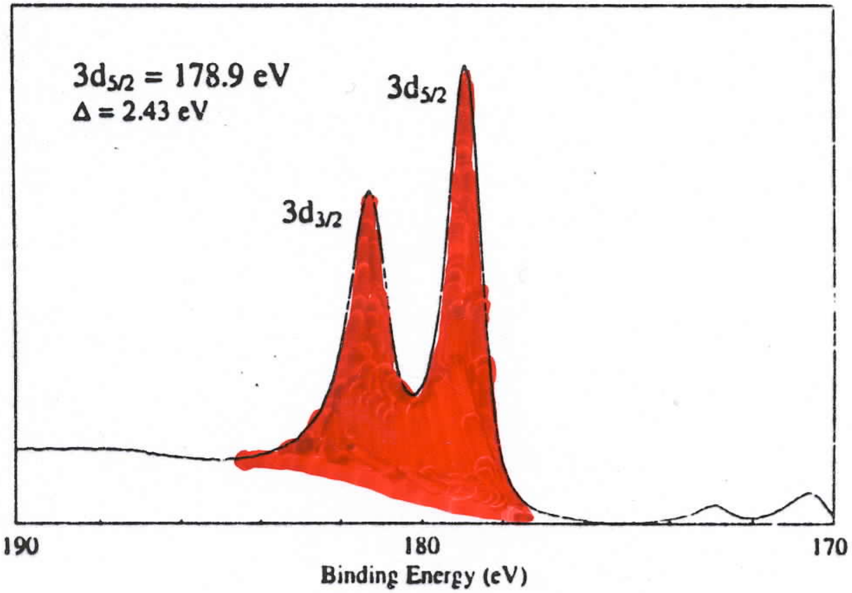
Core level XPS spectrum of zirconium (Zr)



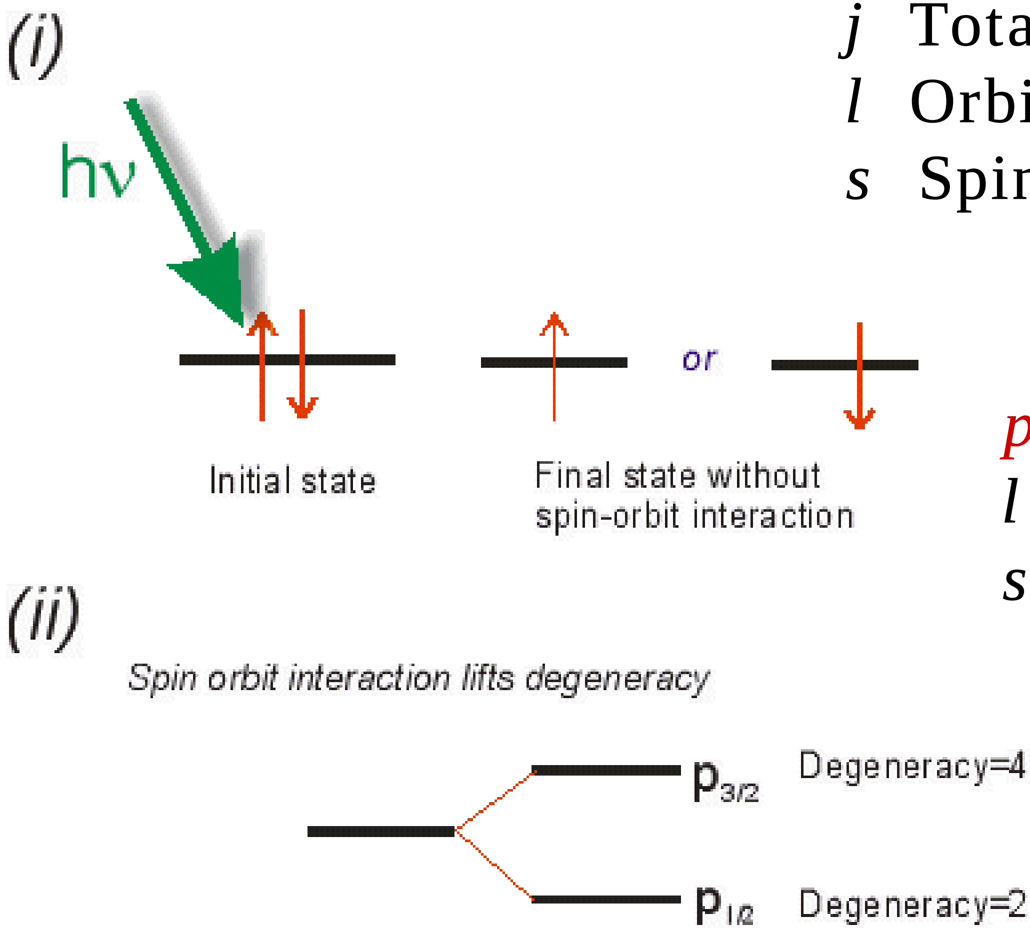
The Zr 3*d* line is characterized by:

1) A specific binding energy which reflects the specific atomic species (Zr) in a specific chemical environment

2) The occurrence of a doublet reflecting the core level spin-orbit splitting

3) A finite width reflecting the instrumental resolution, lifetime broadening and other many-body effects

Spin-Orbit Splitting



Quantum Numbers

j Total Angular Momentum

l Orbital Angular Momentum

s Spin Angular Momentum

$$j = l + s$$

p-symmetry state

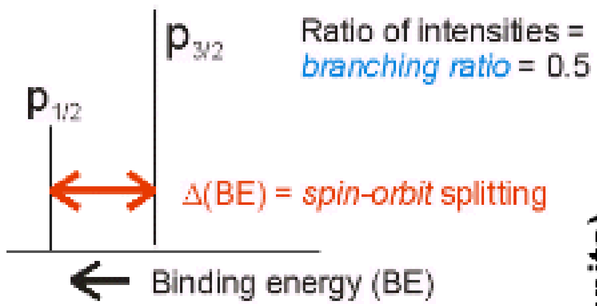
$l = 1$

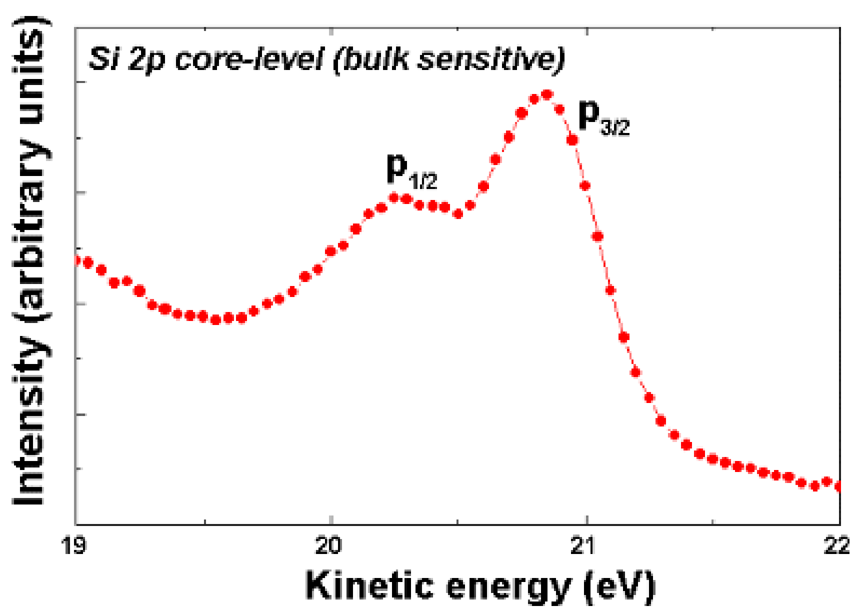
$s = \pm 1/2$

Degeneracy = $|2j+1|$

Spin-Orbit Splitting

(iii) Degeneracies determine relative intensities of peaks comprising doublet



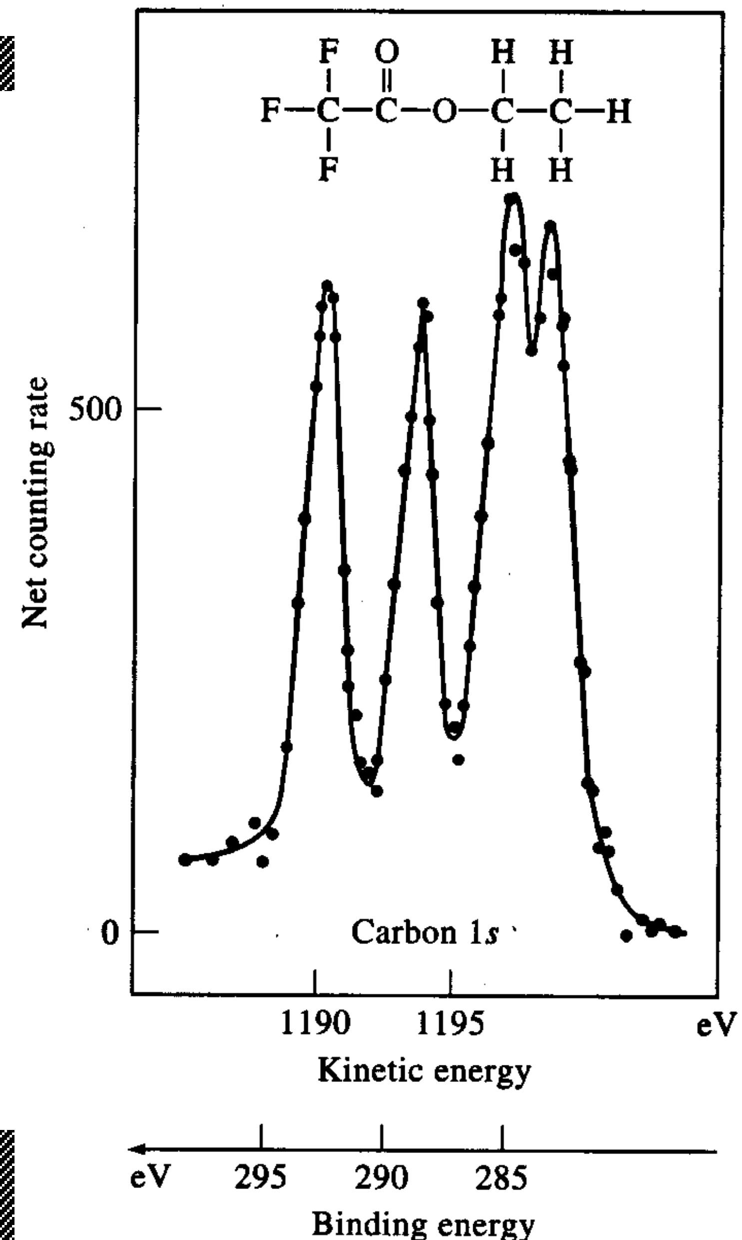


XPS : Chemical shift

Carbon 1s binding energies in ethyl trifluoroacetate

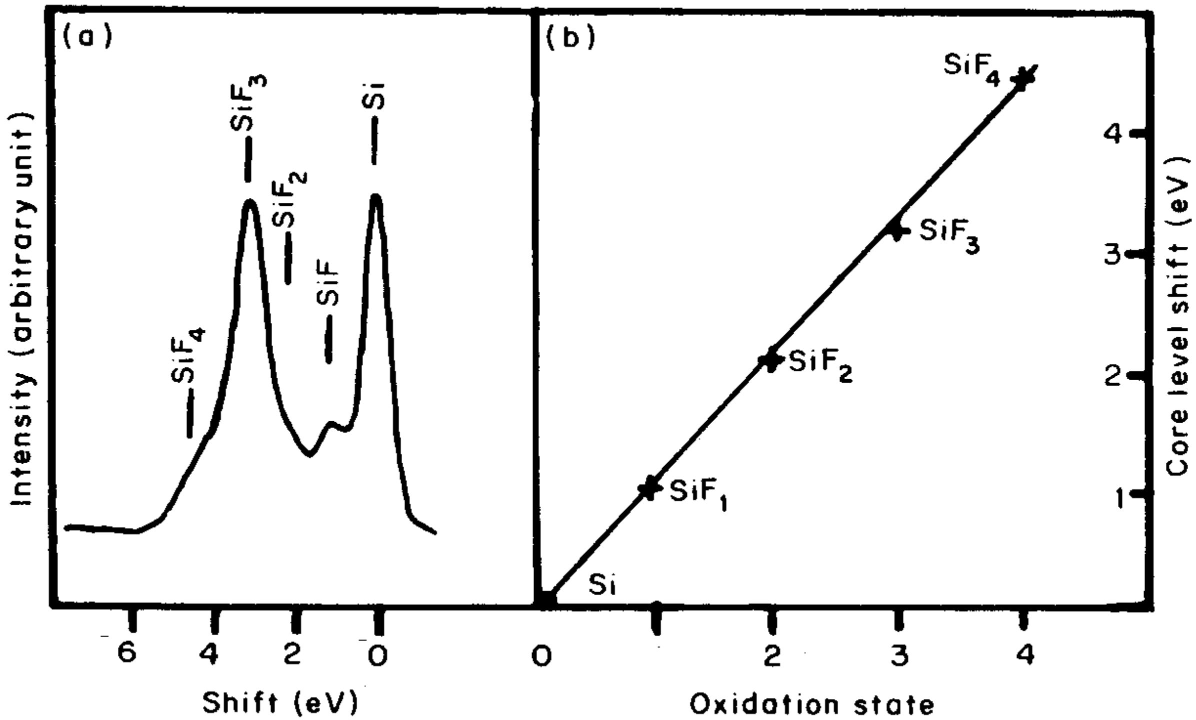
Can be used to quantify different chemical bonds for same element

XPS also called **ESCA** - **electron spectroscopy for chemical analysis**



XPS : Chemical shift

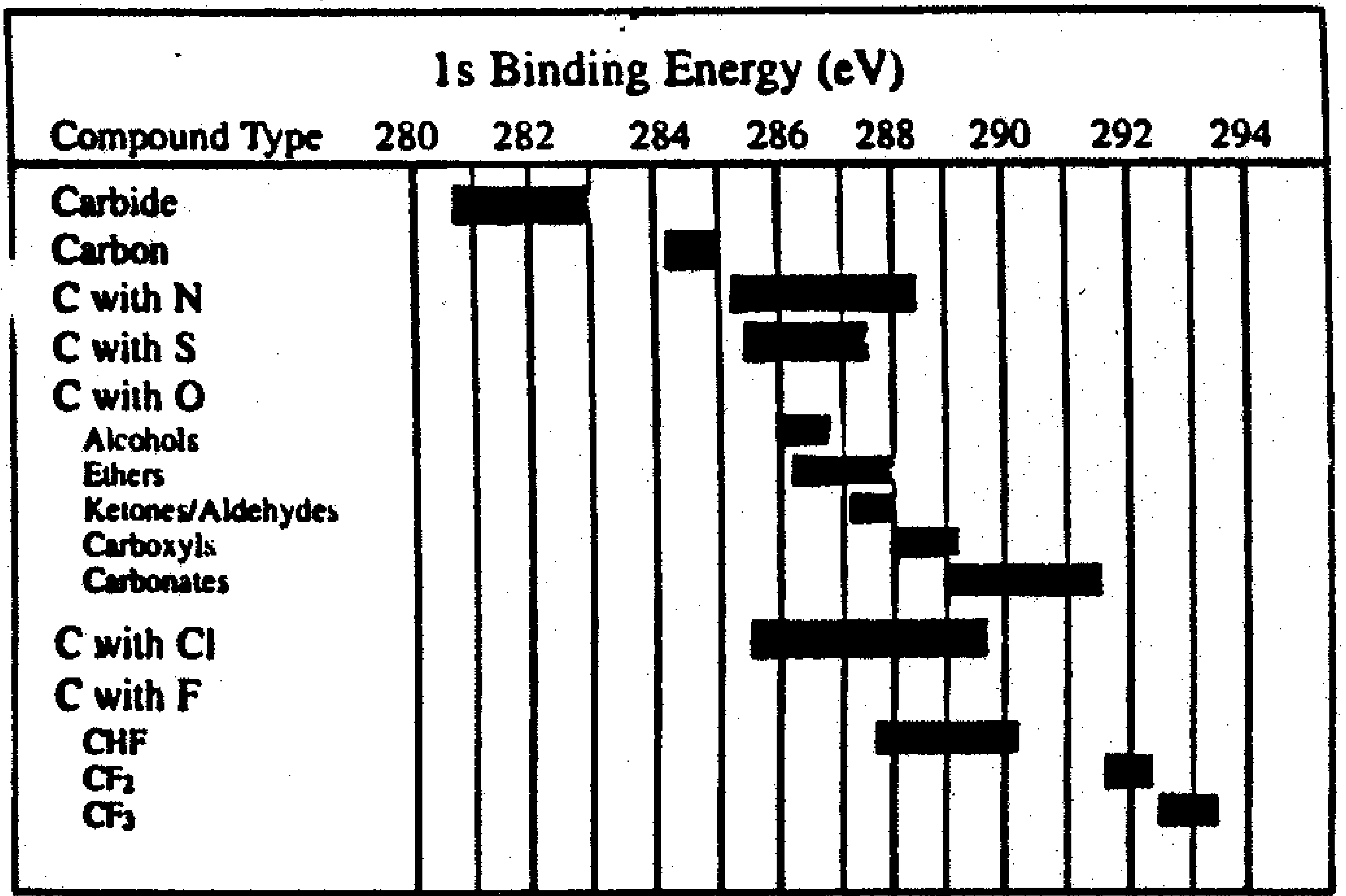
Si 2p spectra for a fluorine-etched silicon wafer



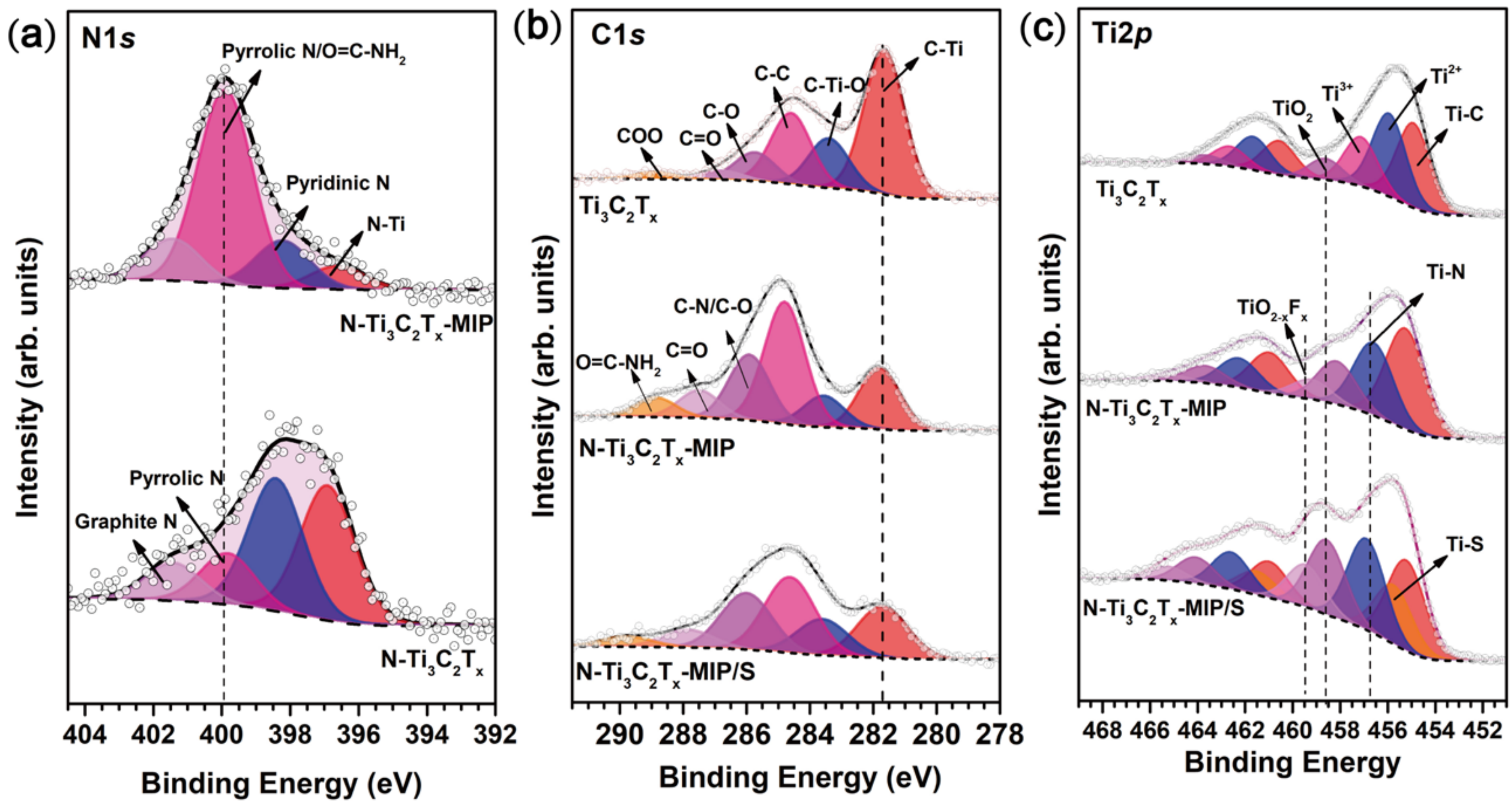
binding energies increase as the oxidation state increases - can be used to determine oxidation state

Chemical Shift (ΔE_b)

How the C 1*s* binding energy reflects differing chemical environment local to the excited C sites



Molecularly imprinted polymer (MIP) in conjunction with 2D material, MXene, developed for cathodes of Li-S batteries



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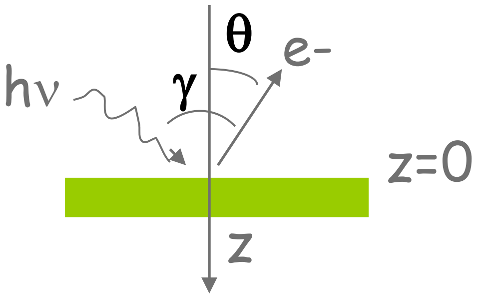

Once the photon flux Φ is given, the photoelectron intensity I_i of the (nl) orbital of the *i*-th atomic species is approximately given by

$$I_i(nl) = C_i \lambda(E_{kin}) \phi(\hbar\omega) \sigma_{nl}(\hbar\omega) T(E_{kin})$$

Where Φ is the photon flux

C_i Atomic Concentration of the *i*-th species

λ Escape Depth

σ_{nl} Orbital Cross Section

T Instrumental Efficiency

sensitivity factor $S_i = \sigma_i(h\nu)\ T\ (E_{kin})$

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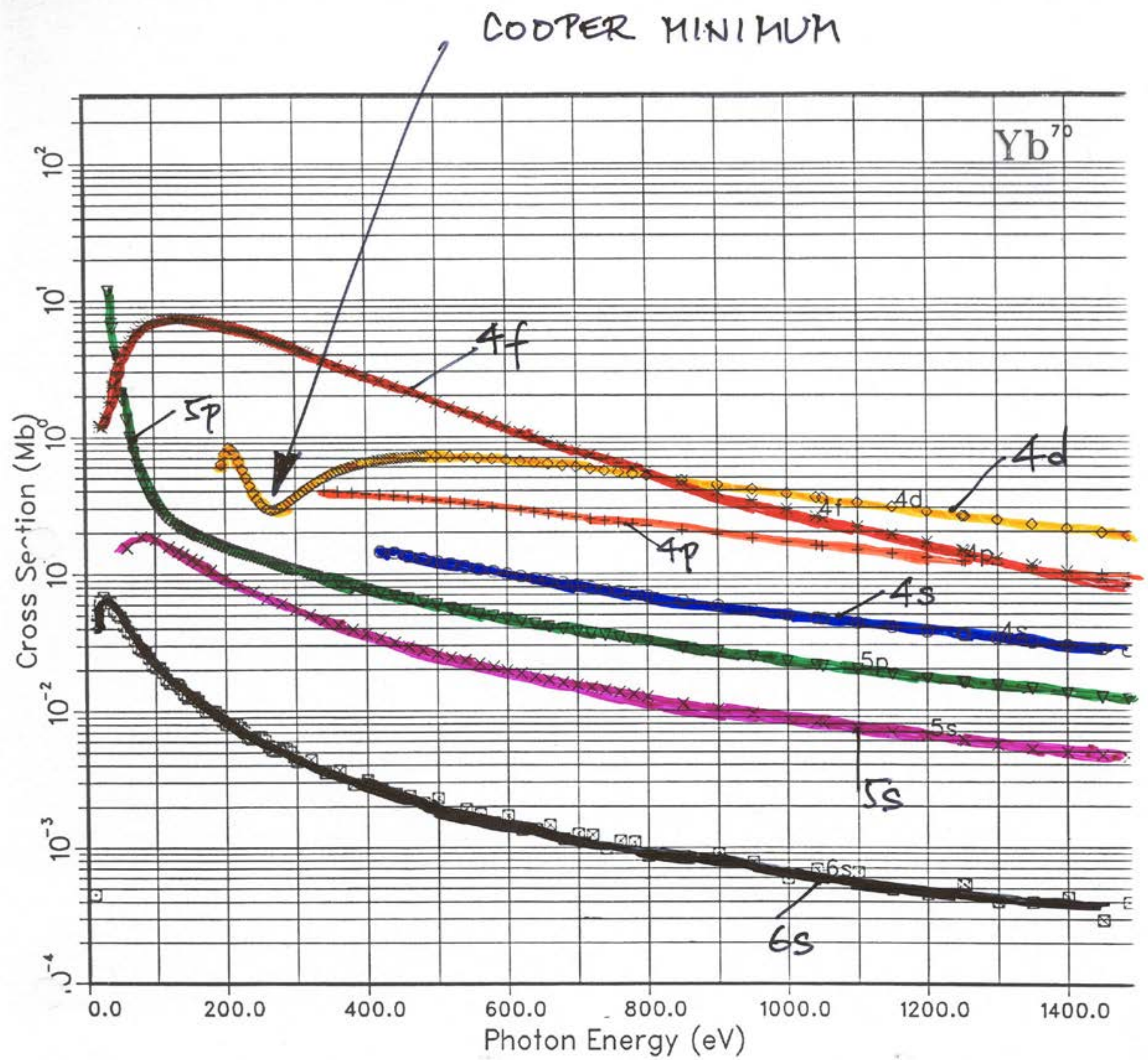

Yb binding energies(eV) are:

1s(2) 57009.8	2s(2) 9290.78	2p(6) 8897.20
3s(2) 2086.76	3p(6) 1904.14	4s(2) 402.610
3d(10) 1561.01	4p(6) 327.461	5s(2) 50.8637
4d(10) 190.652	5p(6) 30.7582	6s(2) 5.16038
4f(14) 15.9818		

Calculated photoionization cross sections for free atoms vs. photon energy (Yeh and Lindau)

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Appendix E. Atomic Sensitivity Factors for X-ray Sources at 90°

This table is based upon empirical peak area values corrected for the system's transmission function. The values are only valid for and should only be applied when the electron energy analyzer used has the transmission characteristics of the spherical capacitor type analyzer equipped with an Omni Focus III lens supplied by Perkin-Elmer. The data are calculated for x-rays at 90° relative to the analyzer.*

Element	Line	ASF
Ag	3d	5.198
Al	2p	0.193
Ar	2p	1.011
As	3d	0.570
Au	4f	5.240
B	1s	0.159
Ba	4d	2.627
Be	1s	0.074
Bi	4f	7.632
Br	3d	0.895
C	1s	0.296
Ca	2p	1.634
Cd	$3d_{5/2}$	3.444
Ce	3d	7.399
Cl	2p	0.770
Co	2p	3.255
Cr	2p	2.201
Cs	$3d_{5/2}$	6.032
Cu	2p	4.798
Dy	4d	2.198
Er	4d	2.184
Eu	4d	2.210
F	1s	1.000
Fe	2p	2.686
Ga	$2p_{3/2}$	3.341
Gd	4d	2.207
Ge	$2p_{3/2}$	3.100
Hf	4f	2.221
Hg	4f	5.797
Ho	4d	2.189
I	$3d_{5/2}$	5.337
In	$3d_{5/2}$	3.777
Ir	4f	4.217
K	2p	1.300
Kr	3d	1.096
La	3d	7.708
Li	1s	0.025
Lu	4d	2.156
Mg	2s	0.252
Mn	2p	2.420
Mo	3d	2.867
N	1s	0.477
Na	1s	1.685
Nb	3d	2.517
Nd	3d	4.697
Ne	1s	1.340
Ni	2p	3.653
O	1s	0.711
Os	4f	3.747
P	2p	0.412
Pb	4f	6.968
Pd	3d	4.642
Pm	3d	3.754
Pr	3d	6.356
Pt	4f	4.674
Rb	3d	1.316
Re	4f	3.327
Rh	3d	4.179
Ru	3d	3.696
S	2p	0.570
Sb	$3d_{5/2}$	4.473
Sc	2p	1.678
Se	3d	0.722
Si	2p	0.283
Sm	$3d_{5/2}$	2.907
Sn	$3d_{5/2}$	4.095
Sr	3d	1.578
Ta	4f	2.589
Tb	4d	2.201
Tc	3d	3.266
Te	$3d_{5/2}$	4.925
Th	$4f_{7/2}$	7.498
Ti	2p	1.798
Tl	4f	6.447
Tm	4d	2.172
U	$4f_{7/2}$	8.476
V	2p	1.912
W	4f	2.959
Xe	$3d_{5/2}$	5.702
Y	3d	1.867
Yb	4d	2.169
Zn	$2p_{3/2}$	3.354
Zr	3d	2.216

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

Provided by the maker of the spectrometer

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$$I_i(nl) = C_i \lambda(E_{kin}) \phi(\hbar\omega) \sigma_{nl}(\hbar\omega) T(E_{kin})$$

Once the efficiency of detection of an atomic species is calibrated via the sensitivity factors one gets

Homogeneous binary compound :

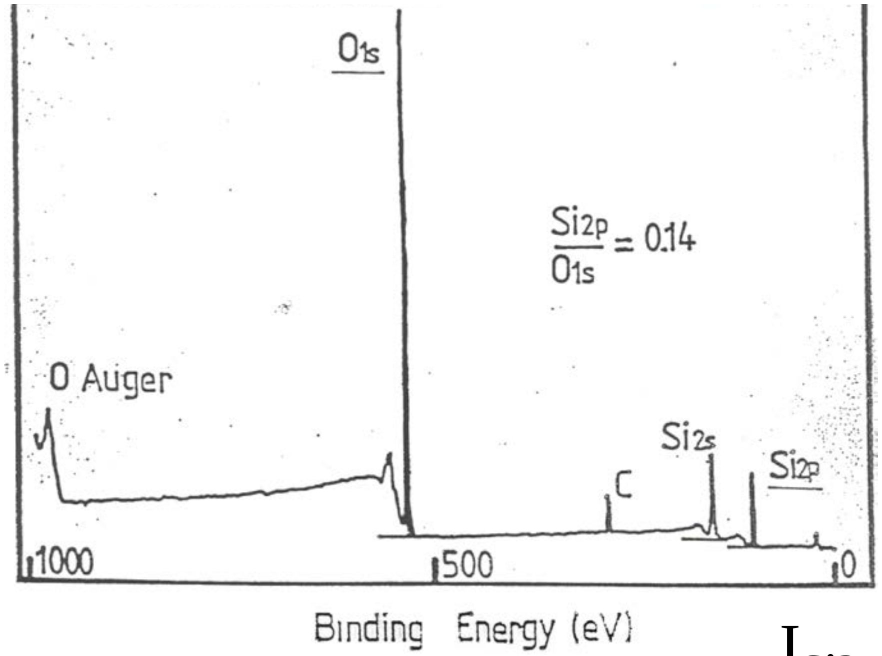
$$\frac{I_A}{I_B} = \frac{S_A N_A \lambda(E_A)}{S_B N_B \lambda(E_B)}$$

Sample with many components :

Atomic concentration C_A for each element can be determined

$$C_A = \frac{N_A}{\Sigma_i N_i} = \frac{I_A/[S_A \lambda(E_A)]}{\Sigma_i I_i/[S_i \lambda(E_i)]}$$

Example: stoichiometry of SiO_2 surface



$$\frac{I_{Si2p}}{I_{O1s}} = \frac{S_{Si2p}\, N_{Si}\, \lambda(Si2p)}{S_{01s}\, N_{O}\, \lambda(O1s)} = 0,14$$

$$\frac{S_{O1s}}{S_{Si2p}} = 5,2 \qquad \frac{\lambda(O1s)}{\lambda(Si2p)} = 0,76$$

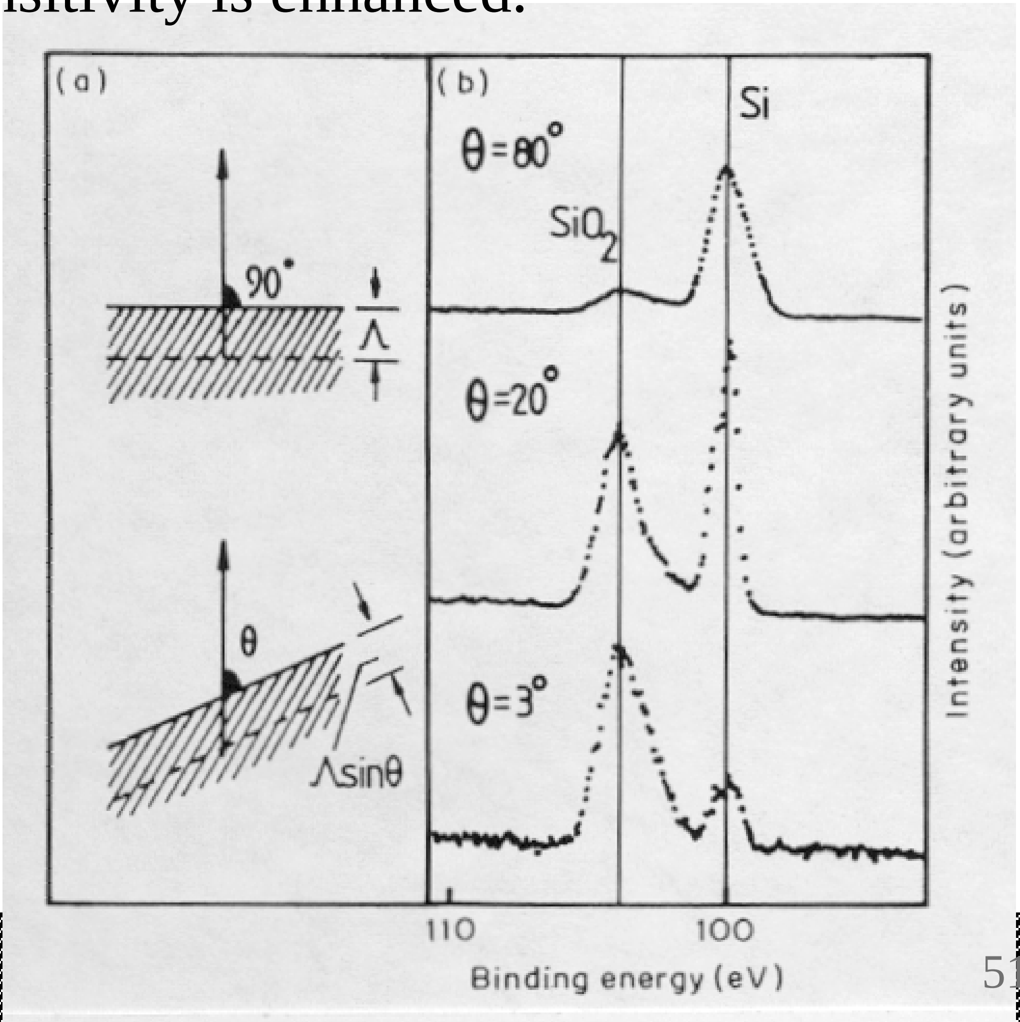
[Si]/[O] = 0,14x5.2x0,76 = 0,55

XPS : depth profiling via angular dependence

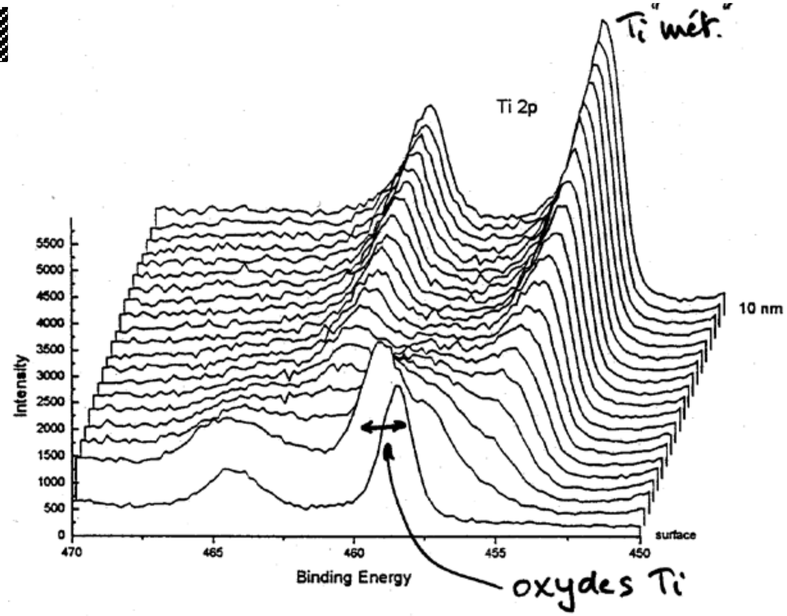
By changing experimental geometry from normal emission to grazing emission surface sensitivity is enhanced.

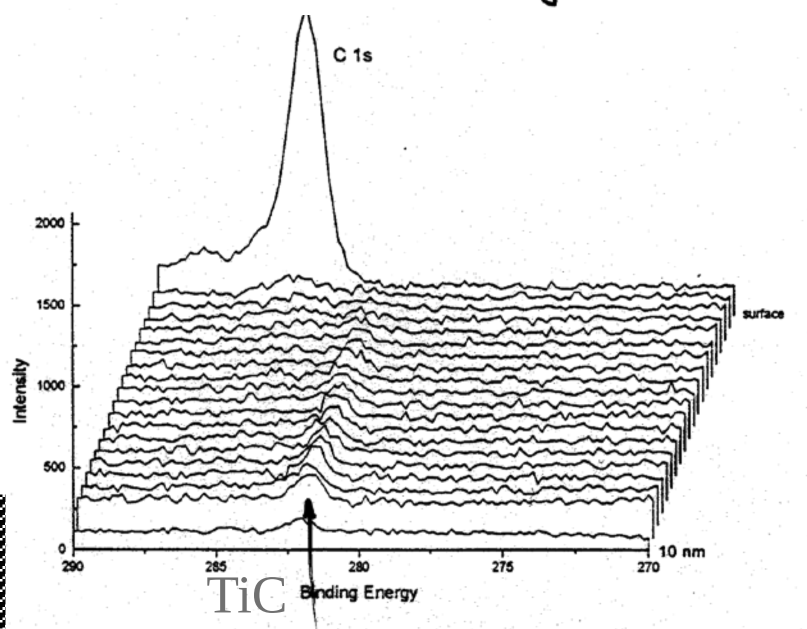
Example:

oxidised Si substrate



XPS : depth profiling via sputtering and measuring cycles - Destructive!





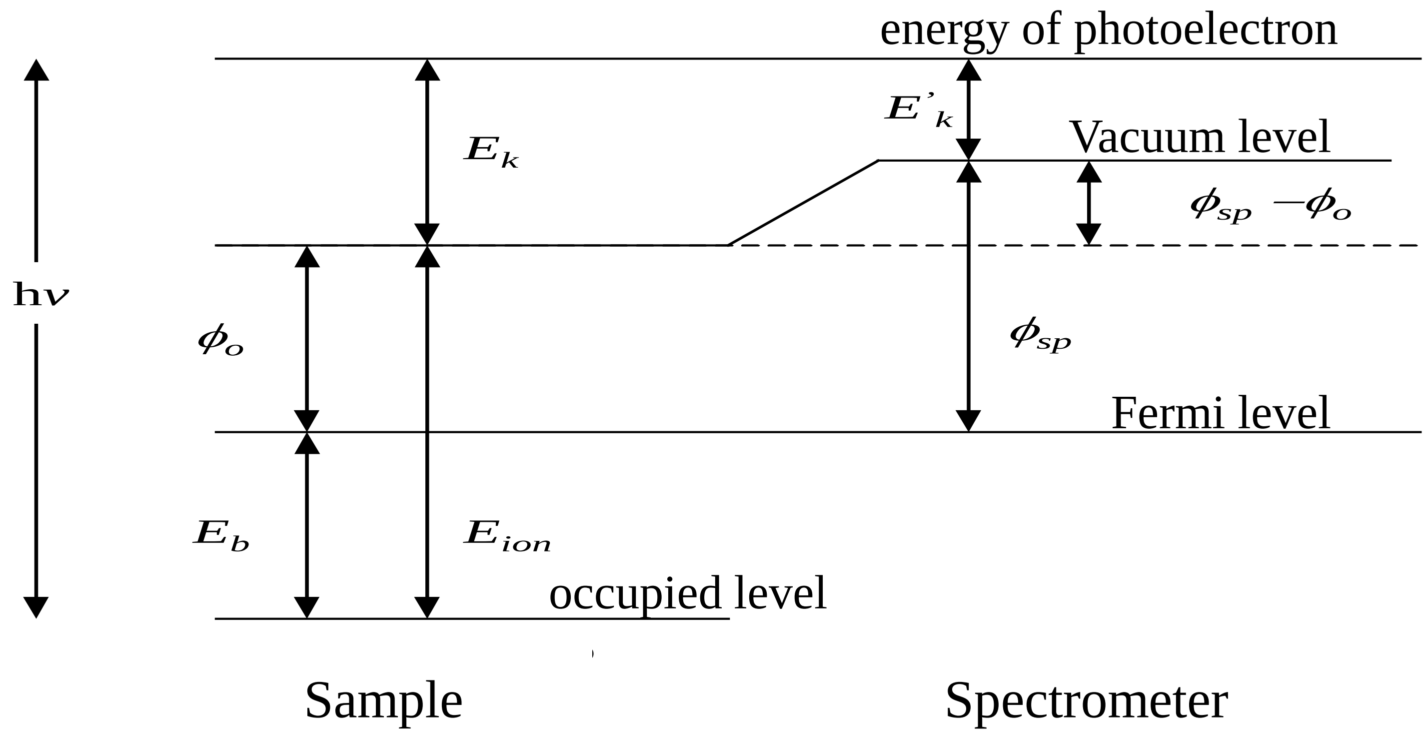
- ion sputtering - removes surface layers
- depth calibrated with reference sample

Ti 2p region

C 1s region

Example: Dental implants, surface oxidized to create porous layer which favours bone adhesion. Can determine thickness of oxide layer; can show hydrocarbon contamination at surface and carbide contamination in bulk

What is the binding energy in XPS ?



$$h\nu = E_b + E_k + \phi_0$$

$$E_b = E_f - E_i = h\nu - E'_k + \phi_{sp}$$

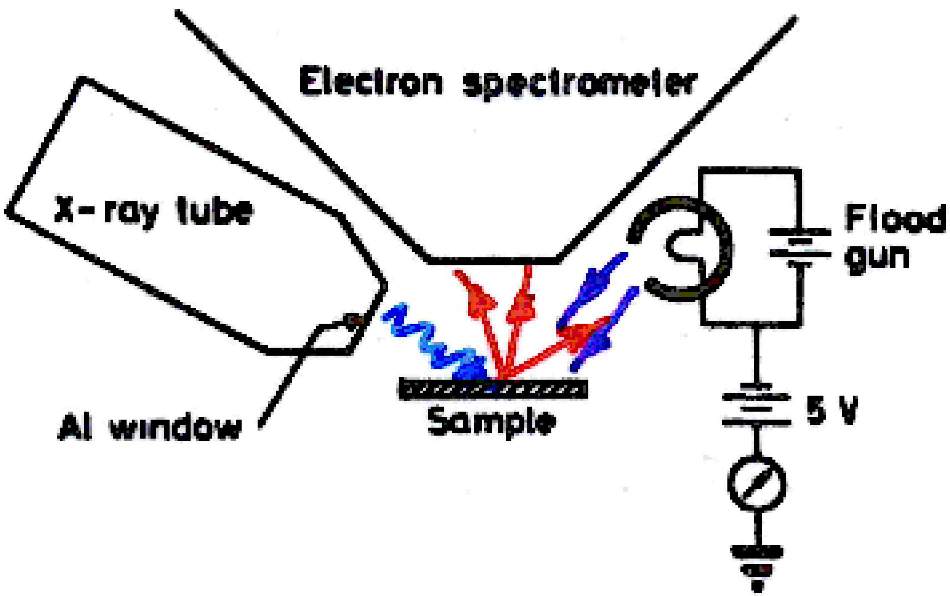
Energy reference

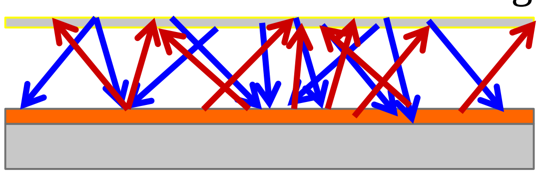
conducting samples : Fermi level

- non-conducting samples : Vacuum level

- insulating samples ⇒ charge effect
- $E_b = h\nu + E'_k - \phi_{sp} + \Delta E$

sample has to be flooded with low energy electrons.



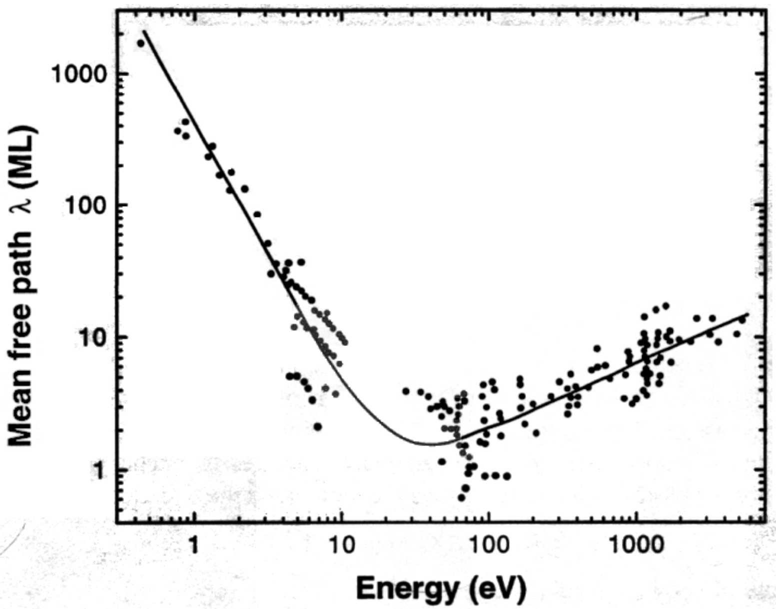


Photoelectrons generate secondary electrons which compensate charge

Some applications

- quantify surface stoichiometry
- verify valence state of metal of nanoparticles
- verify core/shell structure
- determine growth mode of thin film
- verify in-situ ion transport (battery)

High kinetic energy XPS



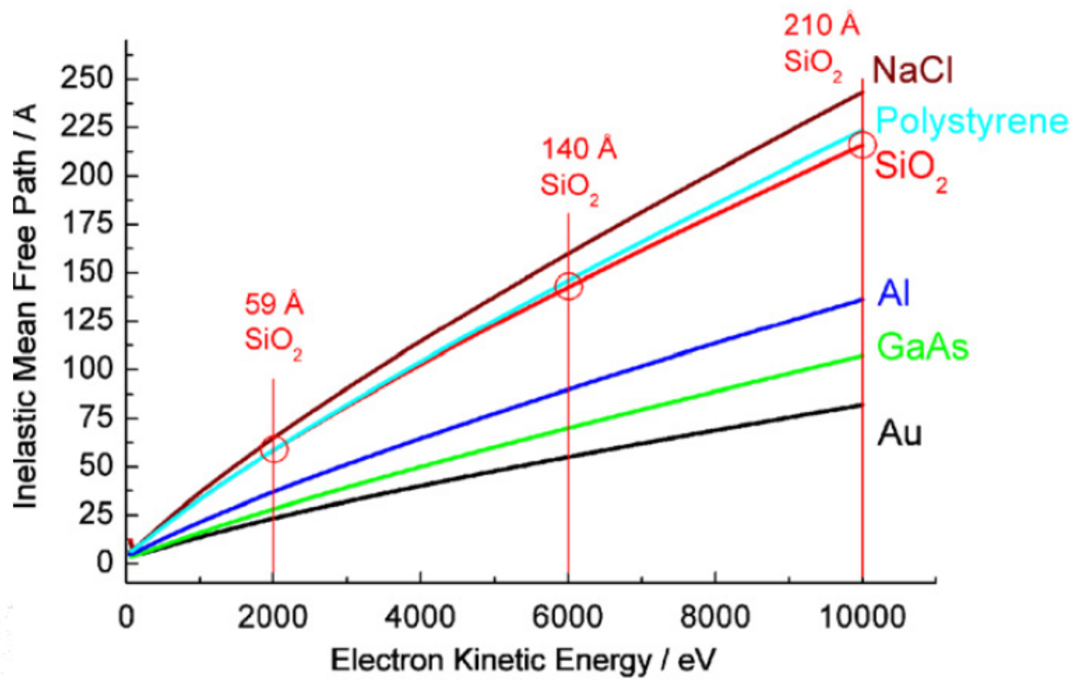


Fig. 1. Inelastic mean free path as function of electron kinetic energy for selected materials. Calculation using the NIST electron inelastic mean-free-path database, version 1.1 [3]. The HIKE facility operates between 2 and 10 keV.

M. Gorgoi et al. / Nuclear Instruments and Methods in Physics Research A 601 (2009) 48–53

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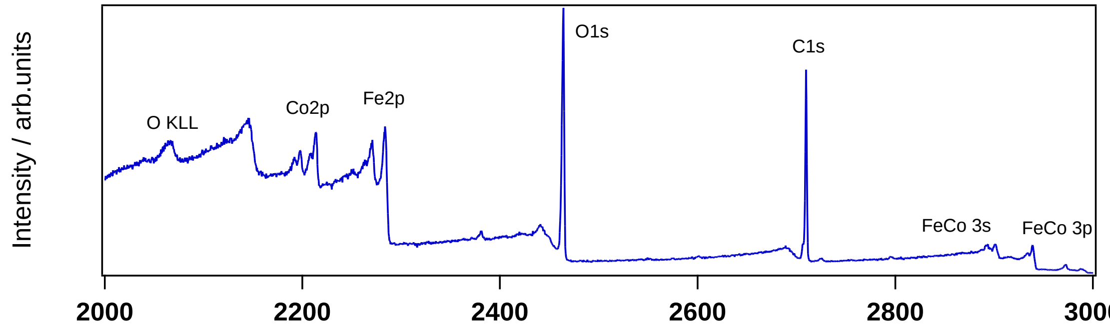
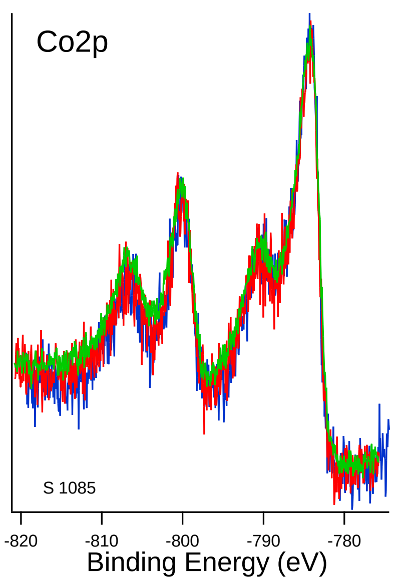
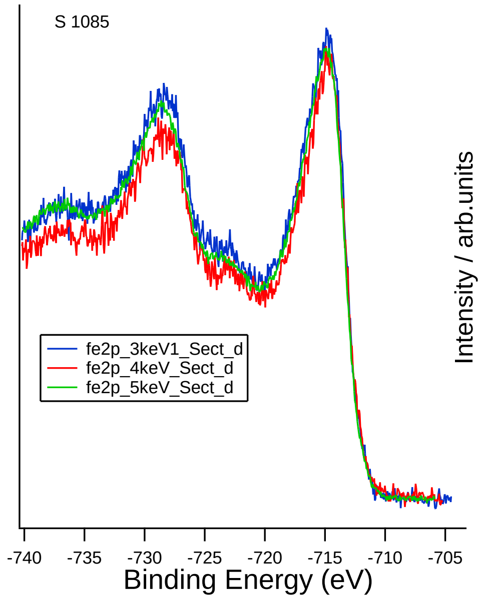
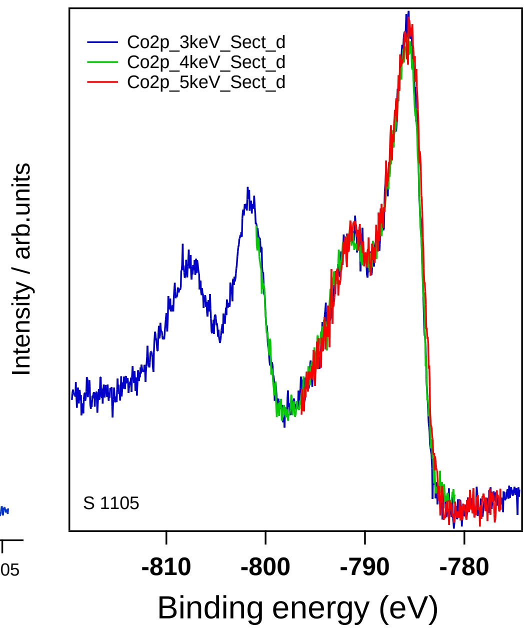
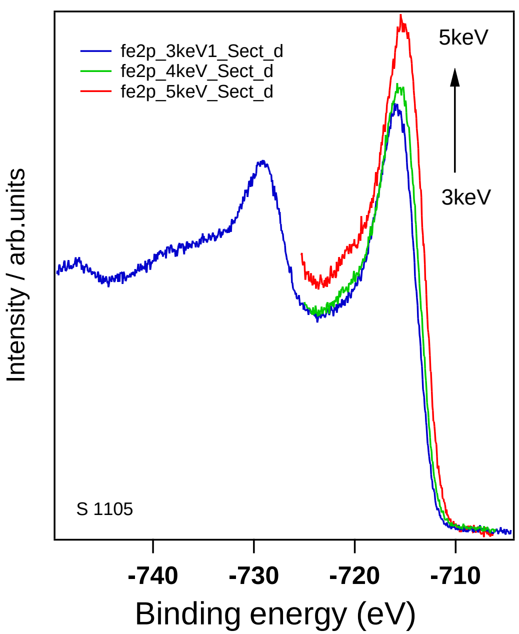
FeCoO/FeO shell-core nanoparticles









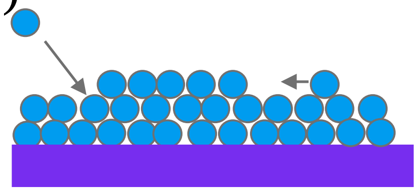


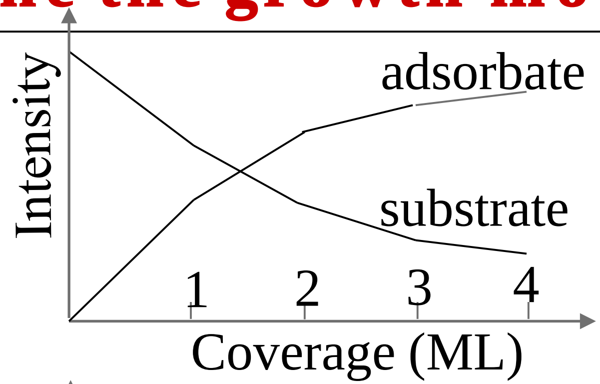
Sample A: No shell-core structure

Sample B: shows the expected shell-core structure. Co2+ and Fe 2+ /3+ are present in the shell and a supposed Fe3+ phase emerge when probing deeper

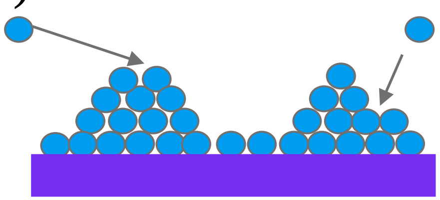
With XPS we can determine the growth mode of a film

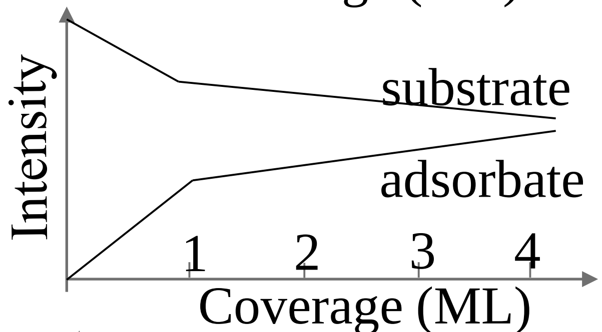
Layer by layer growth (Franck-van der Merwe)



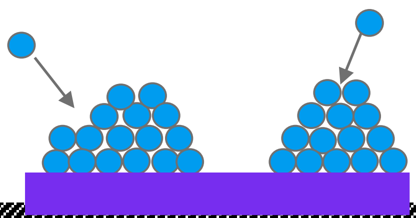


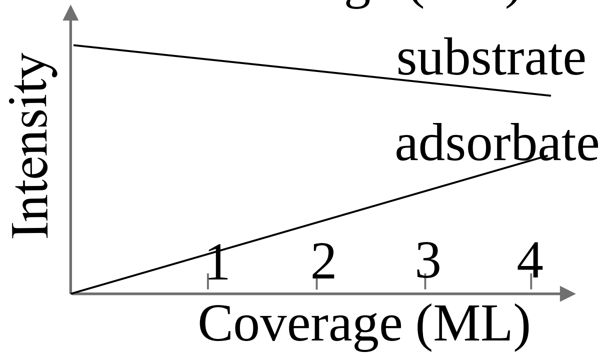
Layer plus island growth (Stransky Krastanov)





Island growth (Vollmer-Weber)





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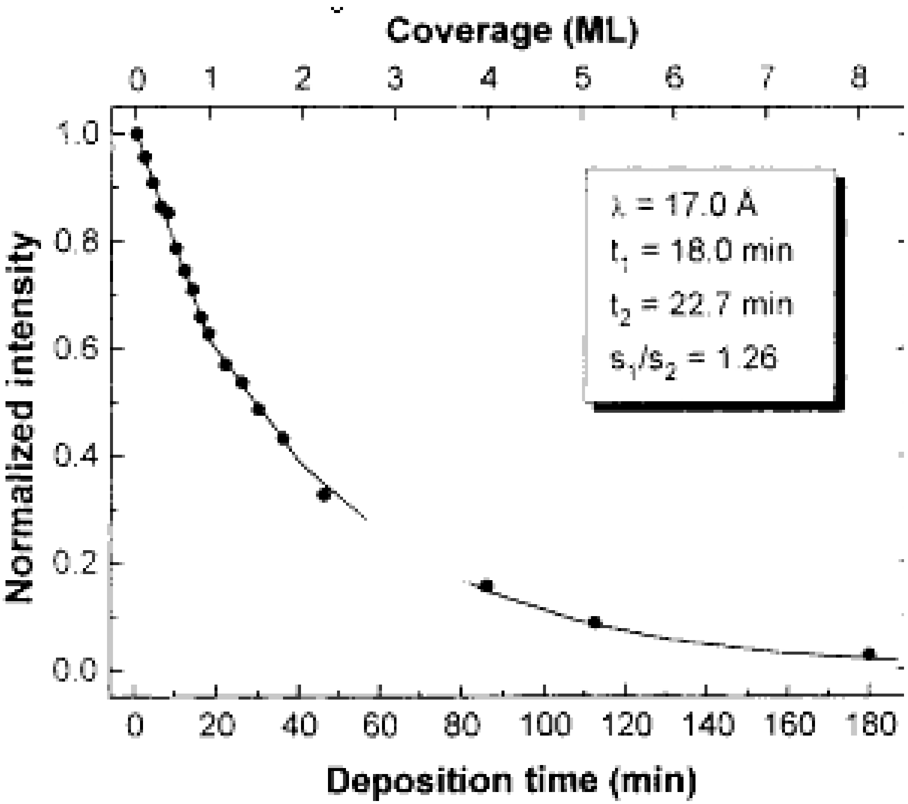
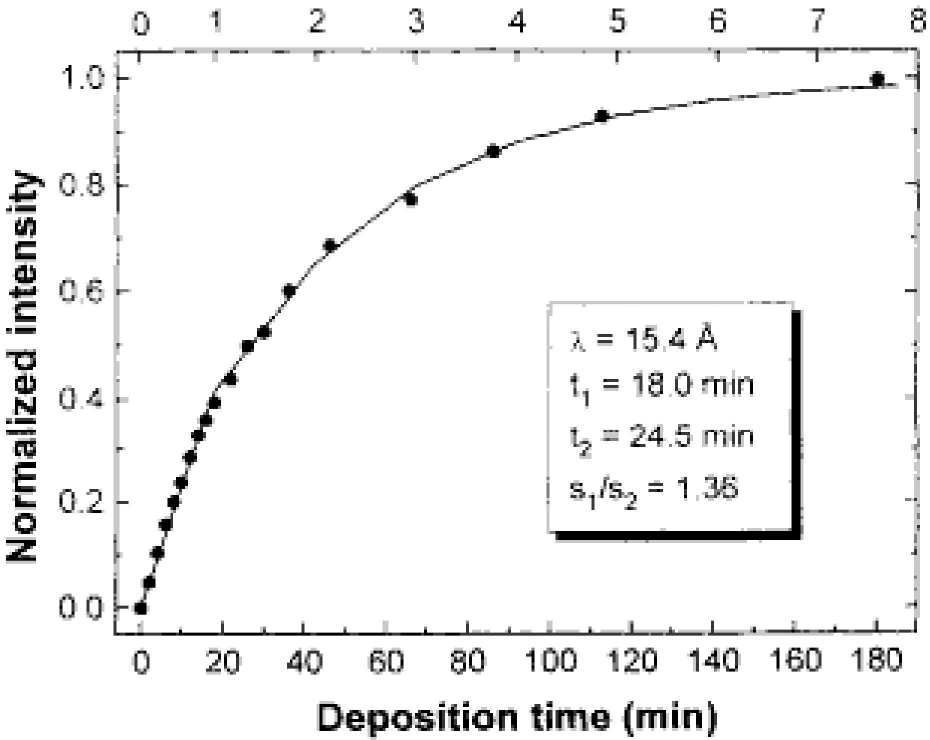
Film growth mode seen in photoemission: C_{60}(111)/GeS(001)





G. Gensterblum et al.,
PRB50 (‘ 94) 11981

Operando XPS of solid electrolyte interphase formation and evolution in Li_2S-P_2S_5 solid-state electrolytes

K.N. Wood *et al.* Nature Commun. (2018) 9, 2490

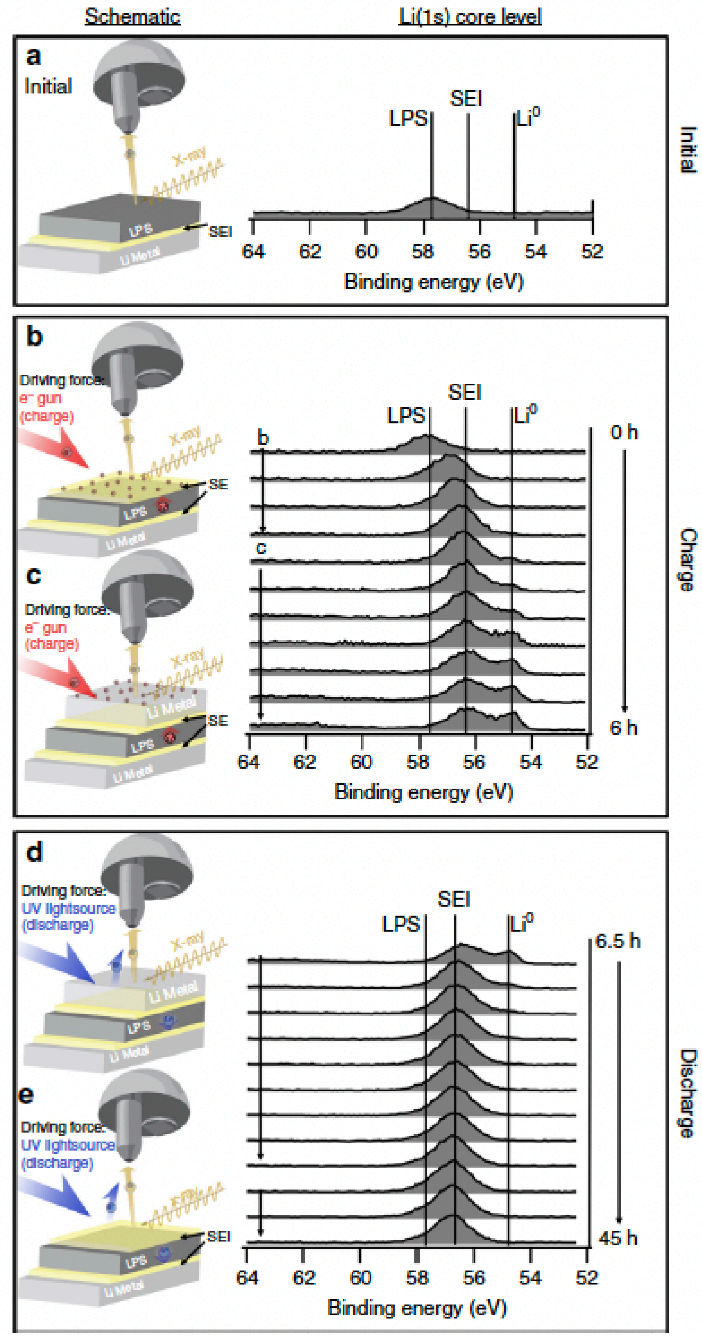


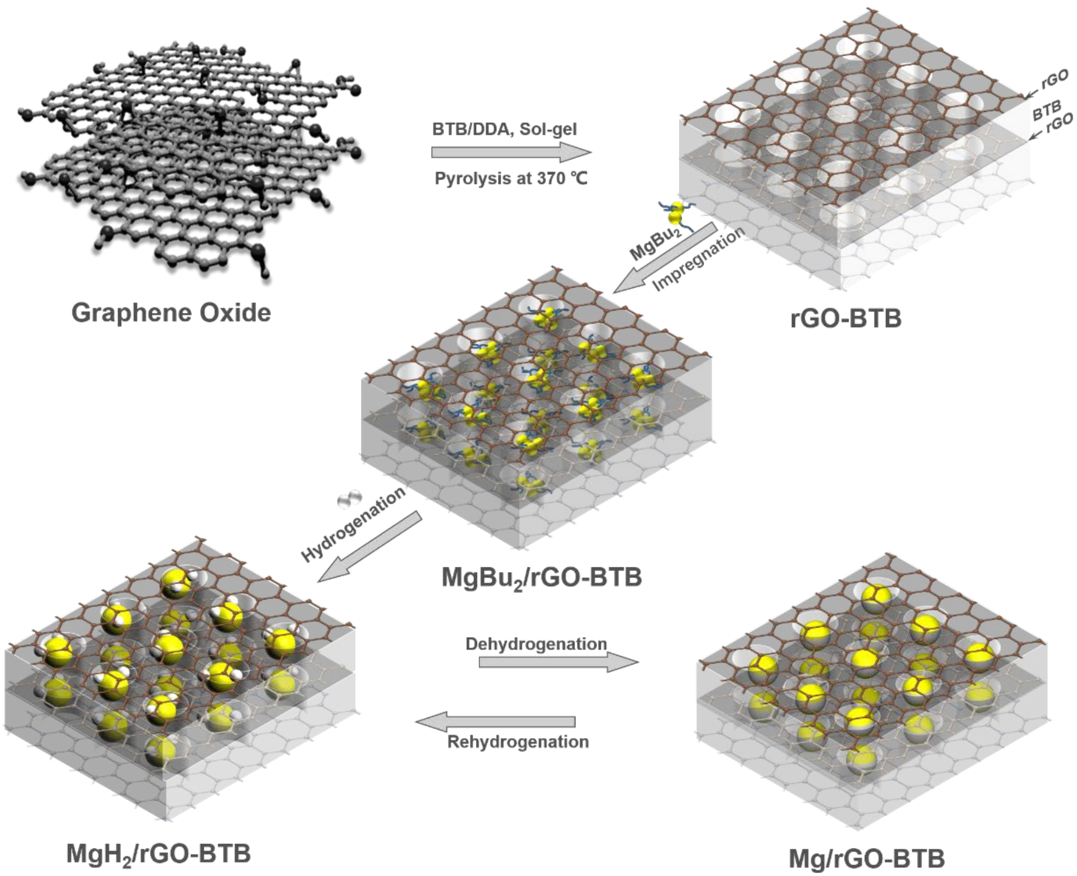
Fig. 2 opXPS schematic and Li 1s core level evolution. **a** Clean LPS surface, **b**, **c** SEI formation during charging, and **d**, **e** SEI evolution during discharging

MgH_2 nanoparticles confined in reduced graphene oxide pillared with organosilica: a novel type of hydrogen storage material

1, 4-bis(triethoxysilyl)benzene (BTB) – pillars to distance GO planes

di-n-butylmagnesium ($MgBu_2$)

$MgBu_2 + H_2 \rightarrow MgH_2 + 2C_4H_{10}\uparrow$



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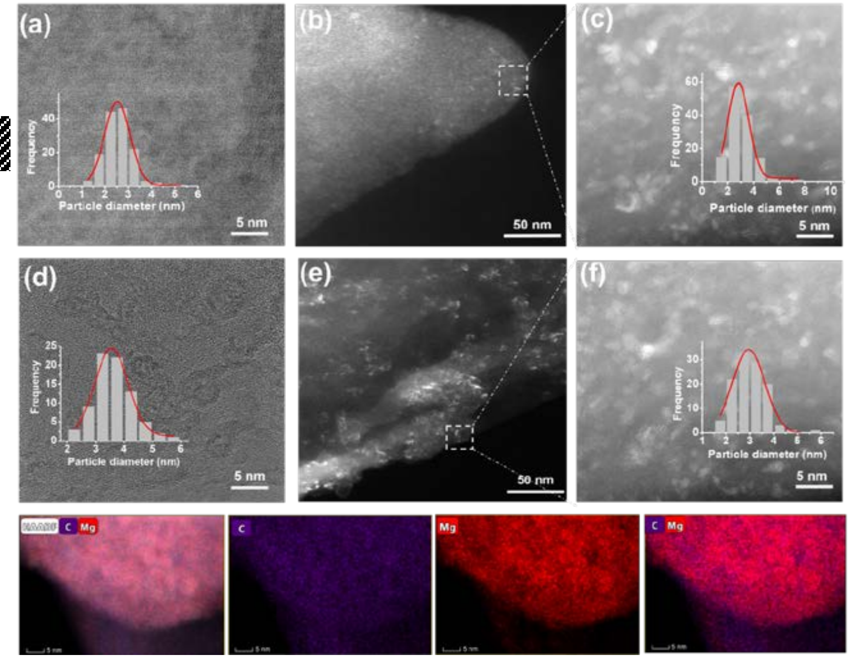
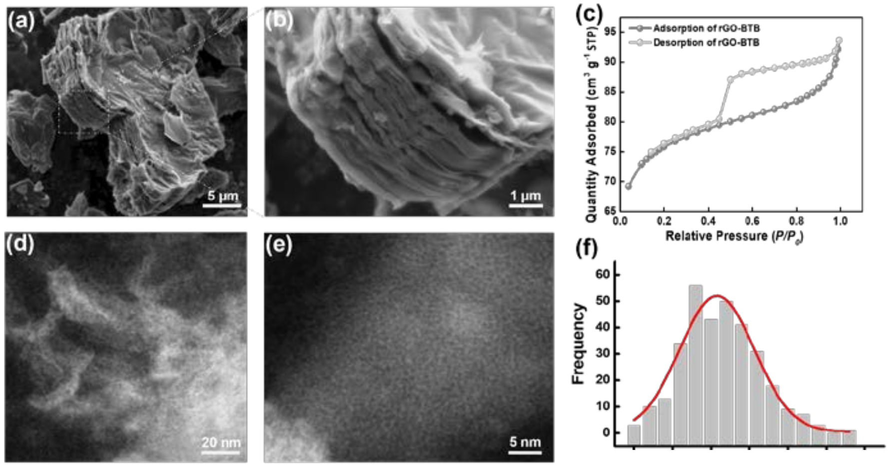
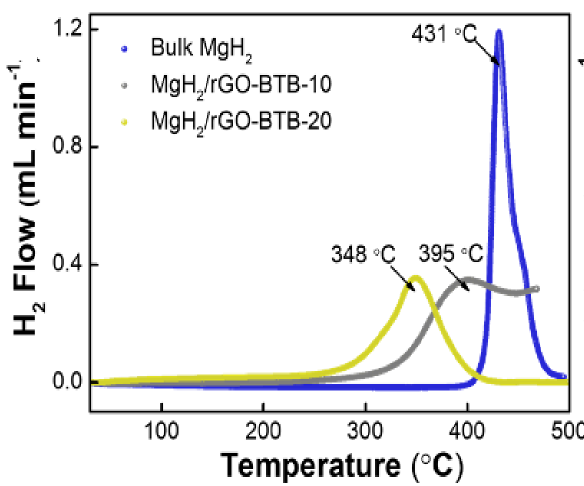
MgH_2/rGO-BTB-10

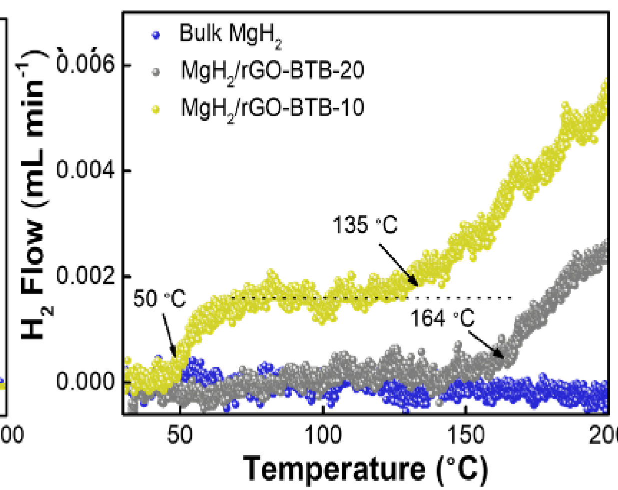


rGO-BTB-10

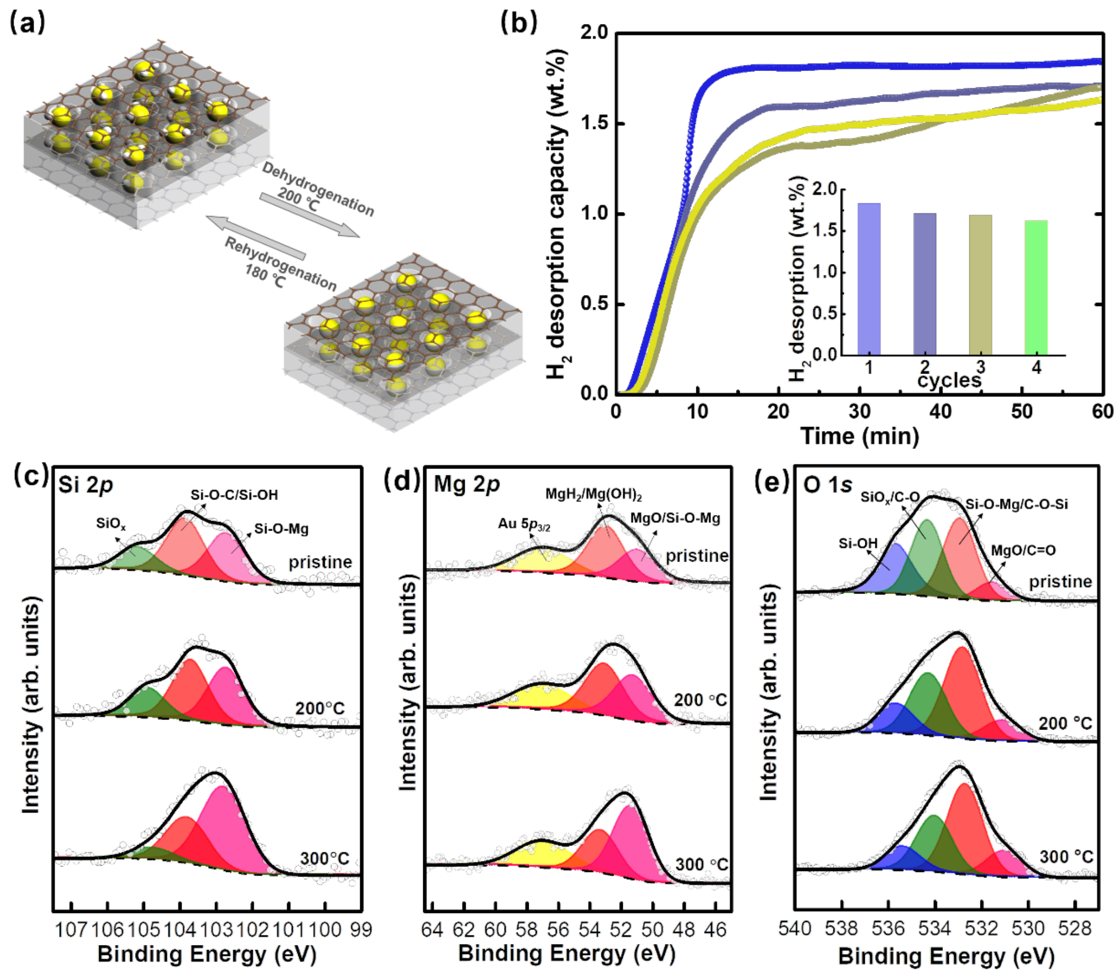


Hydrogen desorption starts at 50 °C ! efficient reversible 1.62 wt.% hydrogen storage can be realized at 200 °C





Above 200 °C Mg reacts with silanol groups



XPS summary

- all kinds of samples: solid, liquid, gases in vacuum (10^{-8} torr)
- both insulating and conducting samples
- can detect most elements at the 0.1% level (not H, He)
- non-destructive (X-ray beam damage possible)
- surface sensitive
- quantitative analysis possible
- determination of oxidation state possible
- depth profiling : through angular dependence (non-destructive) or sputtering-measuring cycles (destructive)

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Thank you for your attention!

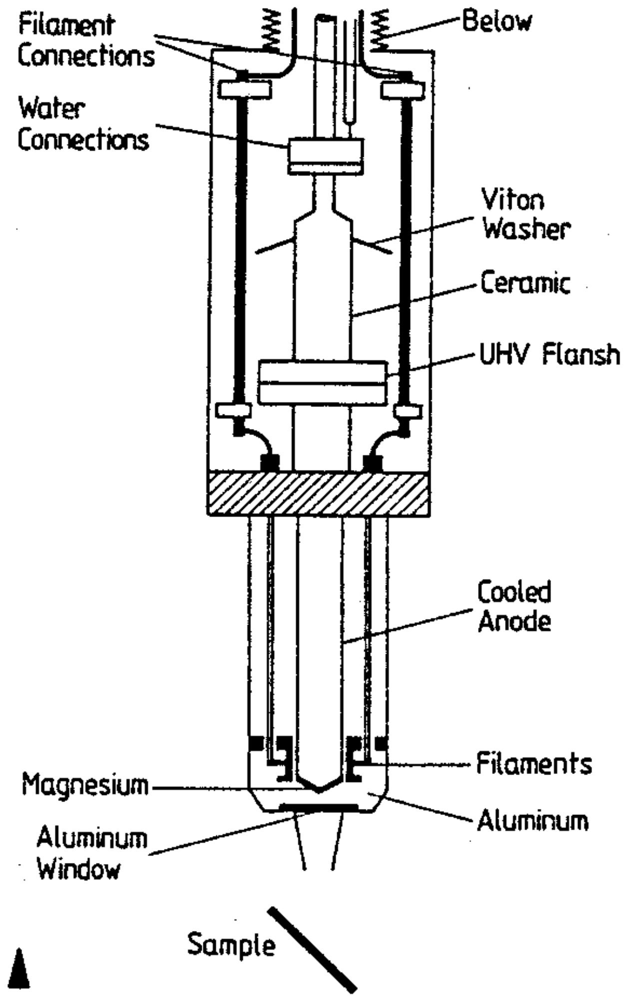
Experimental details

X-ray Sources :

• Monochromatic laboratory sources

Mg K_α 1253,6 eV or Al K_α 1486,6 eV

• synchrotron radiation ⇒ photon energy can be chosen between 200 and 1500 eV



A standard **X-Ray source** – has to be coupled to monochromator

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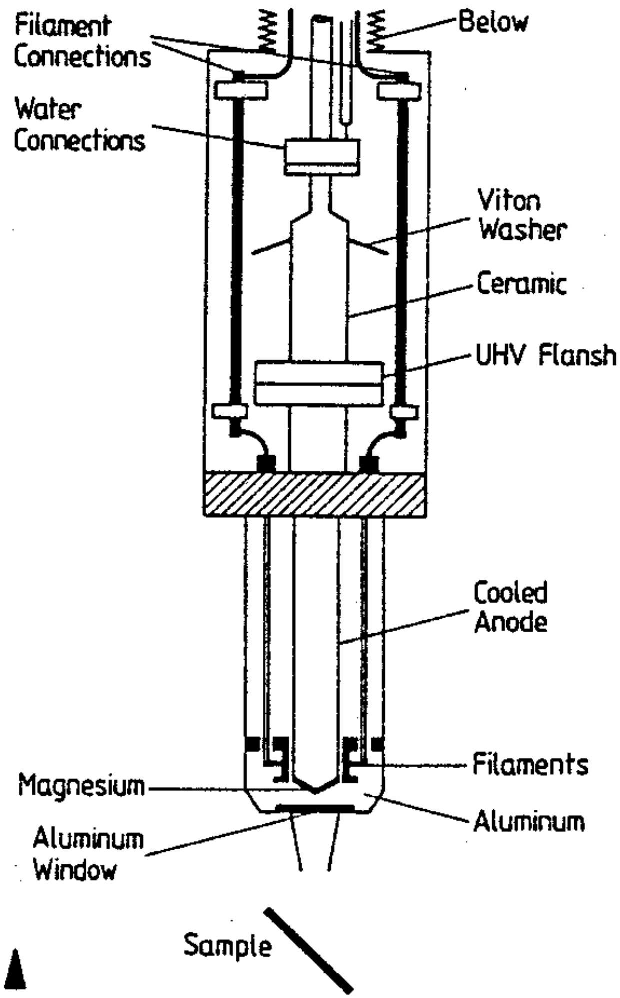
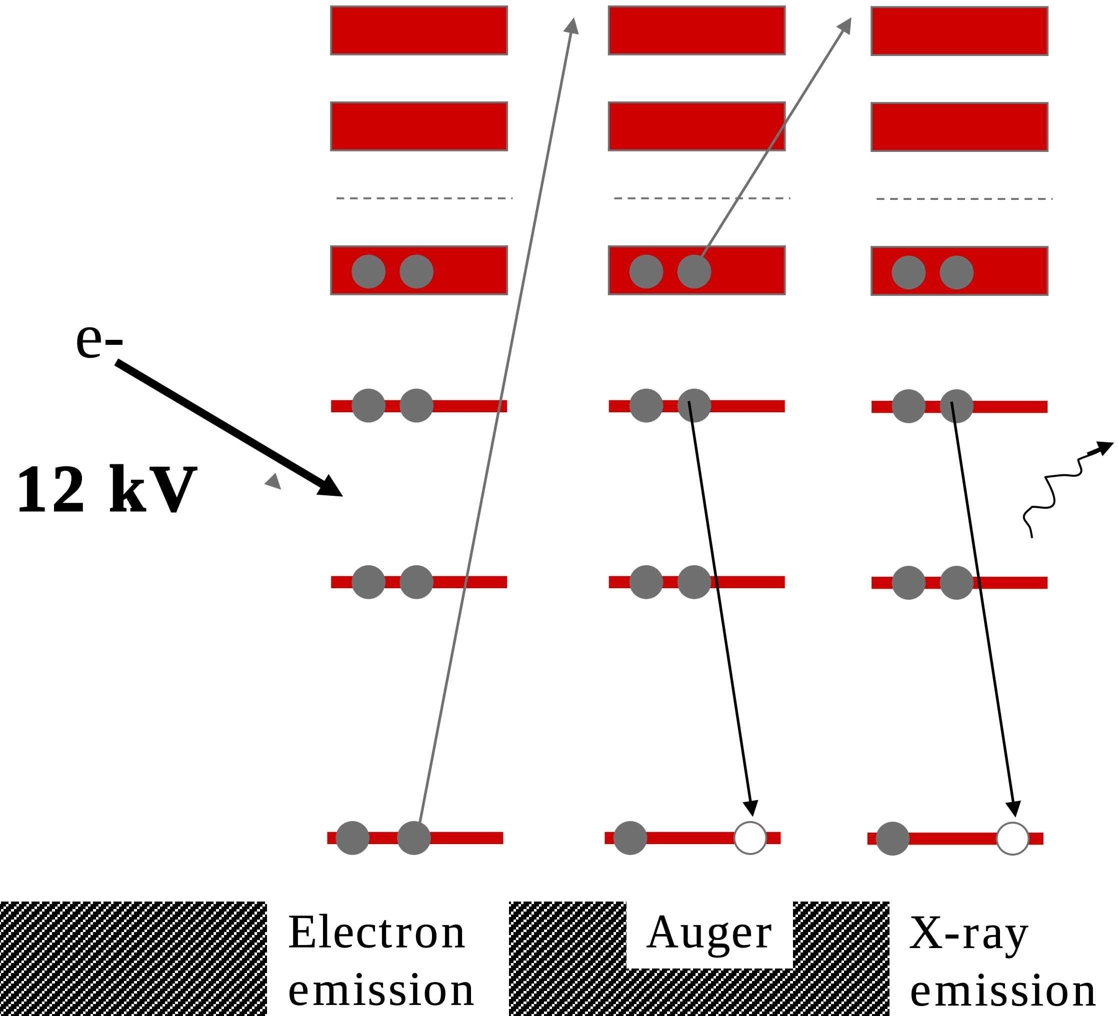
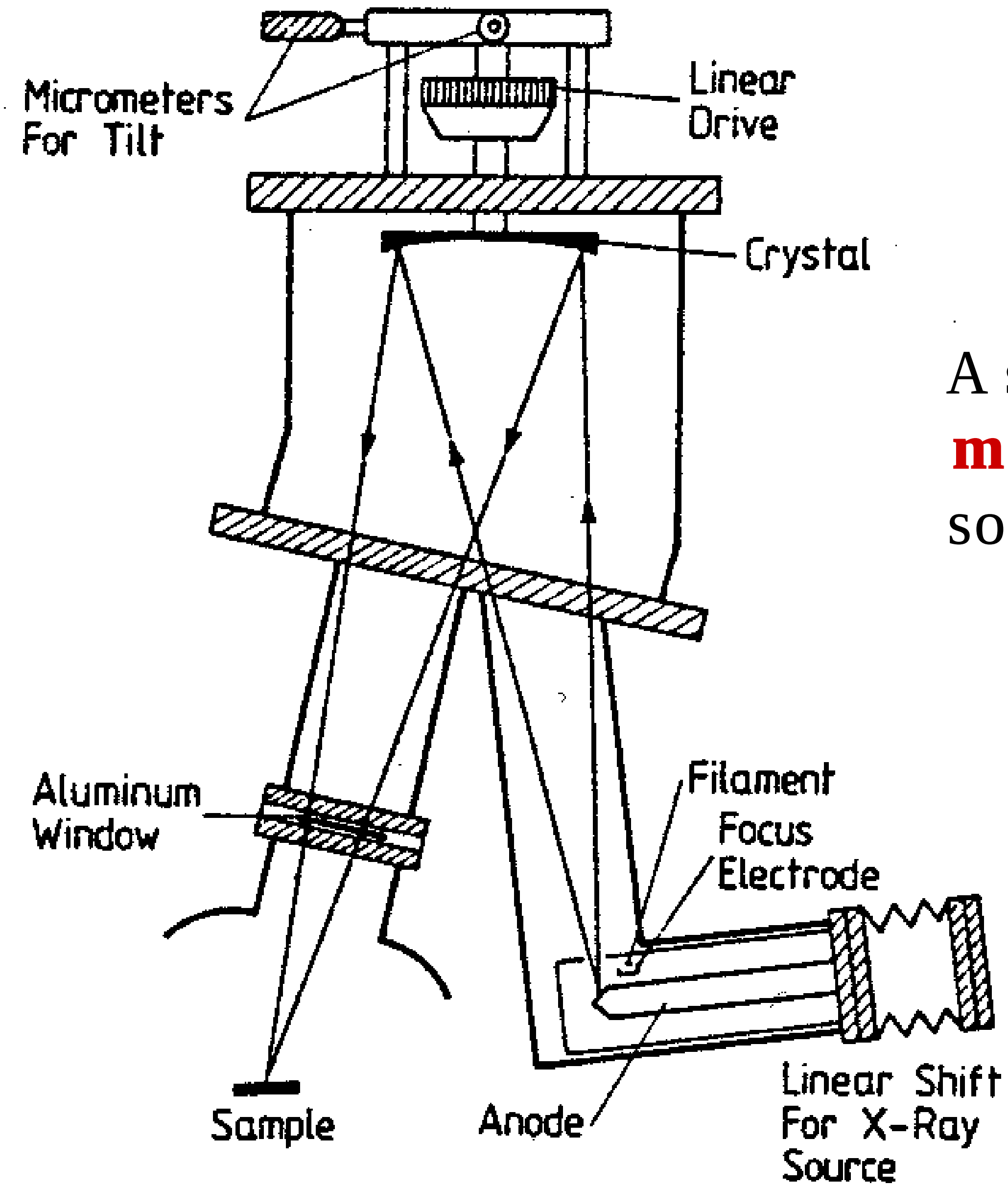
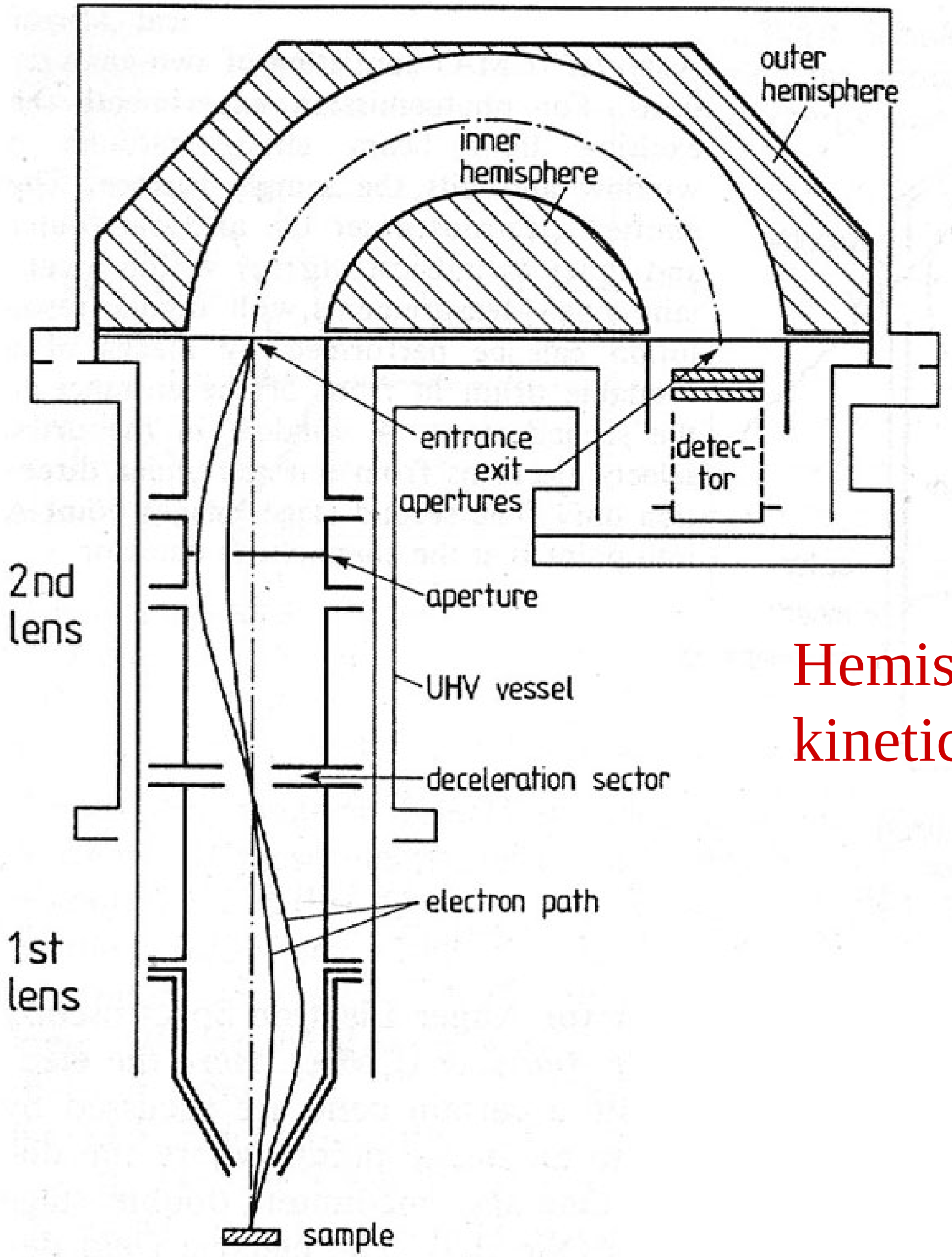
X-Ray source







A standard **monochromator** for X-Ray source



Hemispherical analyzer of electron kinetic energy

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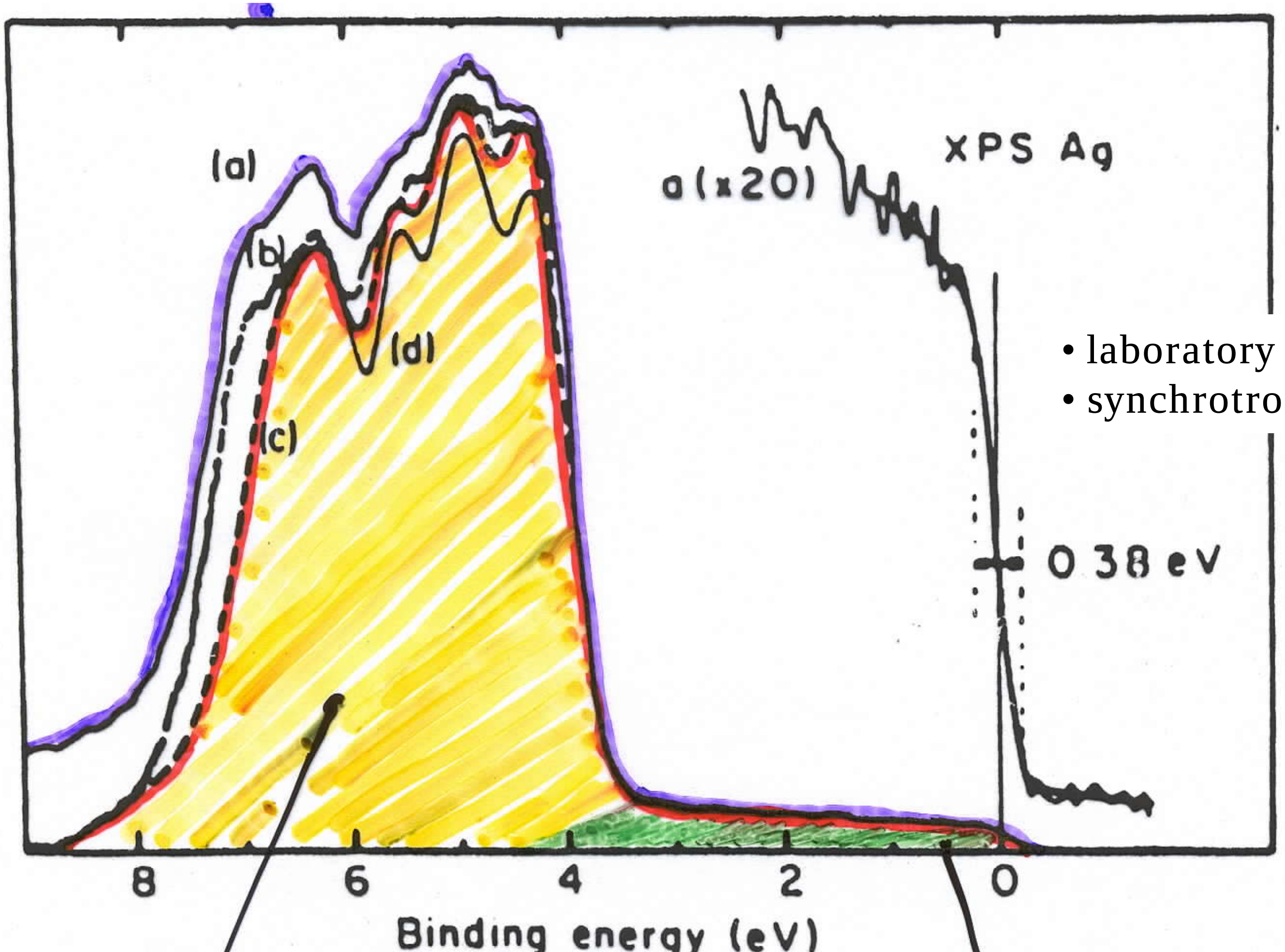
The instrumental resolution can be determined by measuring the Fermi edge of a metallic sample



- laboratory sources 0,3 - 1,2 eV
- synchrotron radiation < 0,1 eV

Ag 4*d*-related manyfold

Ag 5(*sp*)-related manyfold