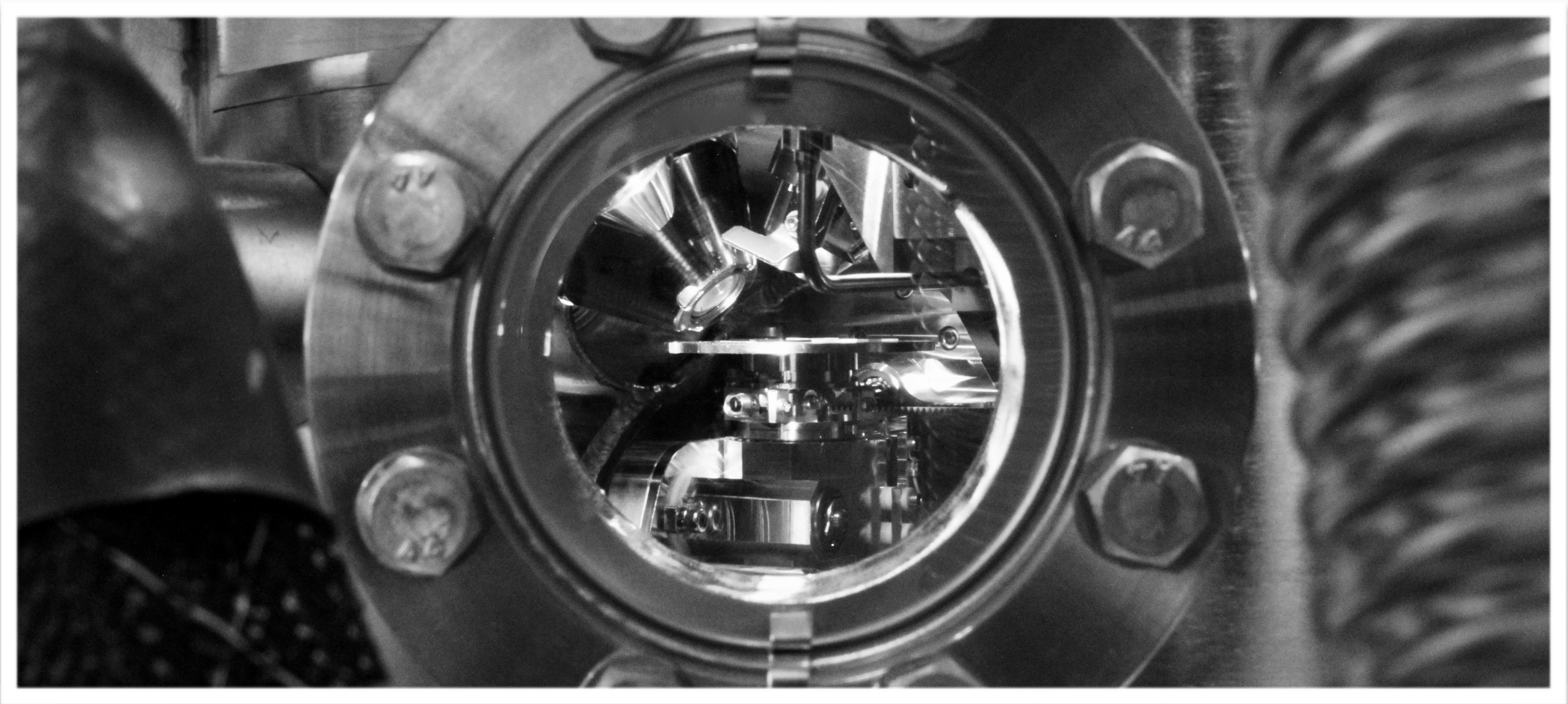

Inside the XPS

Advanced Solid State & Surface Characterization

Pascal Schouwink
Mounir Mensi
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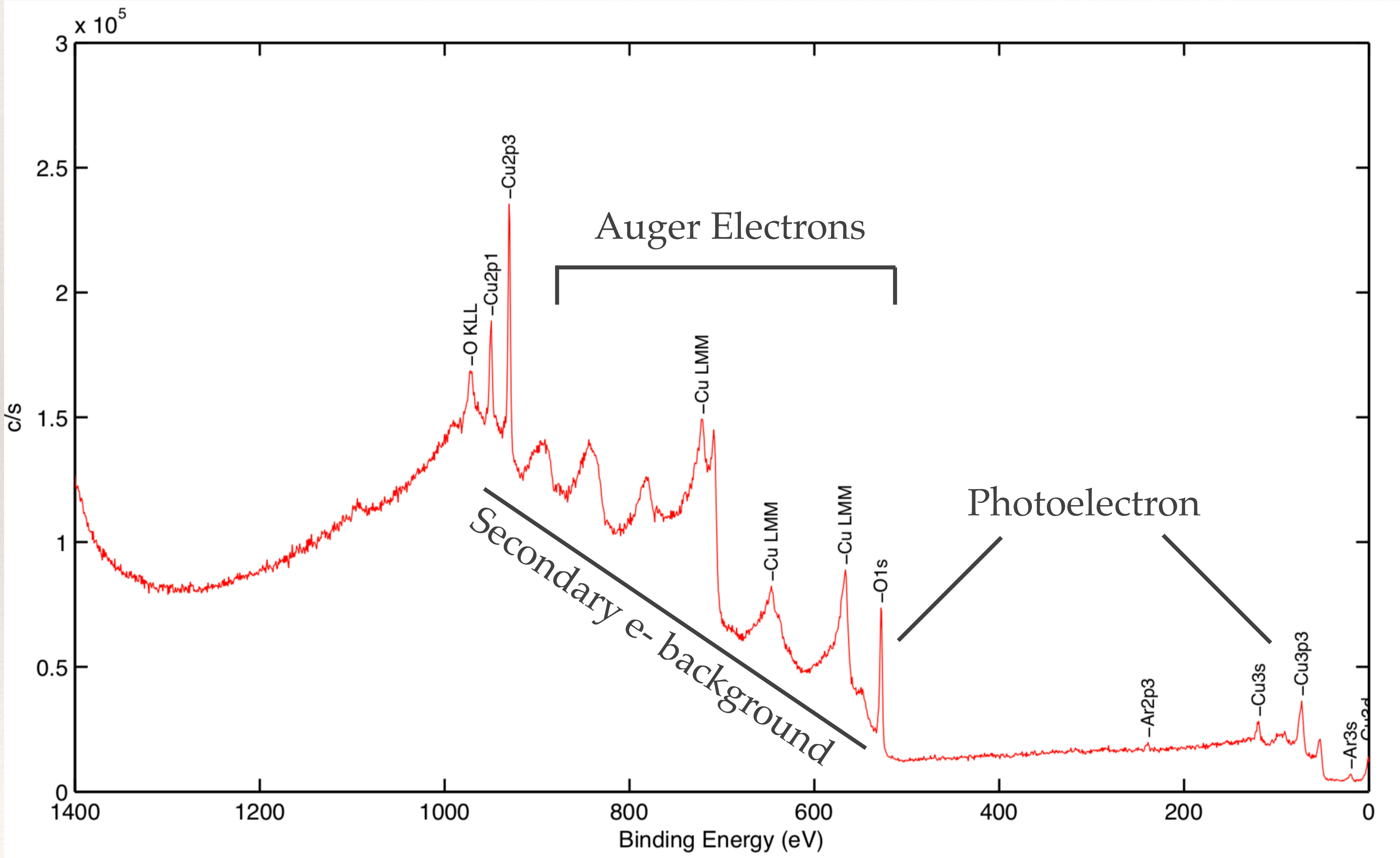
2025 / 03 / 18

Plan

- Main components of an XP spectrum
- PE spectrum detailed
  - PE lines: main features
  - Exercice 1 / resolution
  - PE spectrum: Minor (‘undesired’) features
- The ‘Chemical Shift’
- Surface Contamination
  - Study case I: Clean gloves?
- Beneath the surface
  - Depth profiling

Components of an XPS spectrum

A survey is a spectrum collected over the whole electron kinetic energy range of the instrument. It is presented the binding energy (B.E.) scale, which is independant from the X-ray source energy, and with a reversed abscissa (B.E. increasing from right to left)



Sputter cleaned copper sample showing the presence from Cu, O, Ar

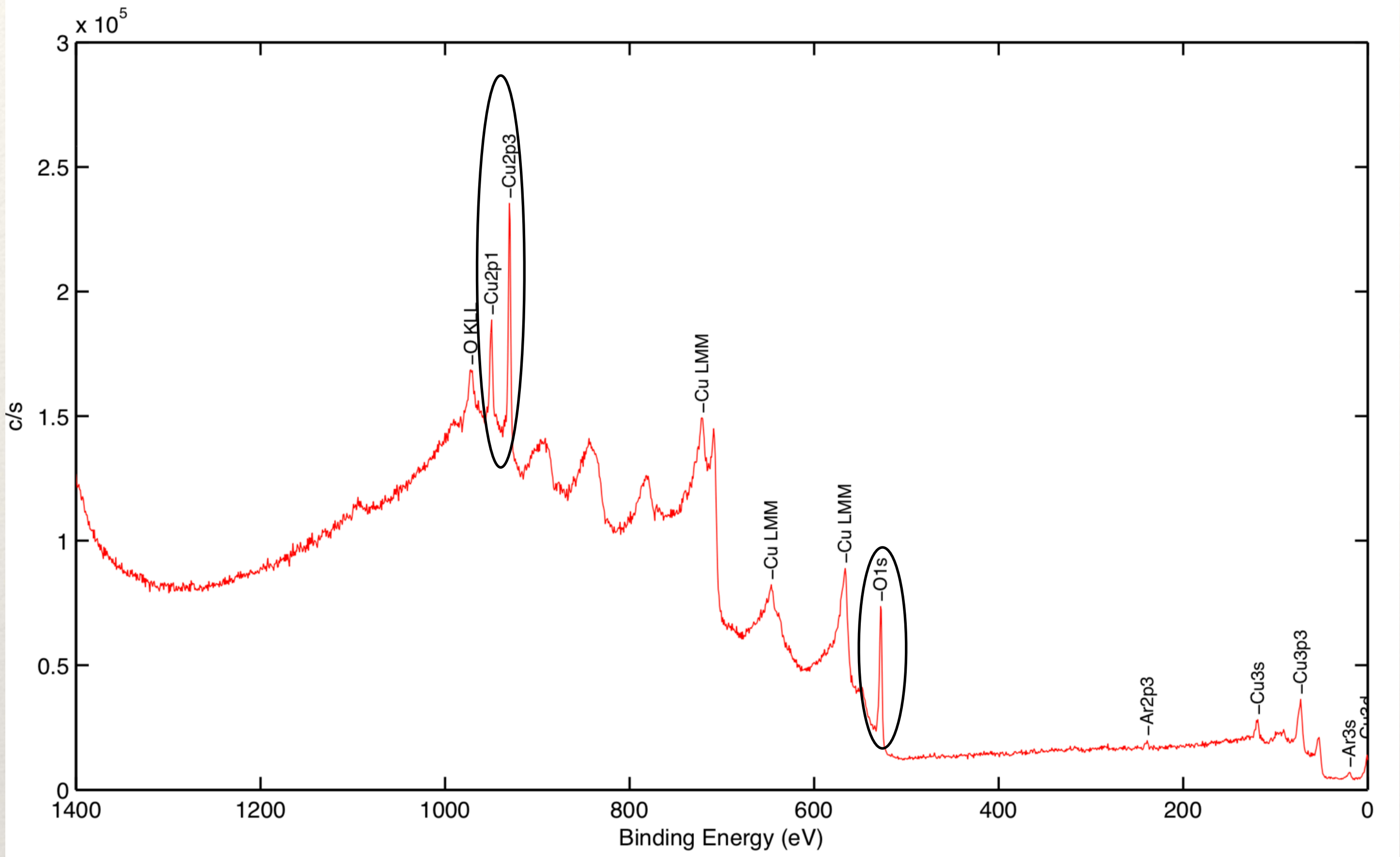
Main contributions

- Photoelectrons
- Auger electrons
- Secondary electrons

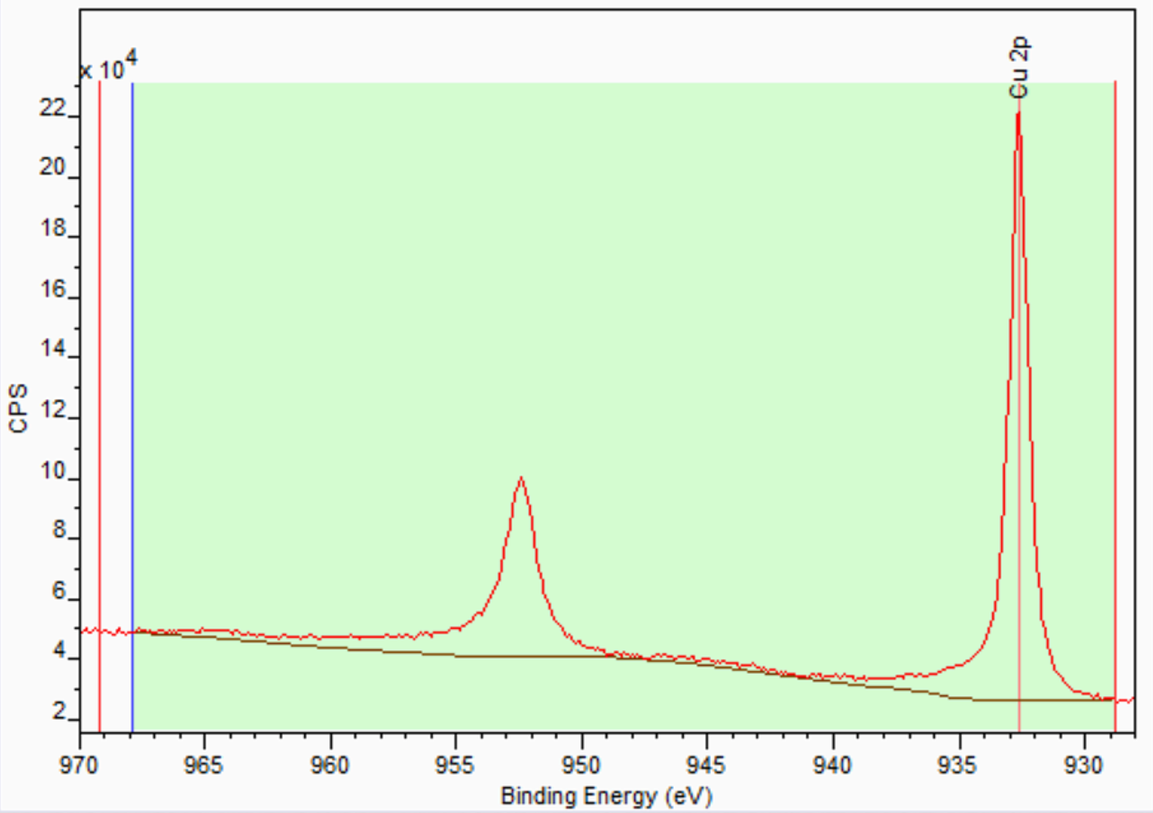
Secondary contributions

- Plasmons losses
- Ghosts
- Satellites

Photoelectron Components



Copper sample showing several photoelectron transitions from Cu, O, Ar



Cu 2p orbital, exhibiting the typical narrow features of PE

- Sharp peaks, uniquely defined for each atomic orbital
- Peak area allow to calculate the **'relative surface atomic concentration'**
- Sensitivity ~ part per thousand

Photoelectron emission (PEE)

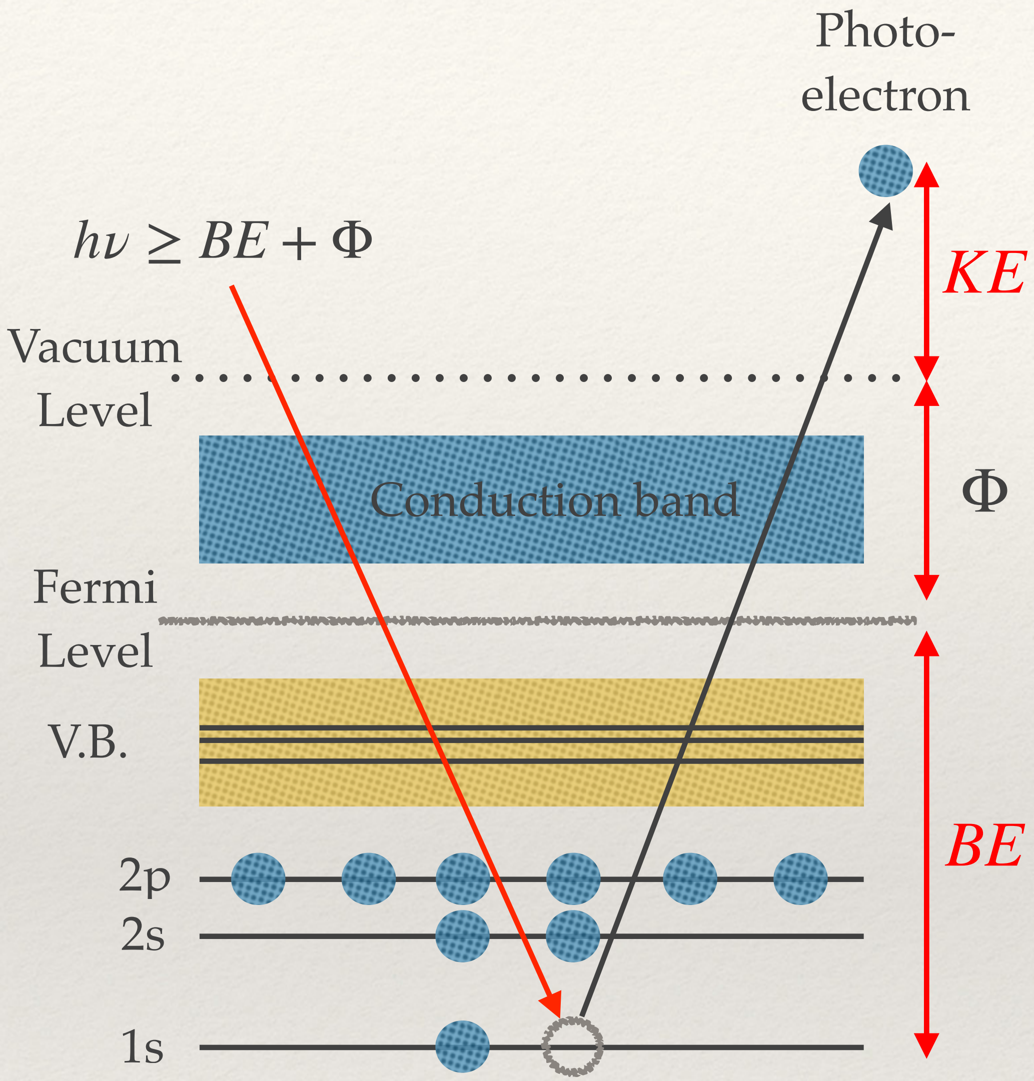


Photo-electron

$h\nu \geq BE + \Phi$

KE

Vacuum Level

Conduction band

Φ

Fermi Level

V.B.

BE

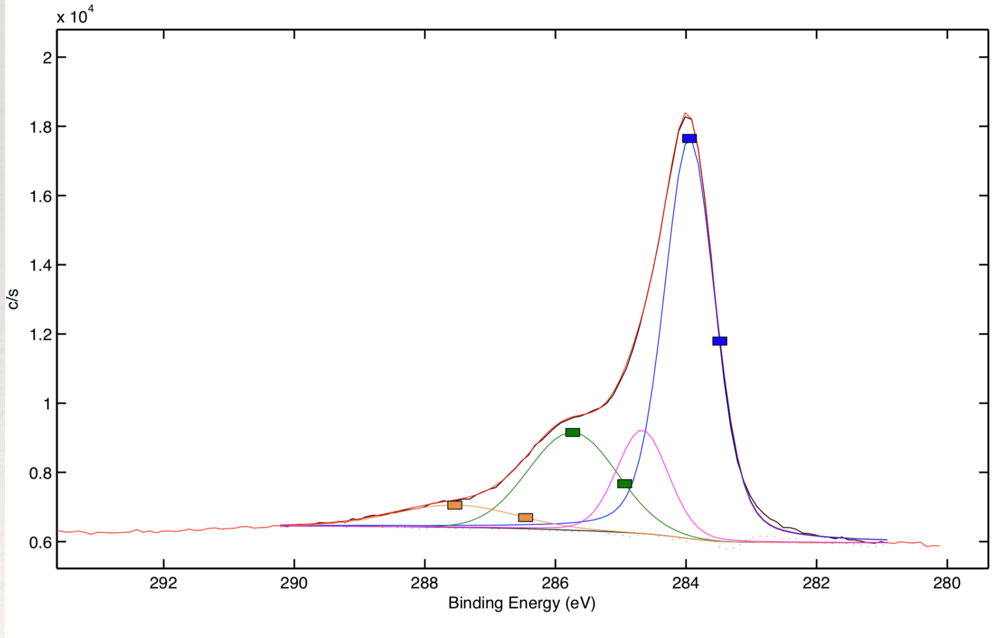
2p

2s

1s

Energy sketch of the photoelectric effect

- Creates sharp peaks in the spectrum, uniquely defined for each atom
- The kinetic energy of the photoelectron depends on the X-ray source, hence the choice of the binding energy scale



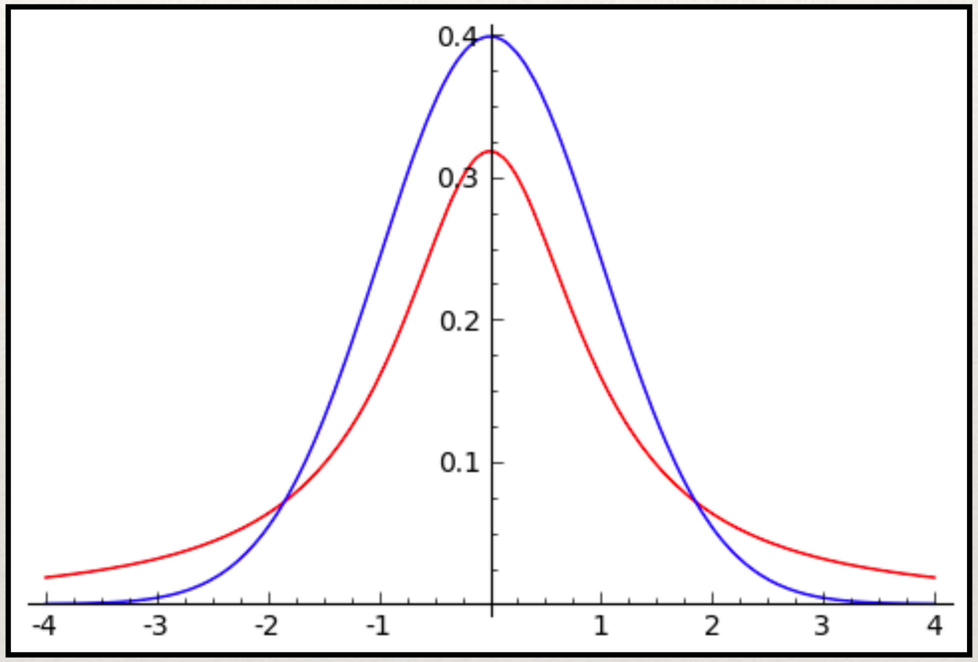
C1s of modified graphene. Courtesy LAS

Photoelectron Linewidth

- The intrinsic energy line width of photoelectrons depends on the lifetime of the core hole state
- From the Heisenberg uncertainty principle:

$$\Delta E \Delta T \geq \frac{\hbar}{4\pi} \Rightarrow \Gamma \geq \frac{2\hbar}{\tau}$$

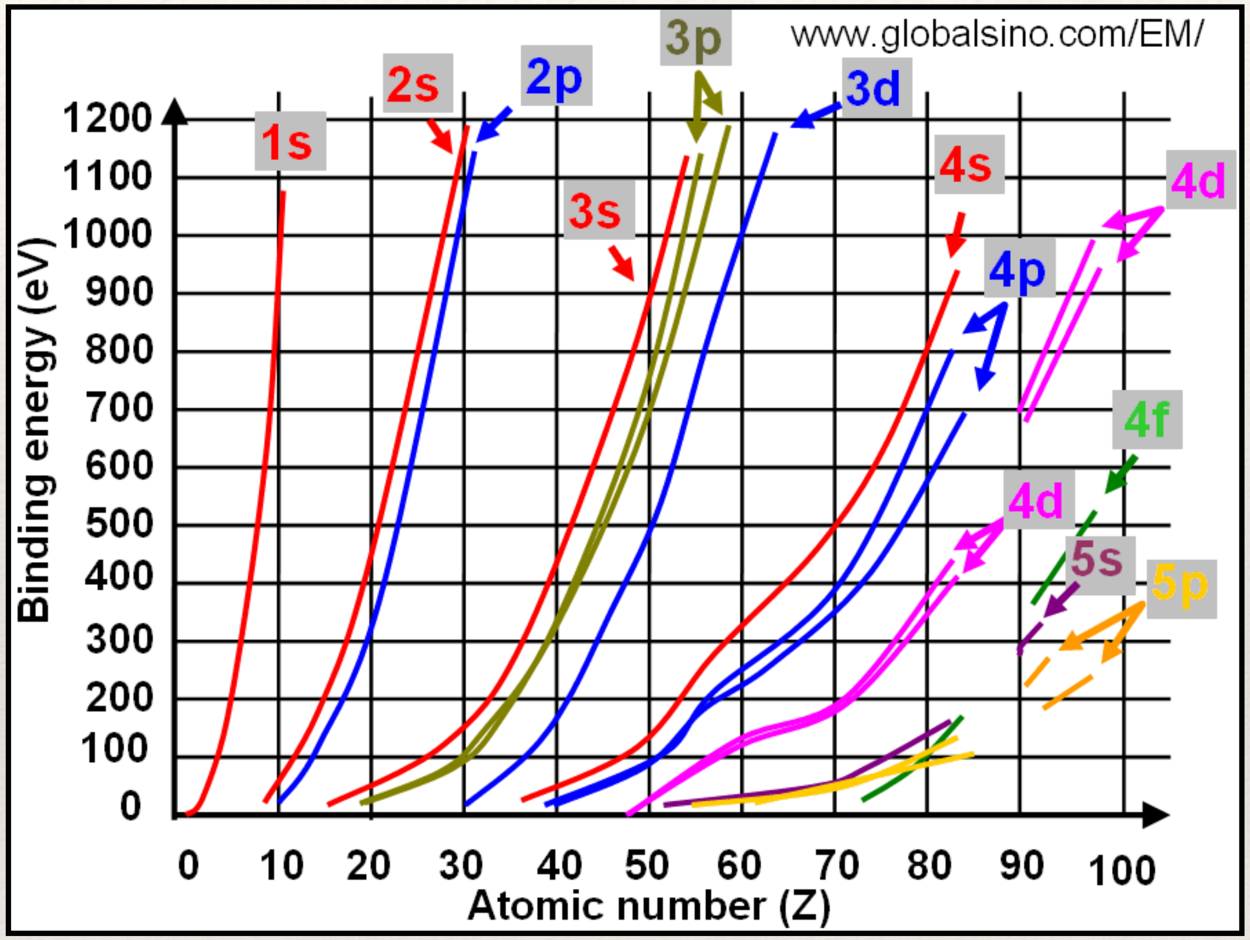
- Lorentzian line shape
- Broadening due to the multitude of decay channels
- Broadening due to phonon excitation (lattice vibrations)
- Inhomogenuous broadening due to chemical shift



Lorentzian (red), Gaussian (blue)

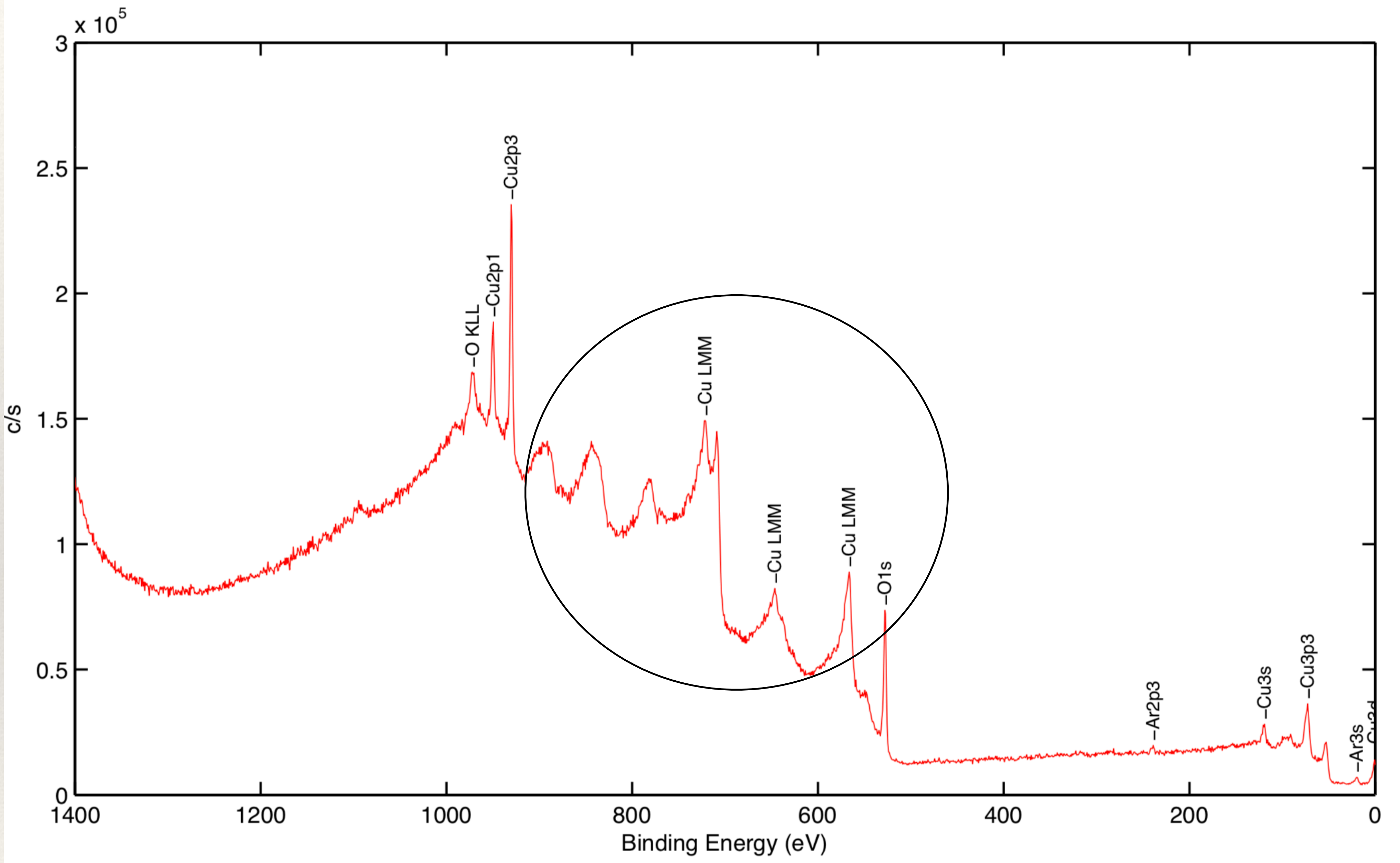
Binding Energy vs Z

- Due to Coulombic attraction between the nucleus and the electronic orbital, the BE increases with Z (for the same line of the periodic table)
- For the same reason the BE remains mostly unaffected by isotopes



Electron binding energy vs atomic number Z, for low binding energies

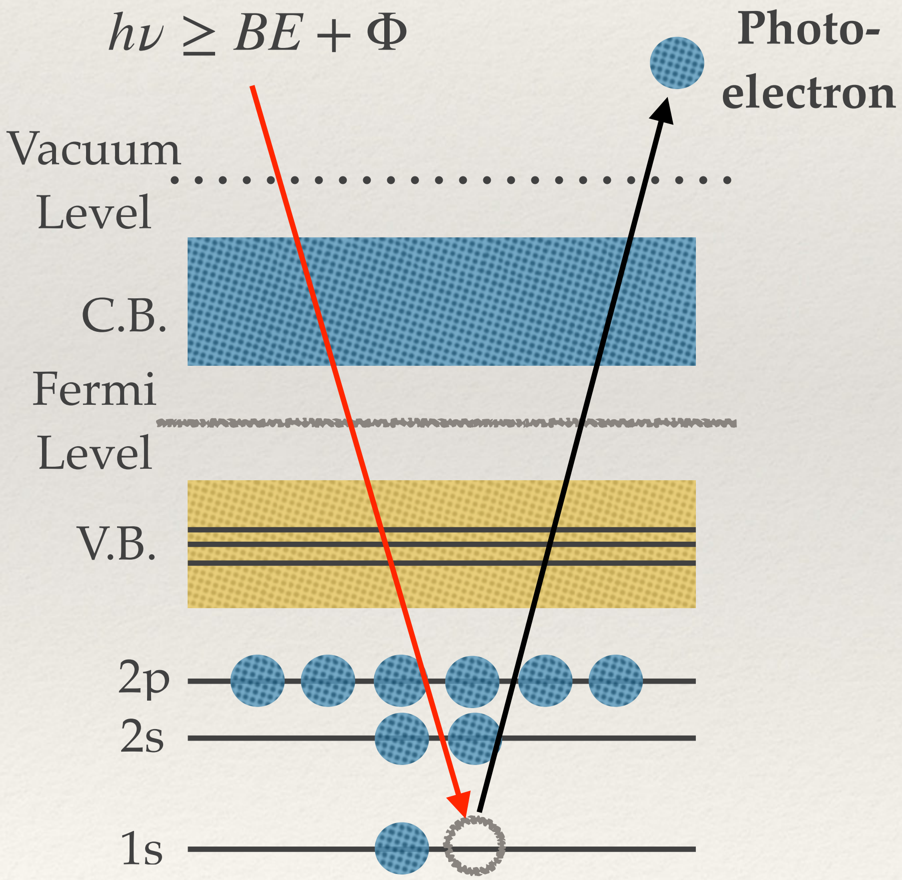
Auger Electrons Components



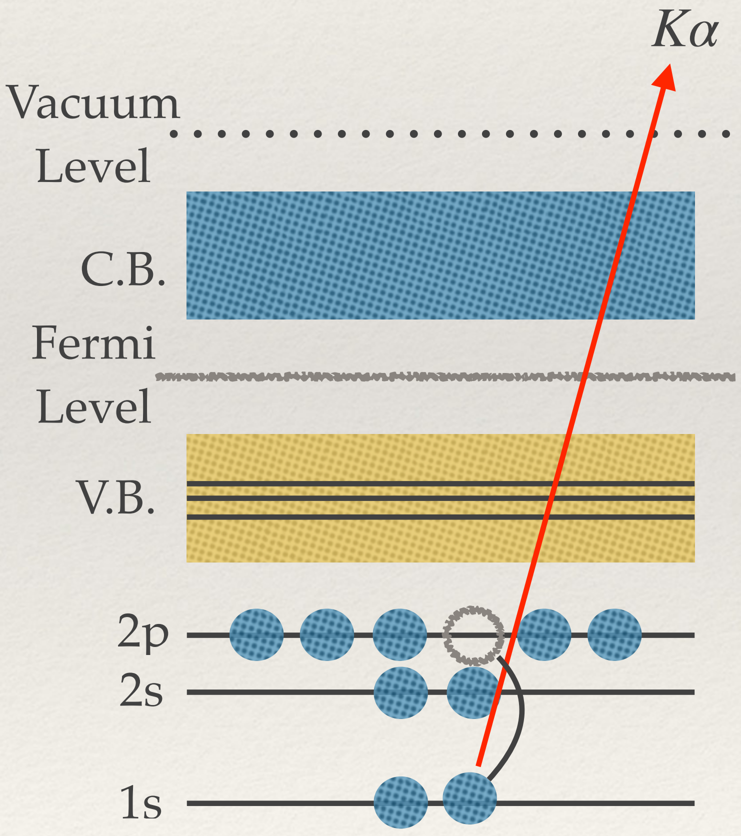
Copper sample showing several X-ray excited Auger transitions lines

Relaxation Paths

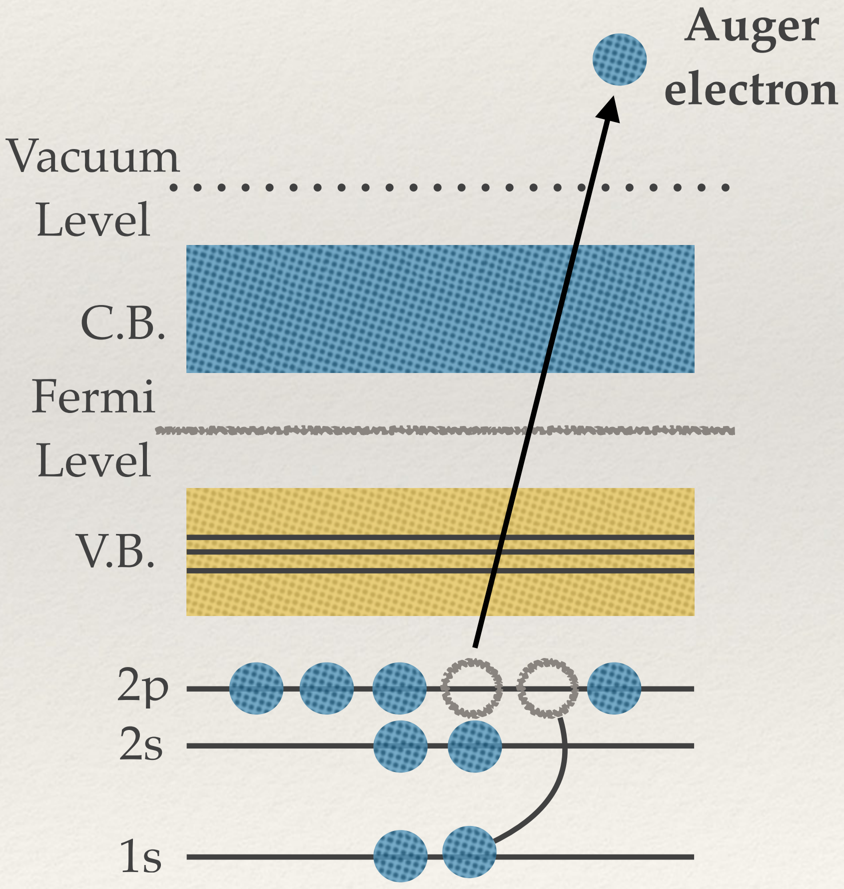
- X-ray induced Auger electron emission is a 3 electrons phenomenon. In a KLL transition:
  - A K level vacancy is created from the emission of a photoelectron (left)
  - An L level electron fills the K level vacancy
  - The released energy is transferred to the L level Auger electron: $E_K = E(K) - E(L_2) - E(L_1)$



Photoelectron Emission



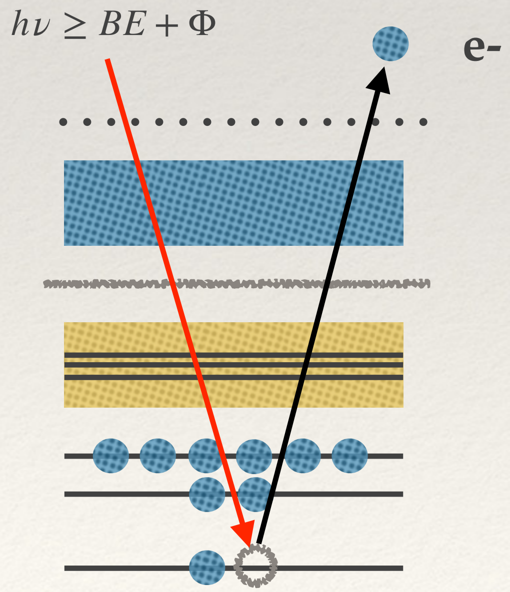
X-Ray relaxation

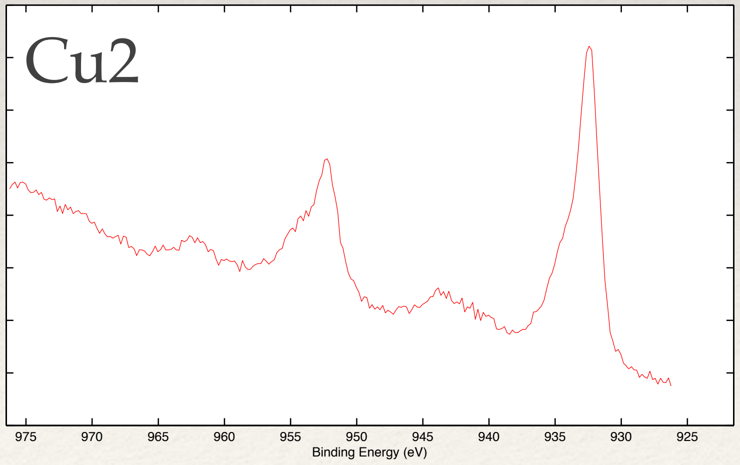


Auger Relaxation

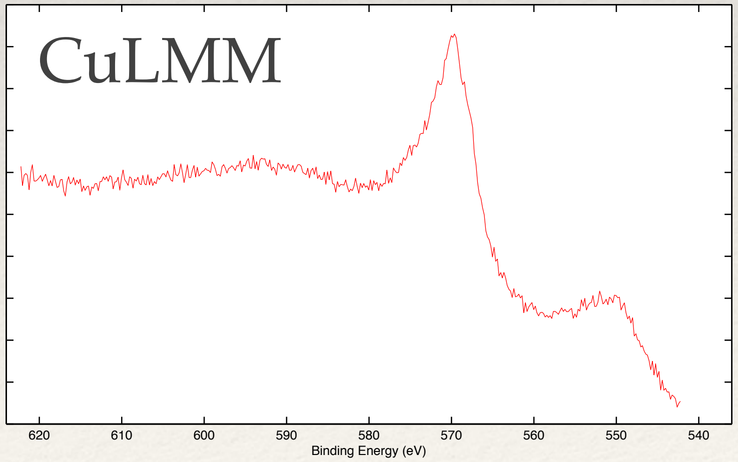
Photoelectrons vs Auger Electrons

- Photoelectron lines depend on the energy of the X-ray source energy: BE independent from source energy
- **Auger electrons lines are independent of the energy of the X-ray source**: KE independent from source energy
- Therefore, represented on the binding energy scale, photoelectron line position are independent of the source, while Auger line position depend on the source. Changing the source changes the Auger vs photoelectron line relationship!

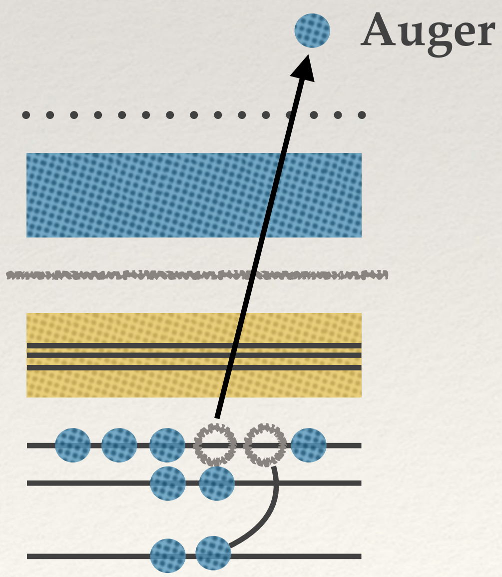




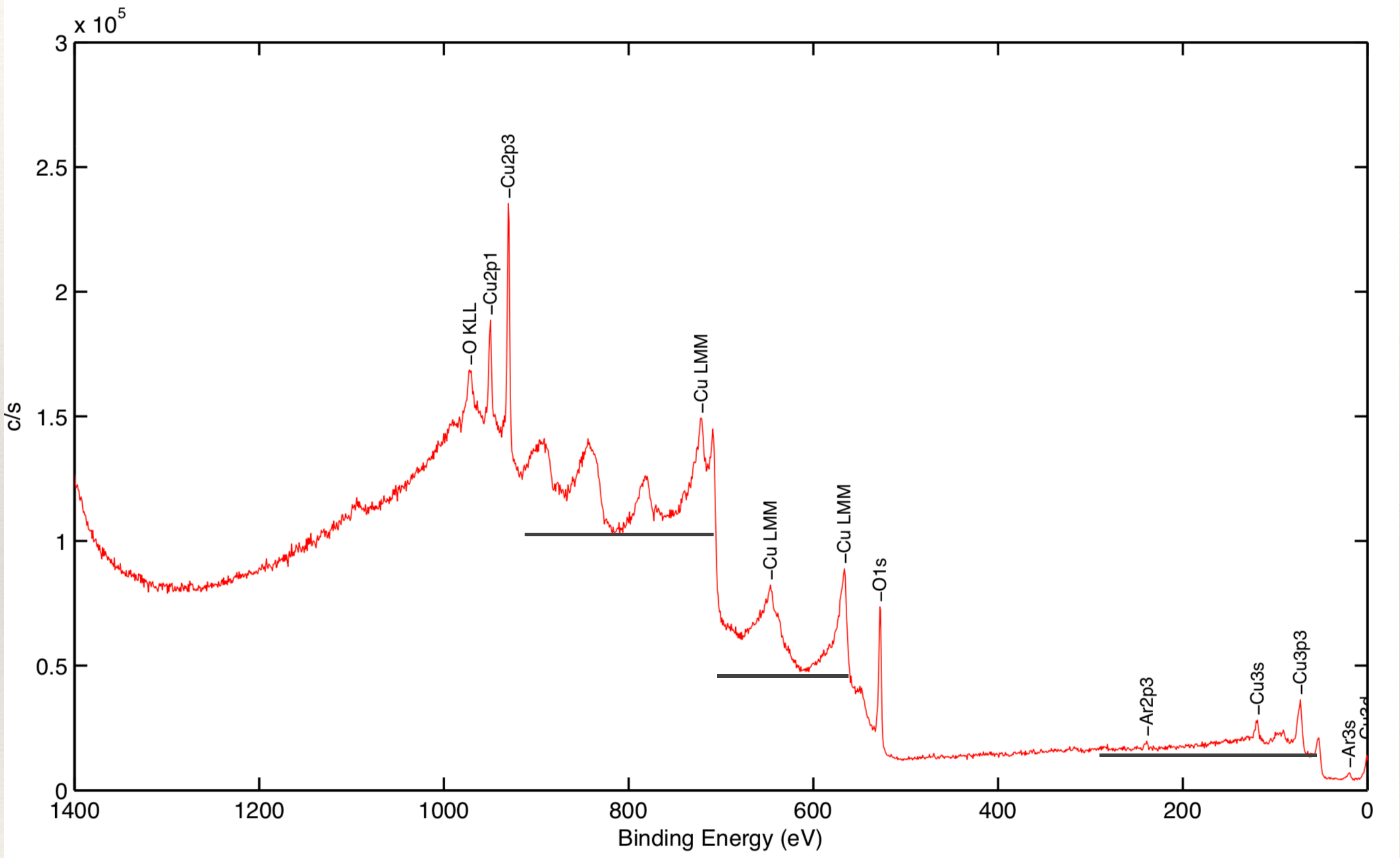
Narrow line feature



Broad line of Auger



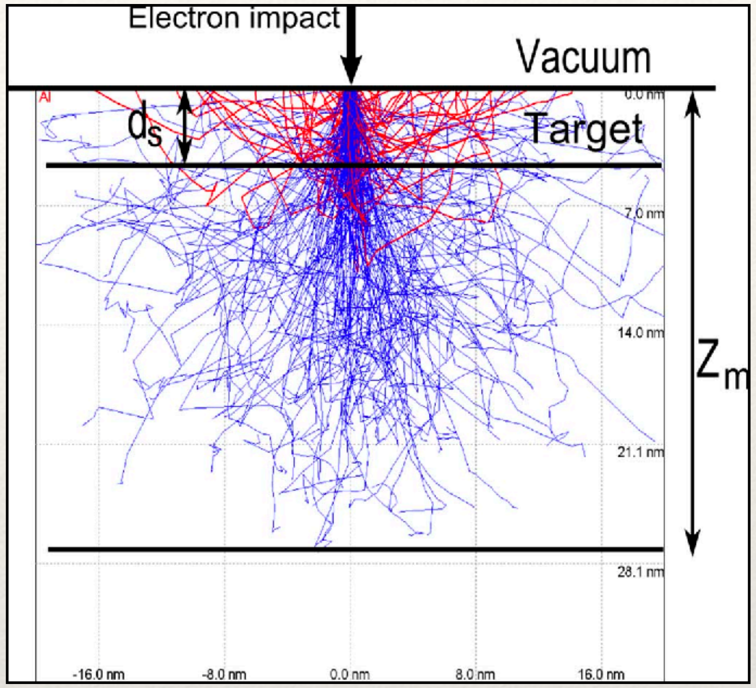
Background from Secondary Electrons

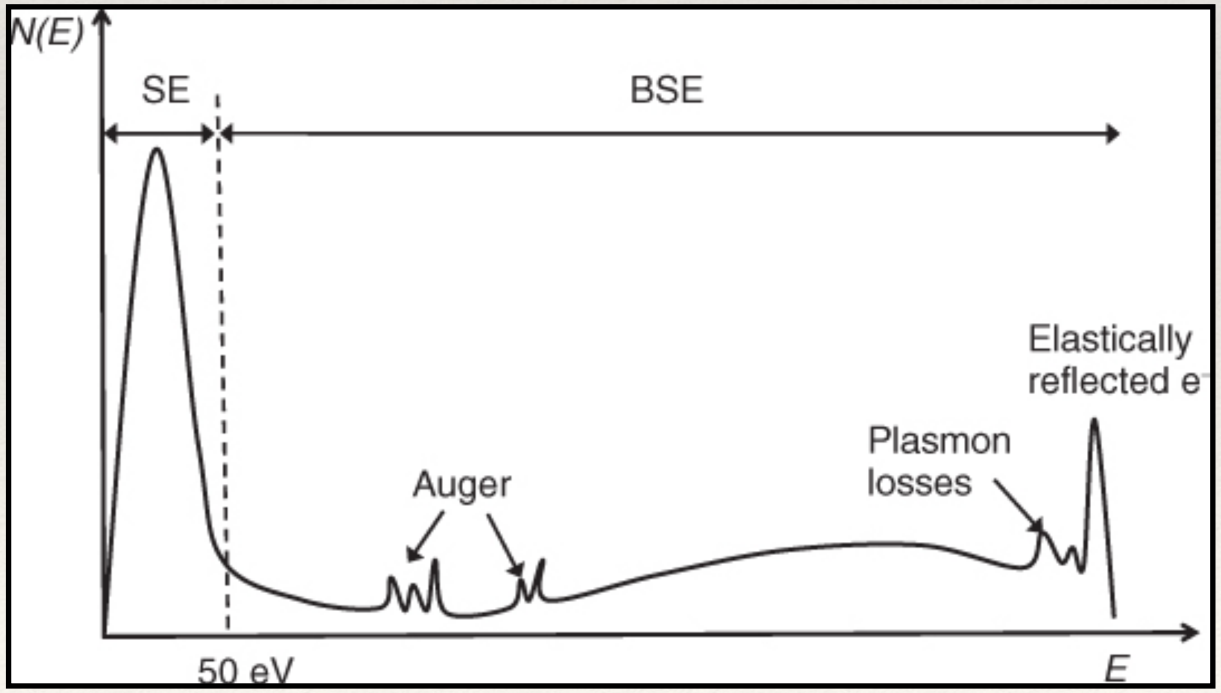


Copper sample showing a pronounced secondary electron background

Secondary Electron Emission

- Most materials undergo a large secondary electron emission yield: SEY>2, i.e. for 1 impinging electron, 2 are emitted
- Energy of 'true' secondary electrons is below 50eV
- Secondary electron form the dominant background in XPS measurement.



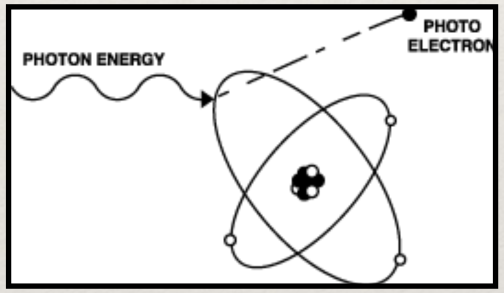


Secondary electron emission energy

Photoemission in the Condensed Phase

Three Steps Model:

1. Ionization, involving photo excitation cross-section, provided the photon energy is high enough:

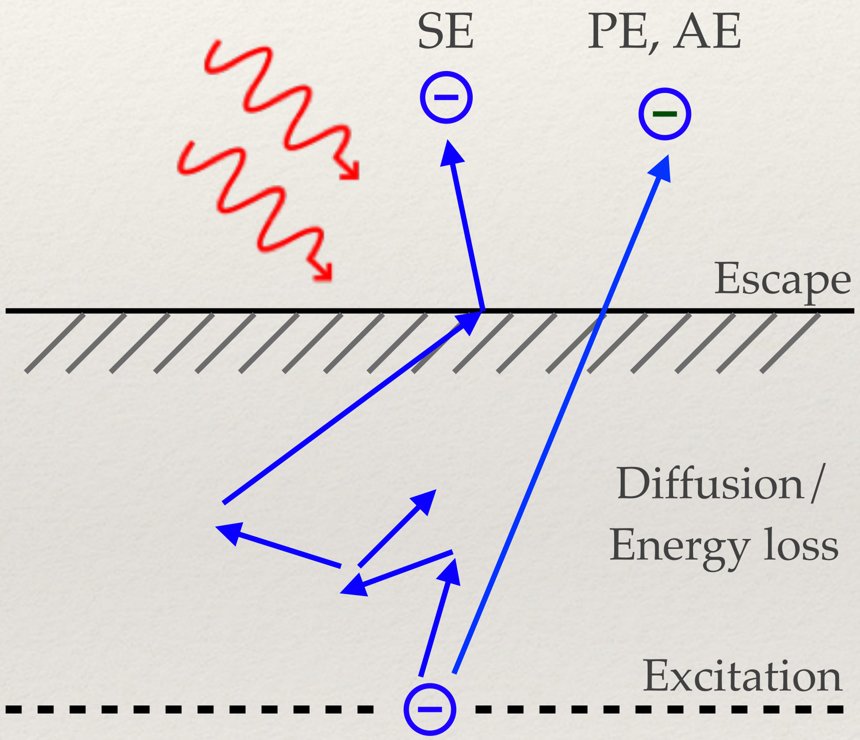


Einstein relationship
on the photoelectric effect

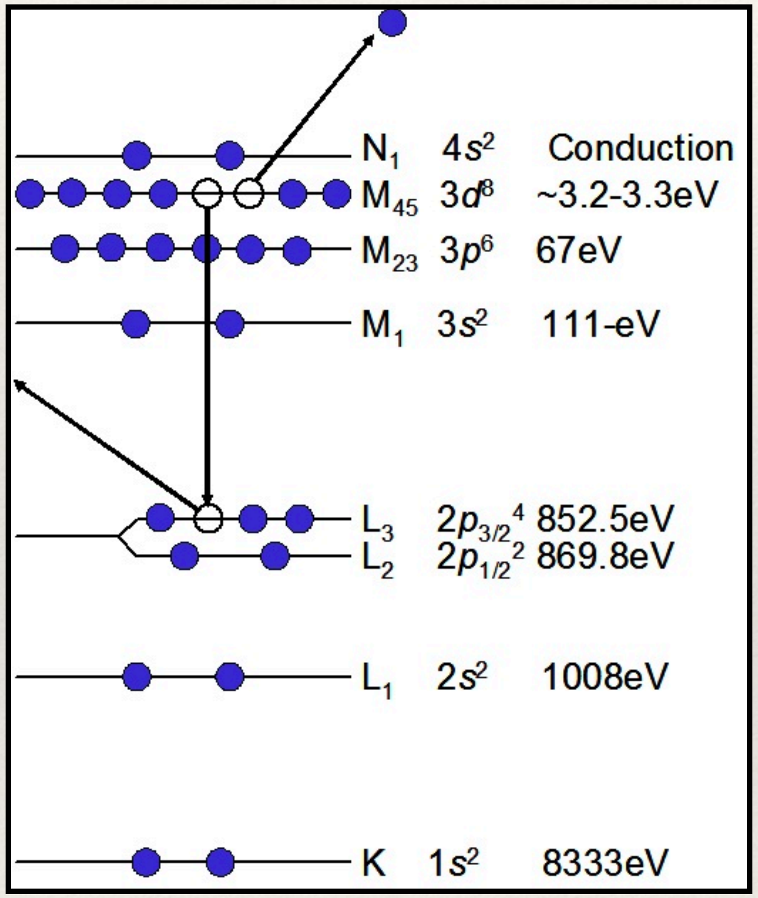
$$E = h\nu - \Phi$$

4. Transport of the electron, involving inelastic and elastic scattering

5. Escape into the vacuum



Exercice



Electronic structure of Ni
Source: CasaXPS

Assuming an Al Ka X-ray source (E = 1486.6 eV) and knowing the electronic structure of Ni, sketch its XPS binding energy spectrum *

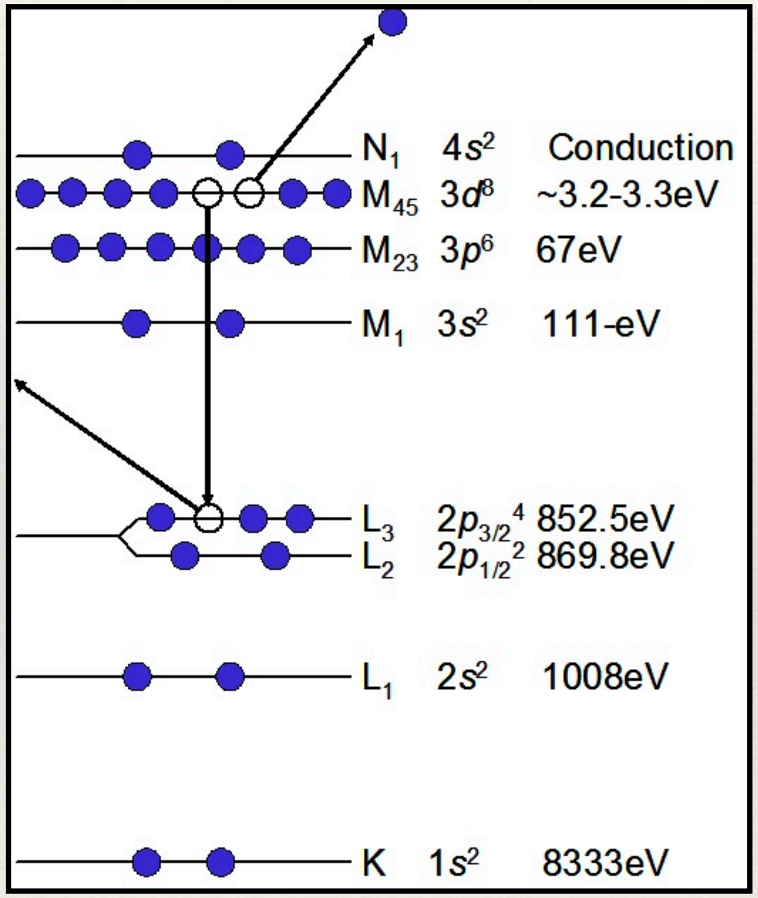
Start with photoelectron lines 2s, 2p, 3s, 3p

- Add the Auger transitions: $L_3M_{23}M_{45}$, $L_2M_{23}M_{45}$, $L_3M_{23}M_{23}$
- Add the secondary electrons background

* *Reminder:* $E_B = h\nu - E_k - \Phi_{spec}$

And neglect the work function (~4.5eV) of the spectrometer

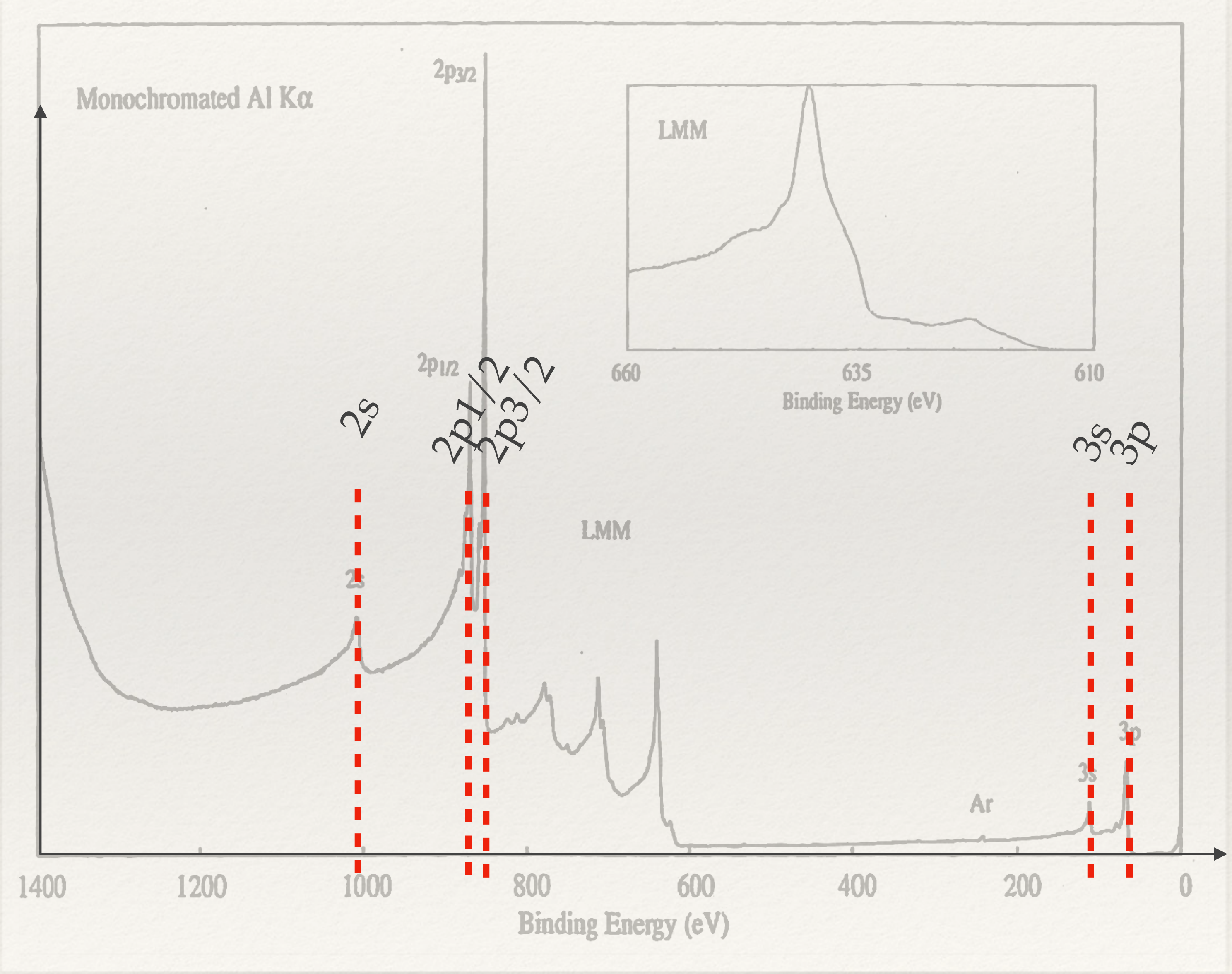
Photoelectron lines



Electronic structure of Ni
Source: CasaXPS

Al Ka X-ray source (E = 1486.6 eV)

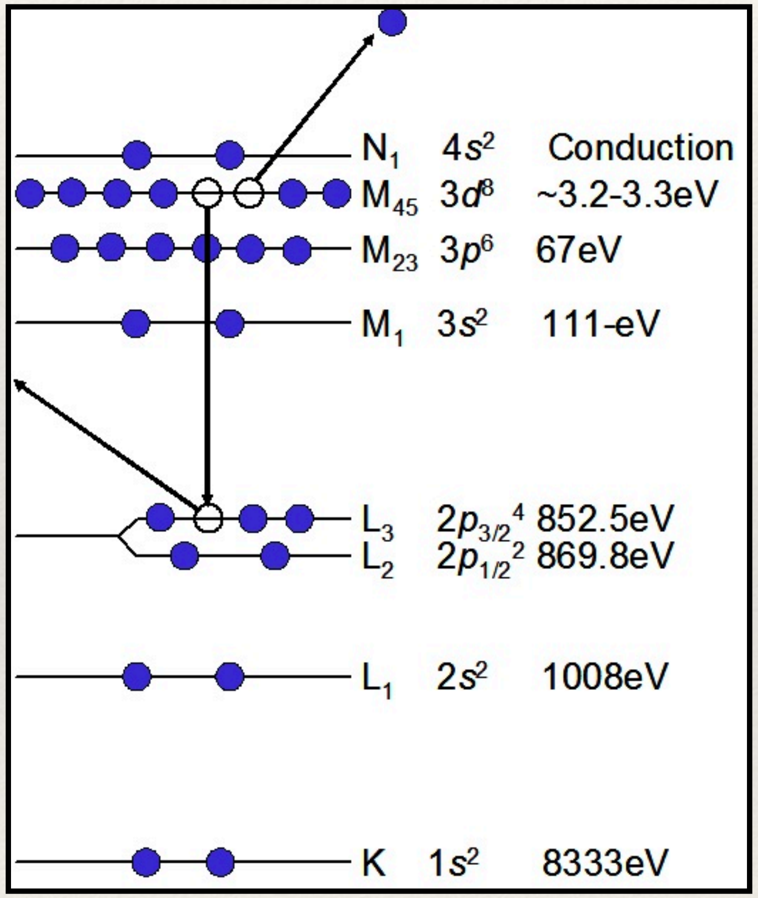
$$E_B = h\nu - E_k - \Phi_{spec}$$



Auger Recombination Lines

Main Auger lines

$L_3M_{23}M_{45}$, $L_2M_{23}M_{45}$, $L_3M_{23}M_{23}$

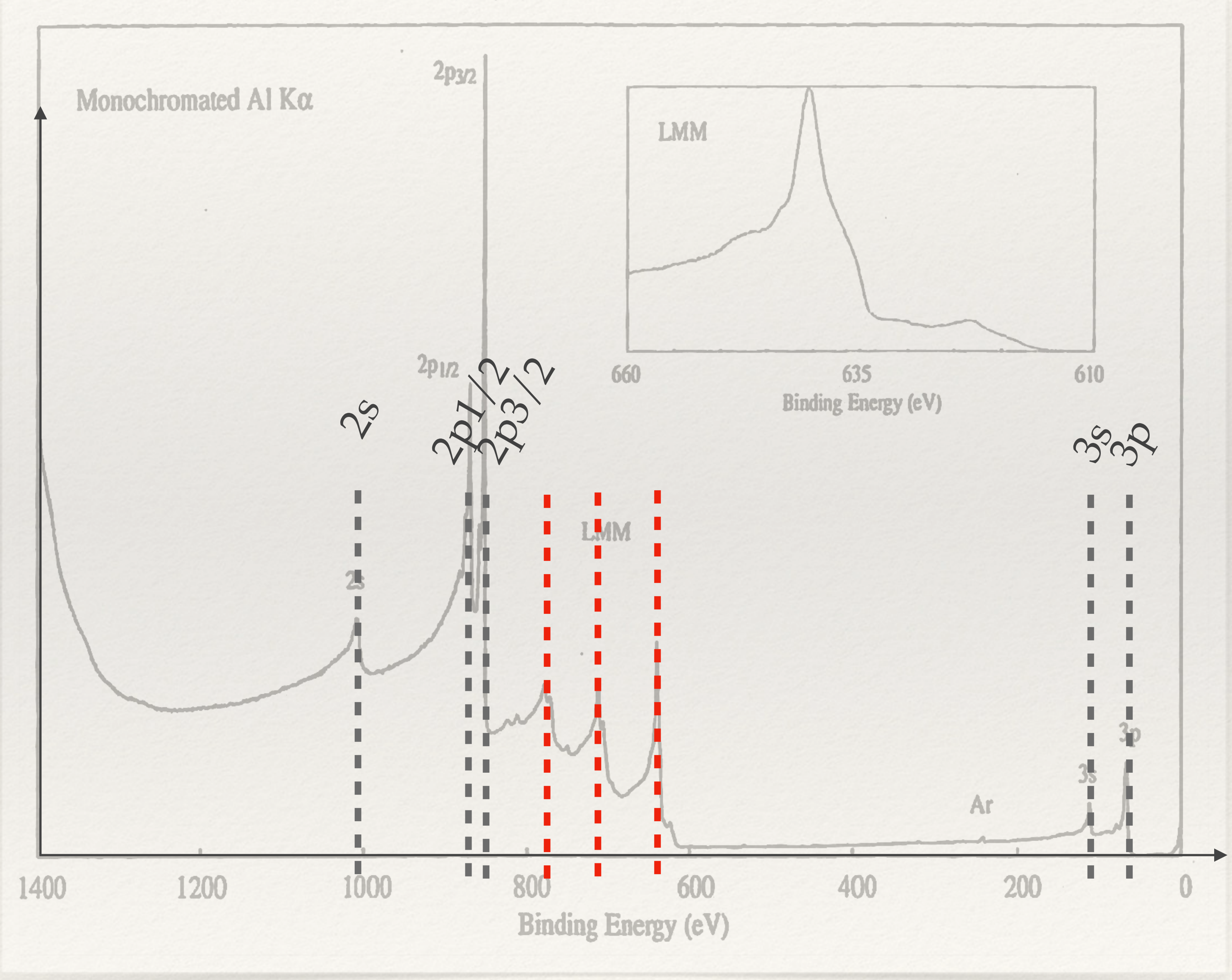


Electronic structure of Ni
Source: CasaXPS

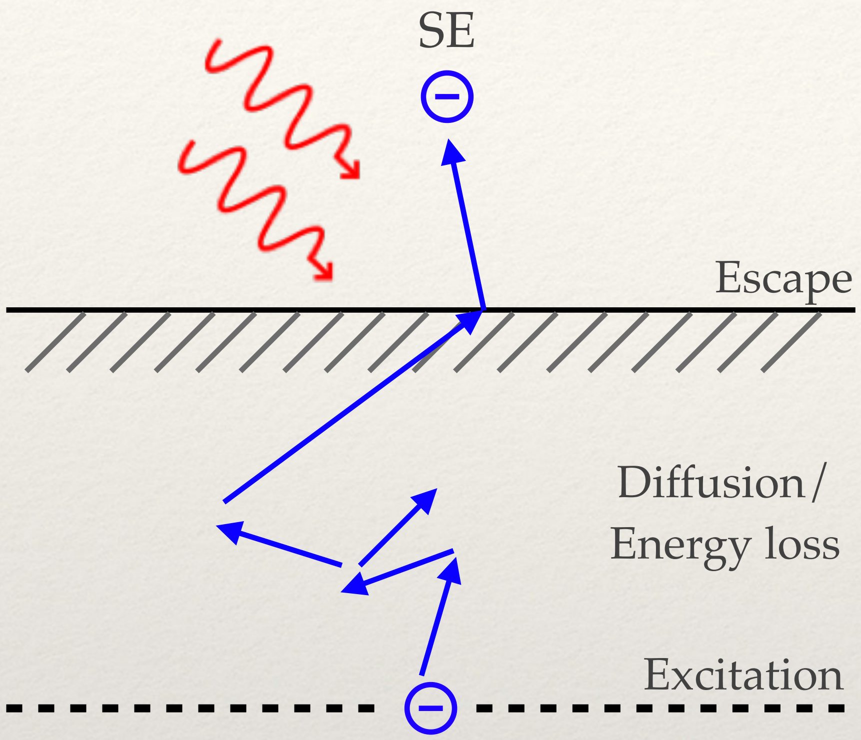
L3M45M45: (852.5 - 3.2) = 849.3 eV -> energy transferred to AE.

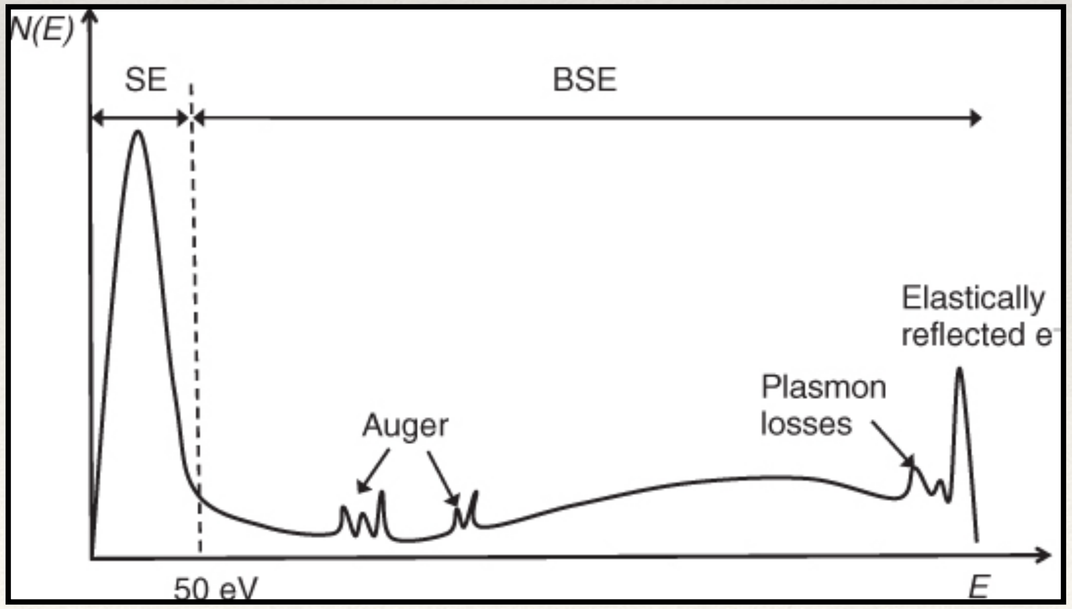
KE ~= 849.3 - 3.2 = 846.1eV

BE = 1486.6 - 846.1 = ~640.5eV



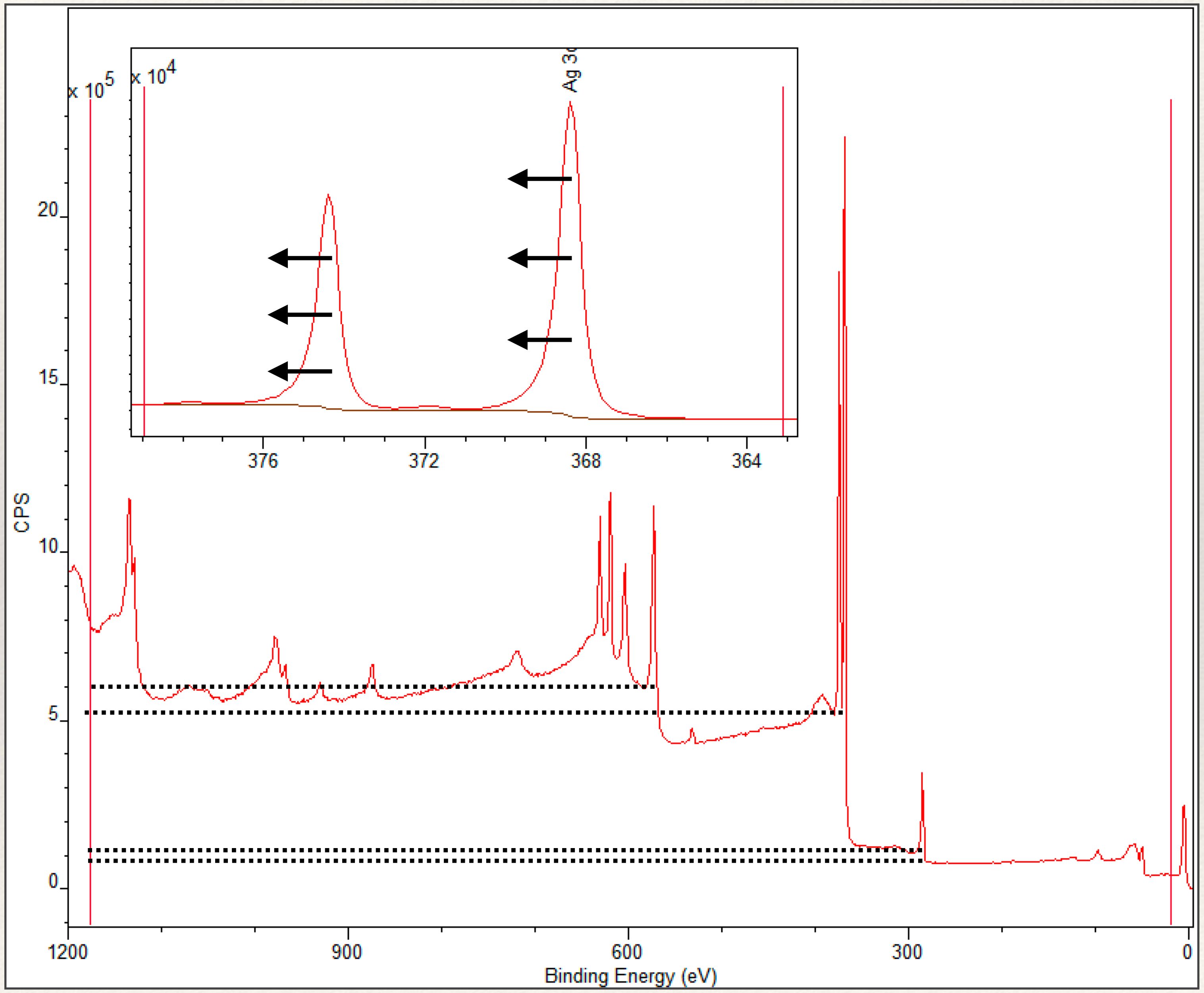
The Background



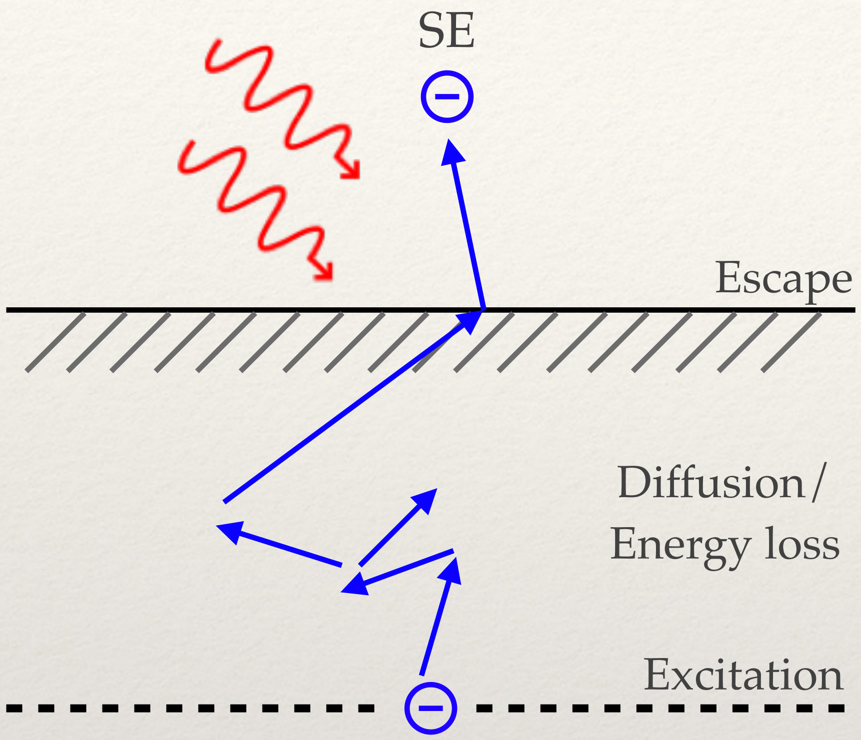


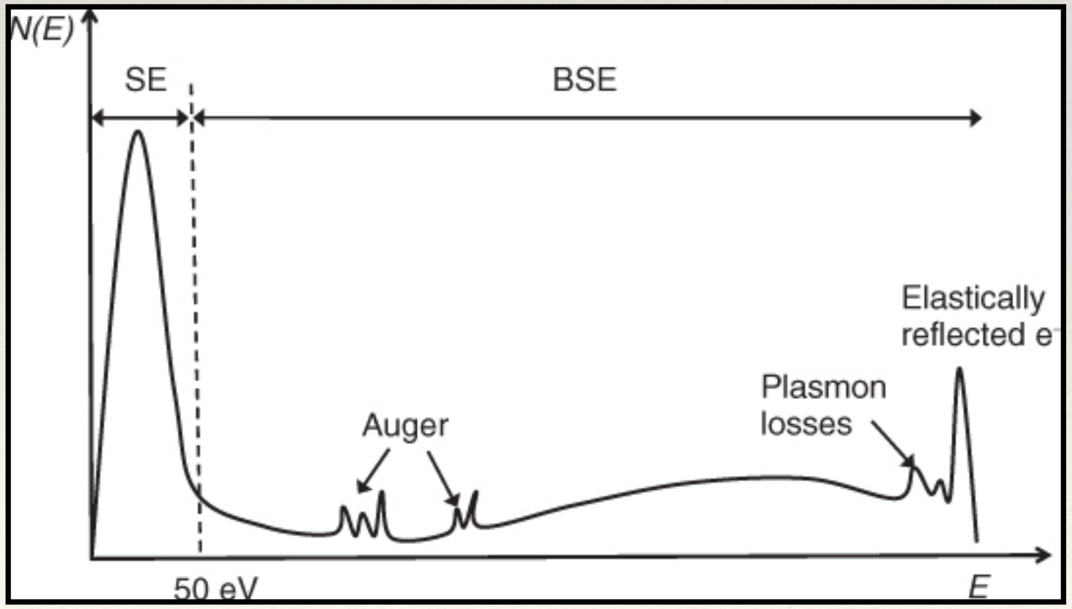
Secondary electron emission energy spectrum

Loss of KE upon inelastic scattering induces the background

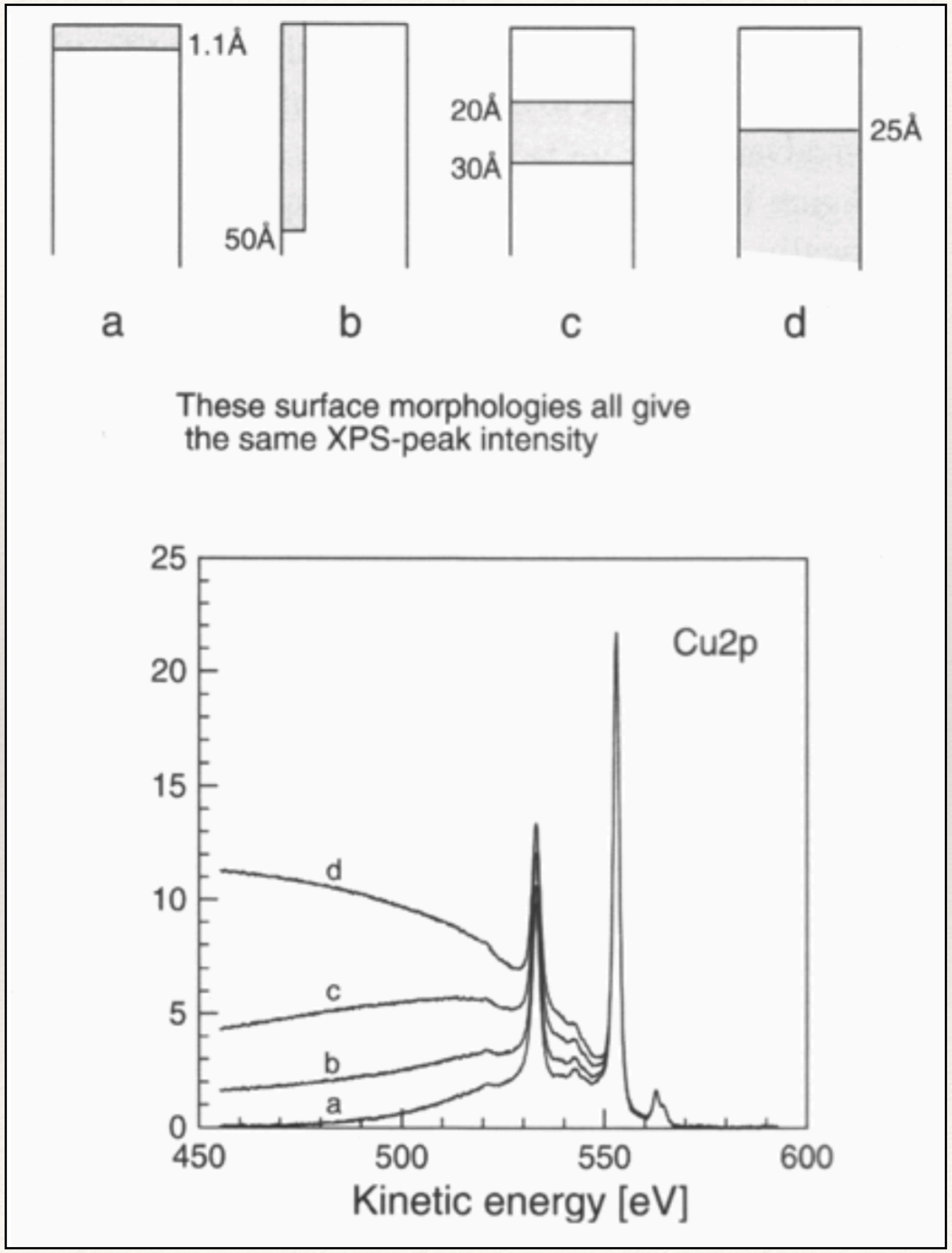


The Background: Shape vs Structure



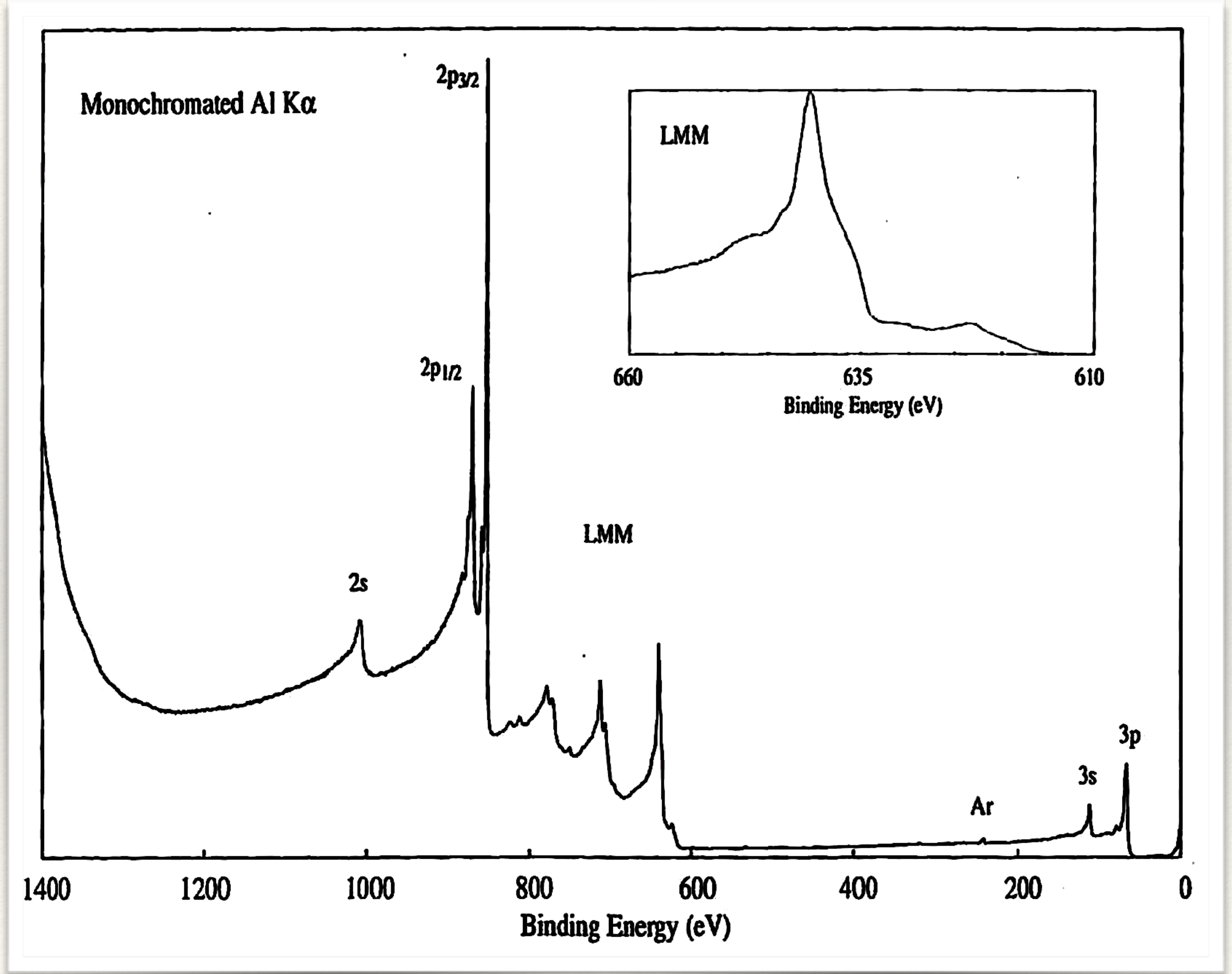


Secondary electron emission energy spectrum



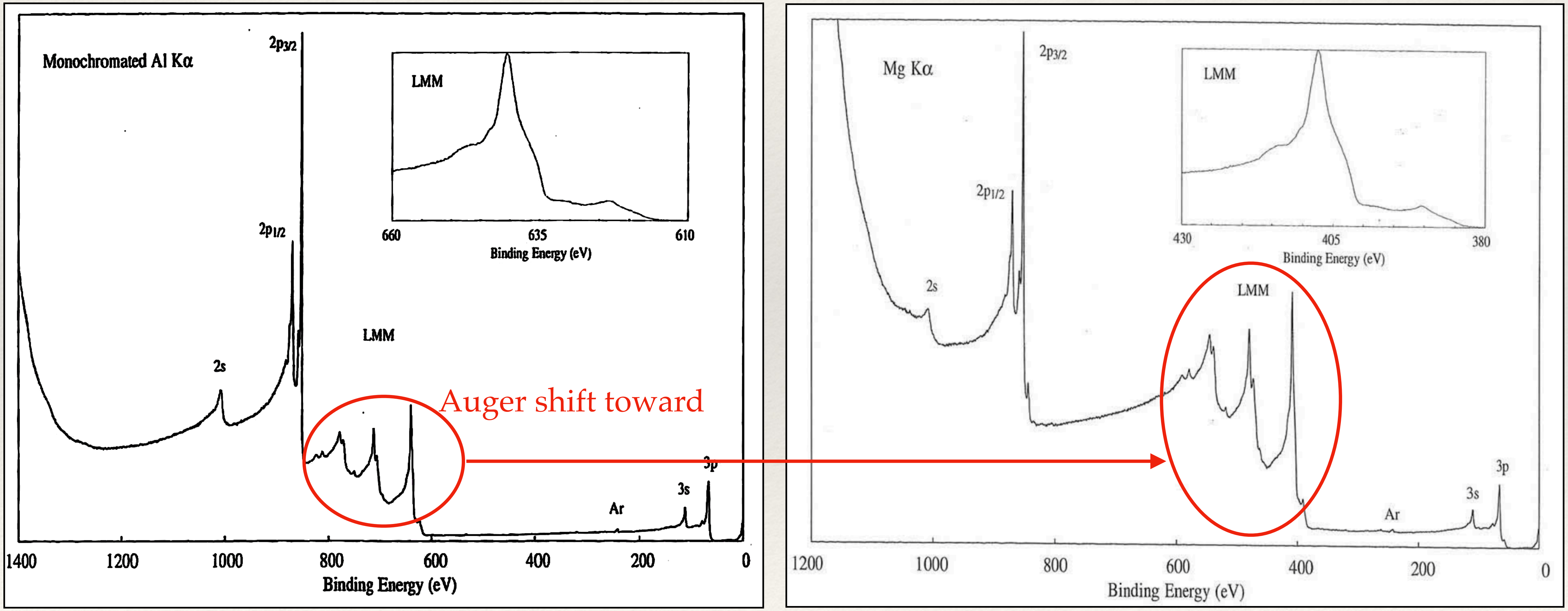
These surface morphologies all give the same XPS-peak intensity

Al Ka XPS Spectrum of Nickel



Al Ka vs Mg Ka

In BE scale, photoelectron line position are independent of the source, while Auger line position depend on the source. Changing the source changes the Auger vs photoelectron line relationship!


Auger shift toward

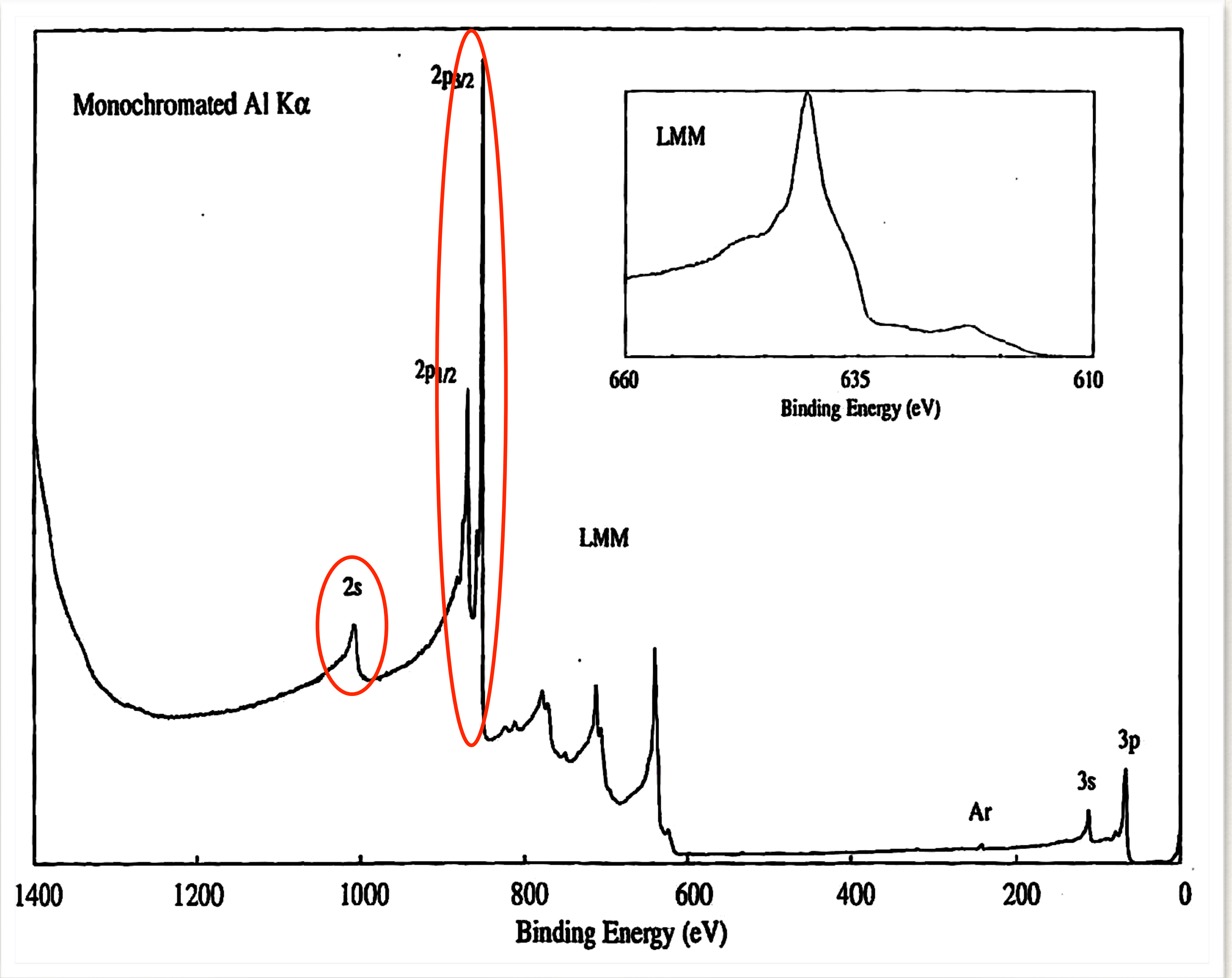
Typical XPS Spectrum

- Sharp peaks from the photoelectron emission
- Broader peaks from X-Rays excited Auger transitions (relaxation)
- ‘Flat’ background due to the secondary electron emission
- **Spin-orbit coupling / ‘spin-splitting’**
- **Multiplet splitting**
- **Satellites**
- **Plasmons loss features**
- **Artefacts**

Typical XPS Spectrum

Among the sharp peaks from the photoelectron emission, some have:

- Single peak
- Double peaks (spin splitting)
- Complex structure with multiple 'peaks'/shoulders (multiplet splitting, shake-up/off)



Spin-Orbit Coupling: 'Spin Splitting'

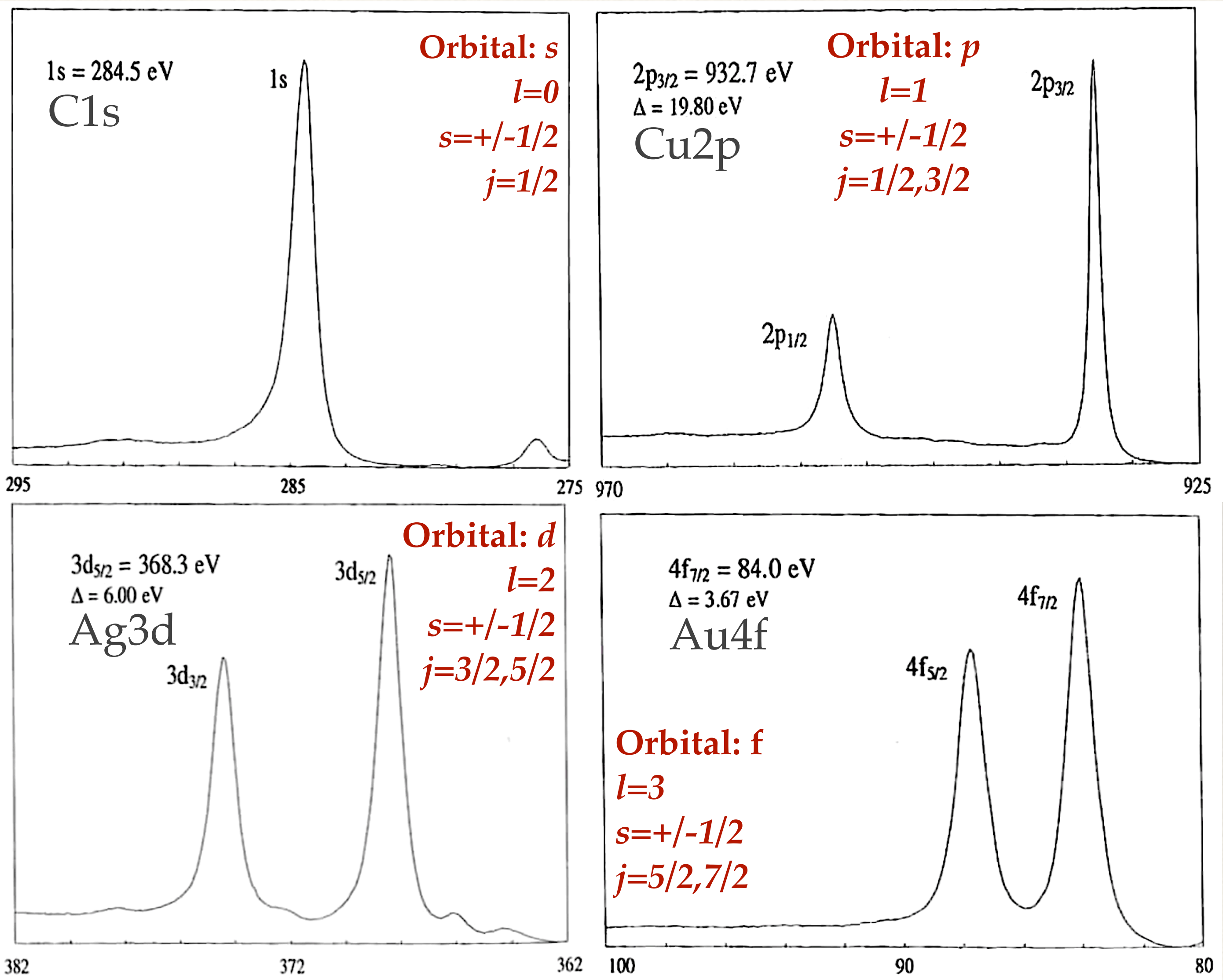
From the quantum mechanics nomenclature: ***nlj***

- *n* is the principal quantum number
- *l* is the angular momentum
- *j*=*l*+*s* is the total angular momentum, with s the spin angular momentum: +- 1/2

All the orbital except s will give rise to spin-splitting with the following area ratio.

Subshell	J value	Aera ratio
s	1/2	1
p	1/2, 3/2	1:2
d	3/2, 5/2	2:3
f	5/2, 7/2	3:4

The separation between the spin-splitted peaks is useful for the elemental determination

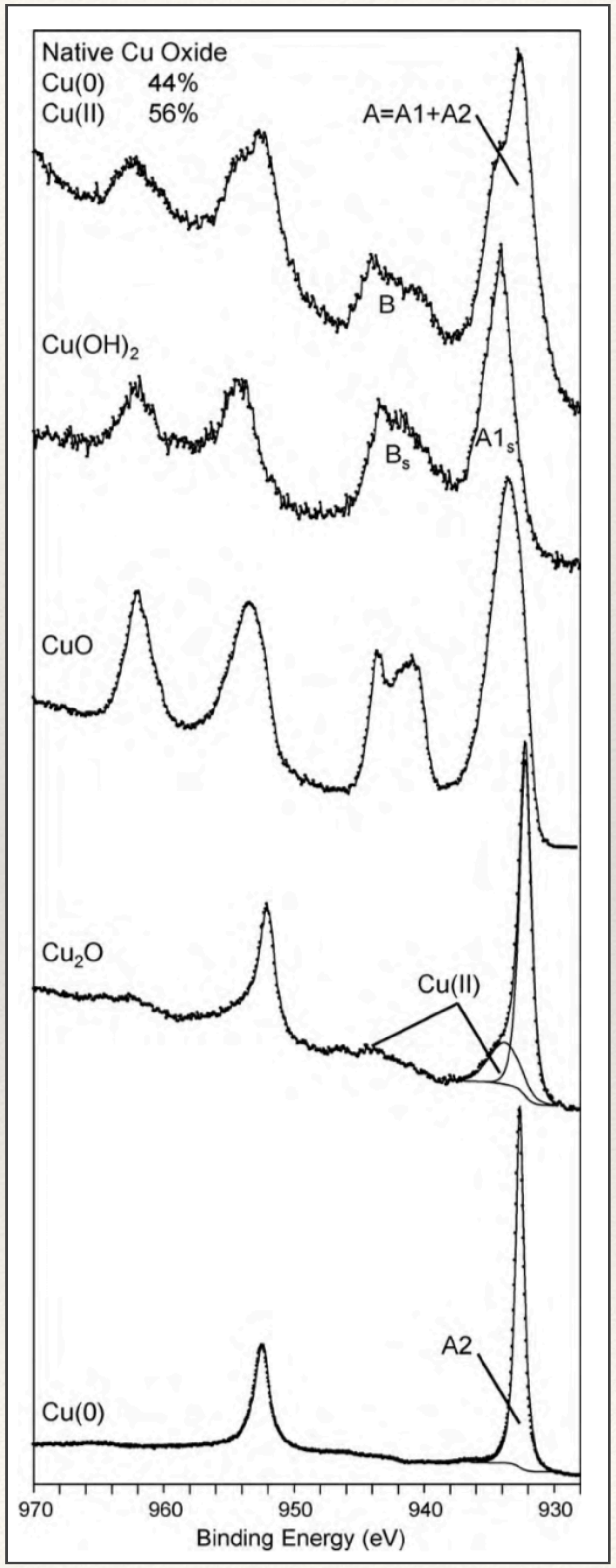


Ref. Spectra: Moulder et al.

Shake-up, Shake-off Satellites

Photoelectric processes do not necessarily lead to the formation of ions in the ground state. The ion might be left in an excited state, decreasing the kinetic energy of the emitted photoelectron. These line are the so-called shake-up satellite peaks.

- Copper oxide and hydroxide have large shake-up peaks, that might be used to determine its chemical state
- Aromatic carbon compounds have a characteristic shake-up line related to the energy of the $\pi \rightarrow \pi^{\star}$ transition.

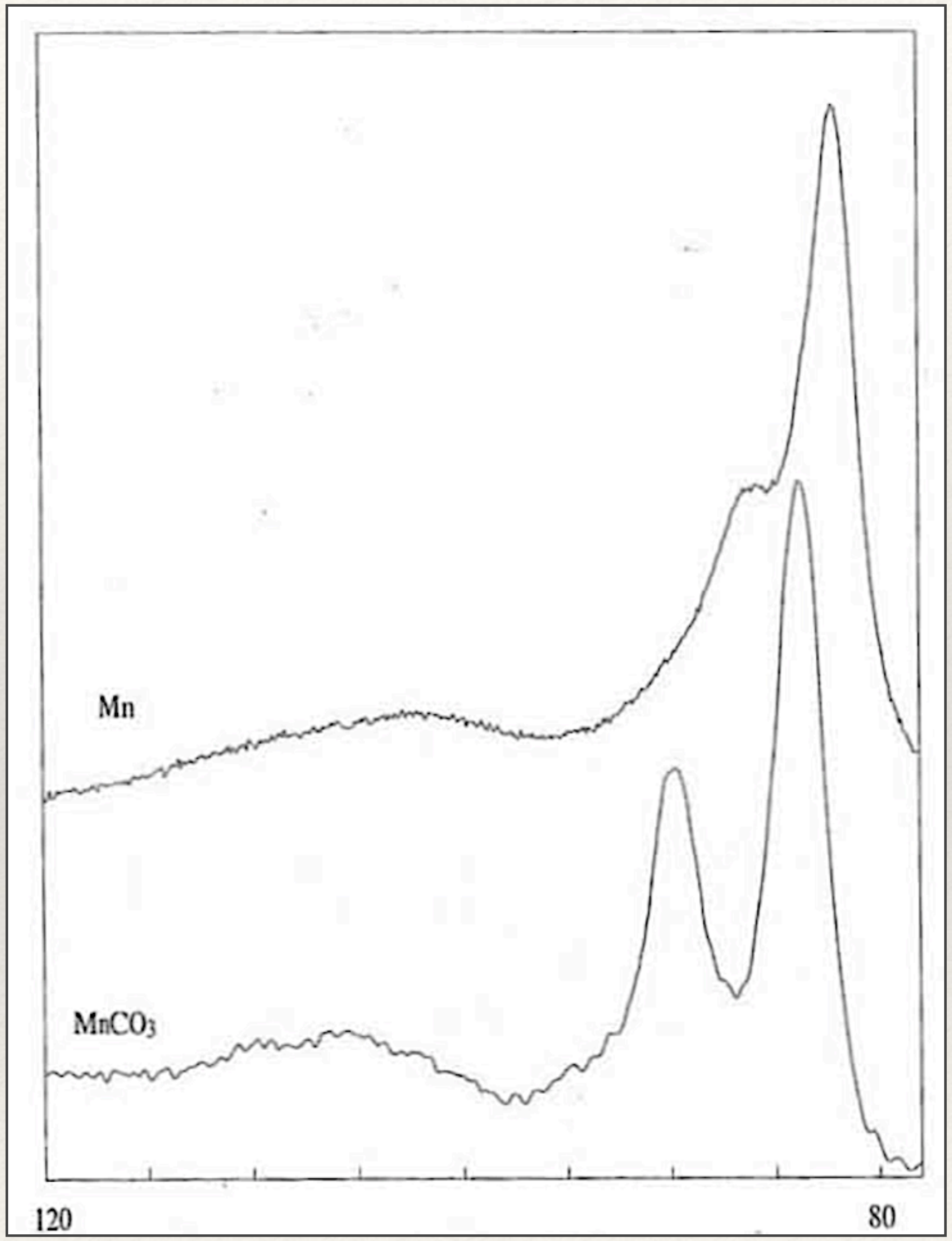


Ref: M. Biesinger et al. *Resolving surface chemical states in XPS analysis of first row transition metals, oxides and hydroxides: Sc, Ti, V, Cu and Zn.* Applied Surface Science 257 (2010)

Multiplet Splitting

The emission of a core level electron from an atom that has unpaired electrons in valence levels can create a vacancy in two or more ways. The coupling of the new unpaired electron left after photoemission from an s-type orbital with another unpaired electrons in the atom can create an ion with several possible final state configurations.

This results in a photoelectron line which splits asymmetrically into several components.



Mn 3s multiplet splitting, Moulder et al.

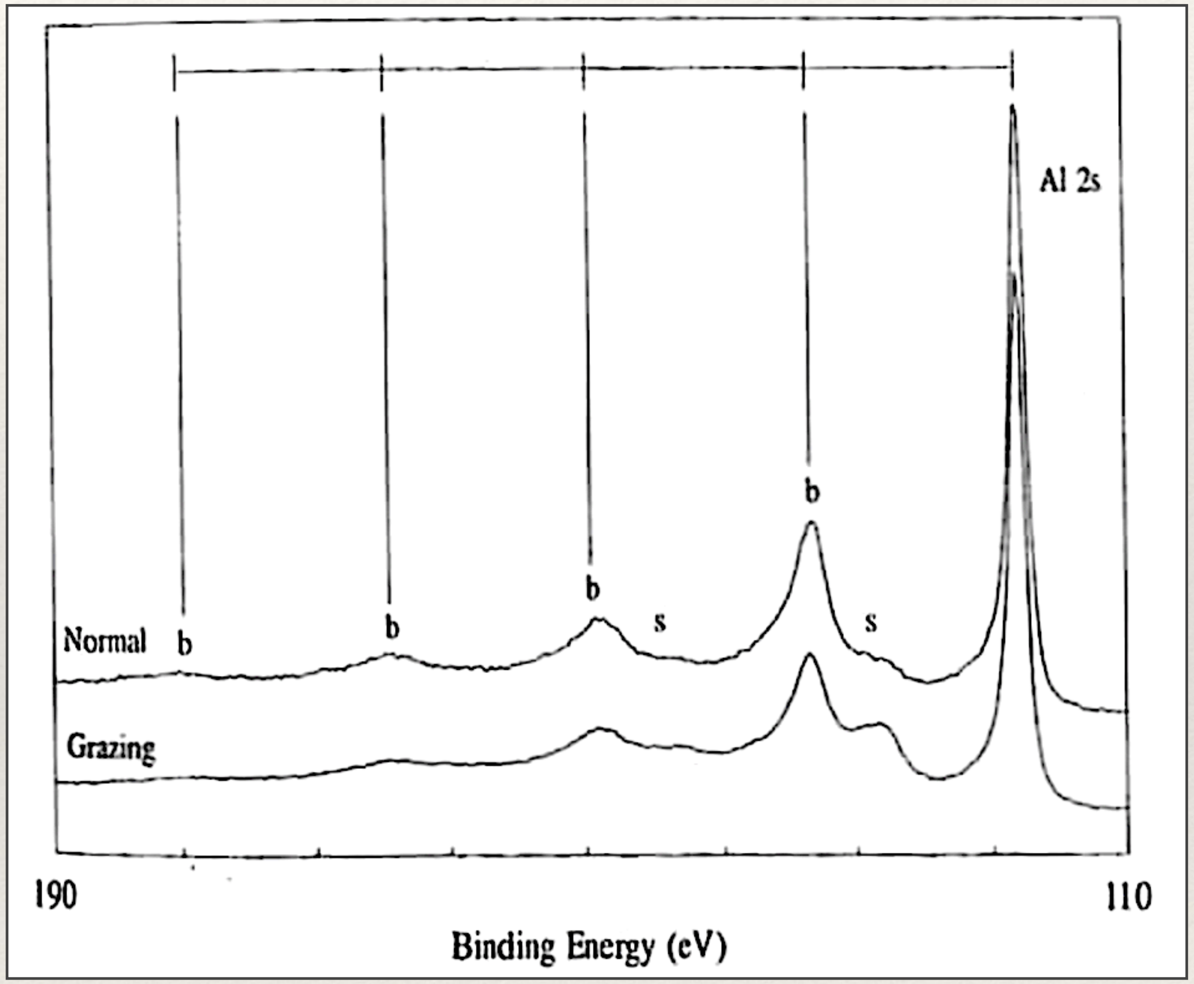
Energy Loss lines

The emission of secondary electrons from the interaction between matter and primary electron gives rise not only to the 'flat' background but also to the so-called energy loss peaks when a photoelectron, or an energetic secondary electron excites an electronic transition through some inelastic scattering:

$$e_{ph} + e_{solid} \rightarrow e^{\star}_{ph} + e^{\star\star}_{solid}$$

The excitation of plasmons (collective electronic oscillation) occurs in a quantified manner. The PE line is repeated at the interval of the plasmon energy with reduced intensity. The so-called bulk plasmons, B_p, are dominant, while the so-called surface plasmon $S_{p,}$ are minor lines

$$S_p = \frac{B_p}{\sqrt{2}}$$

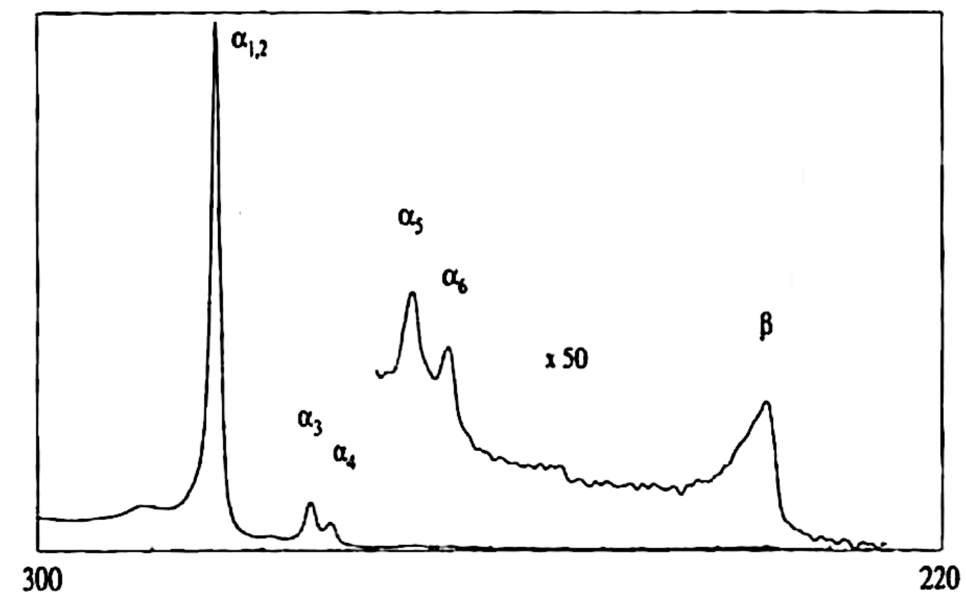


Bulk and surface plasmon in Al. Moulder et al.

Artefacts: X-Ray Satellites & Ghosts

Satellites: X-ray emission spectrum from a non-monochromatic source exhibits not only the characteristic X-ray but also some minor X-ray components at higher photon energies. Intensity and spacing are characteristics of the X-ray anode material.

Ghosts: X-ray from an element other than the anode material impinges upon the sample, resulting in small peaks displaced by a characteristic energy interval. These lines may result from Mg/Al, or Ag/Al anode cross-contamination, from the anode base structure, oxidation of the anode, generation of X-ray photons in the X-ray window (Al foil), or seldom from X-rays generation within the sample itself.



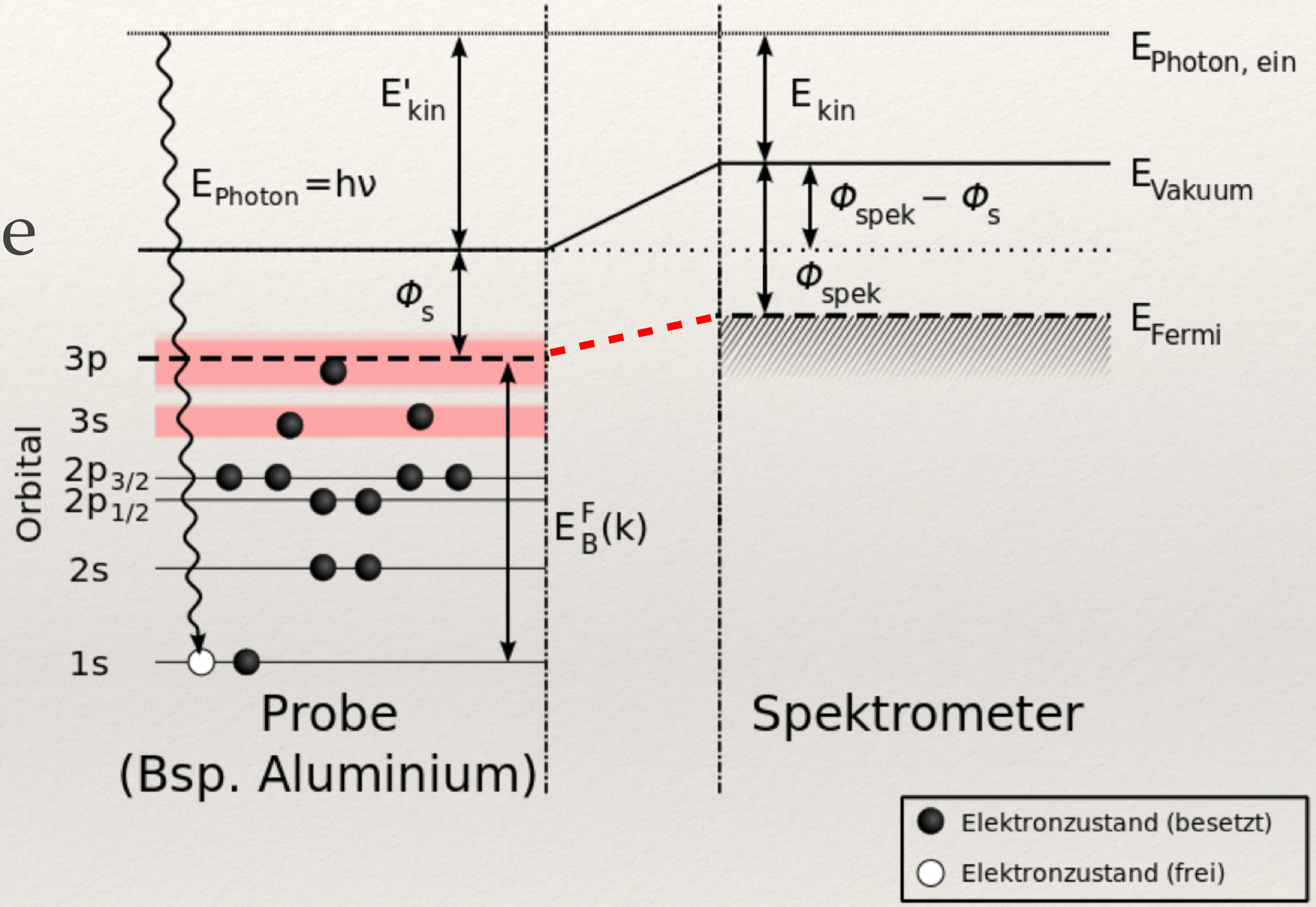
Mg X-ray satellites as observed in the C1s spectrum of graphite. Moulder et al.

	$\alpha_{1,2}$	α_3	α_4
Mg shift eV	0	8.4	10.1
Relative height	100	8.0	4.1
Al shift eV	0	9.8	11.8
Relative height	100	6.4	3.2

Table of the relative displacement of different X-ray transitions

Artefacts: Sample Charging

- Photoelectrons, X-Ray excited Auger electrons and secondary electrons contribute to a positive charging of the top surface of the sample
- Conductive samples can be grounded to balance the charging effect
- Insulating samples present a challenge



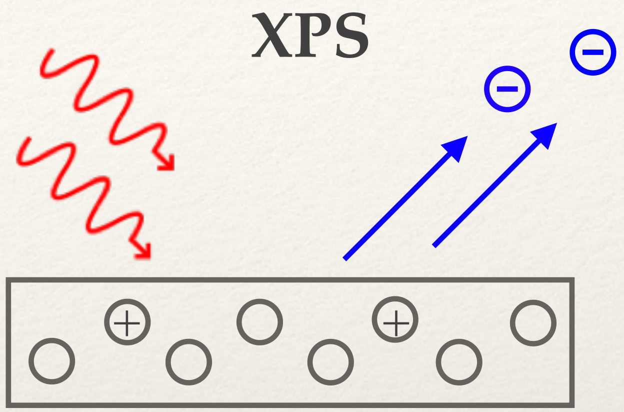
Energy referencing between an insulating sample and the spectrometer; Fermi levels are NOT aligned.

Static Charging

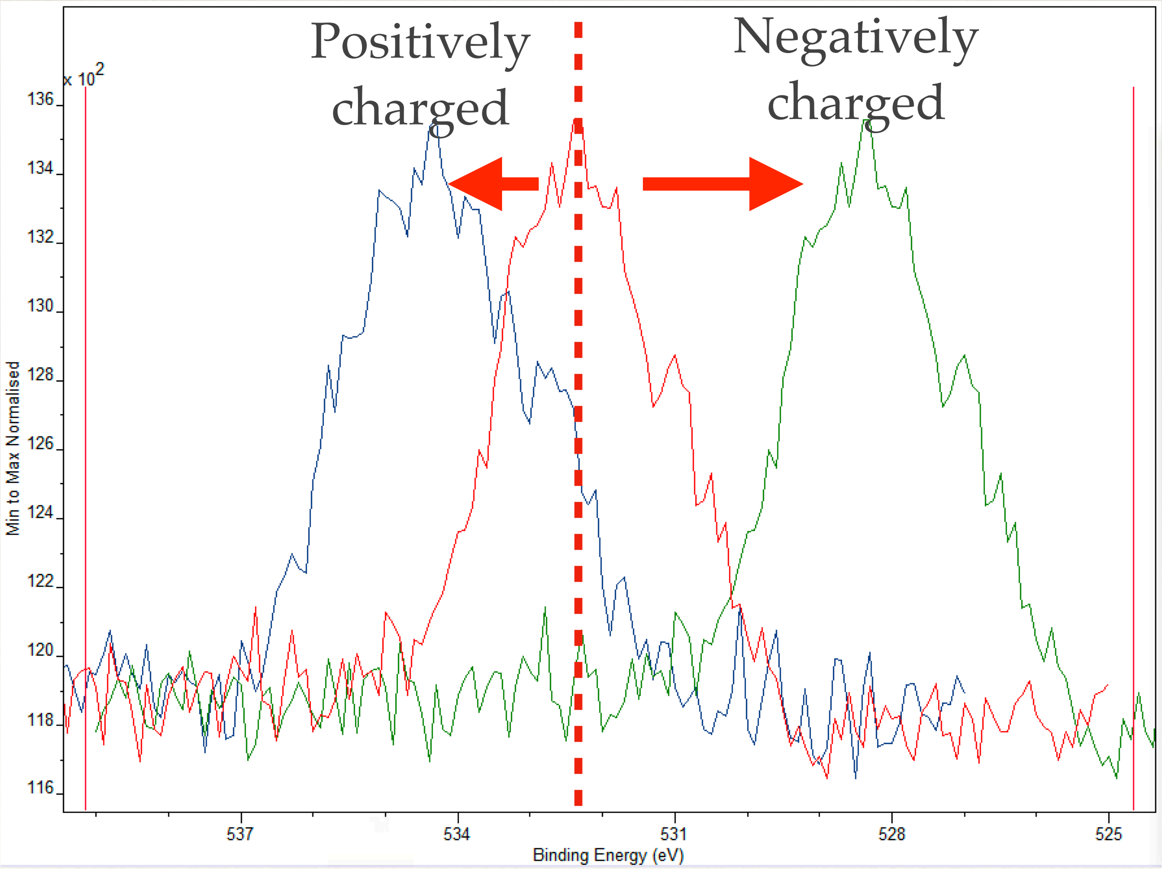
Sample charging is a function of the photoelectron and subsequent secondary electrons emission. In XPS, the charge build up shifts the KE (BE) energy towards lower (higher) energy. Charging induces peak shift, peak broadening and asymmetries, multiple peaks, reduced intensity etc…

Solutions:

- Thin gold or conductive coating
- Neutralize the charges, then:
- Calibration, e.g on C-C bound of the C1s line (not necessarily the best solution)



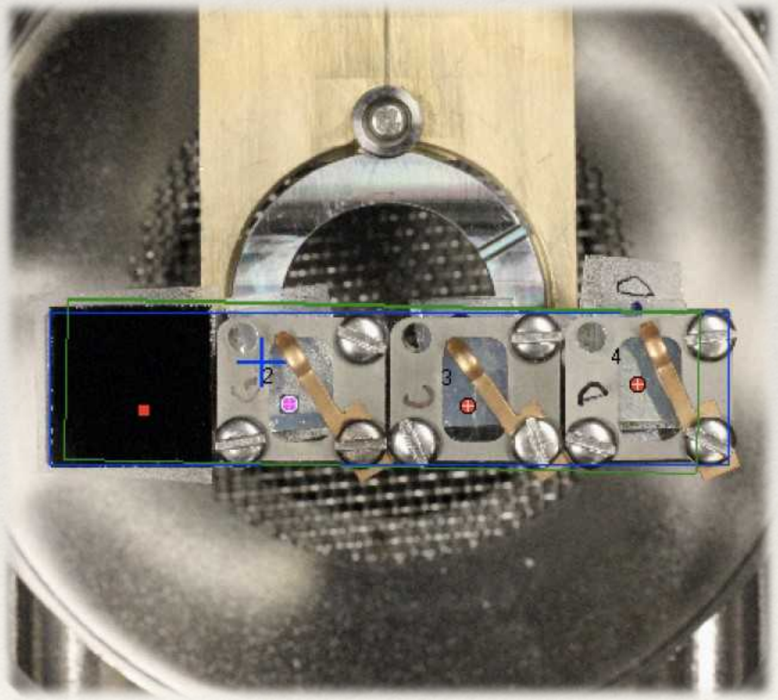
Photoelectrons interact with matter, generating secondary electrons



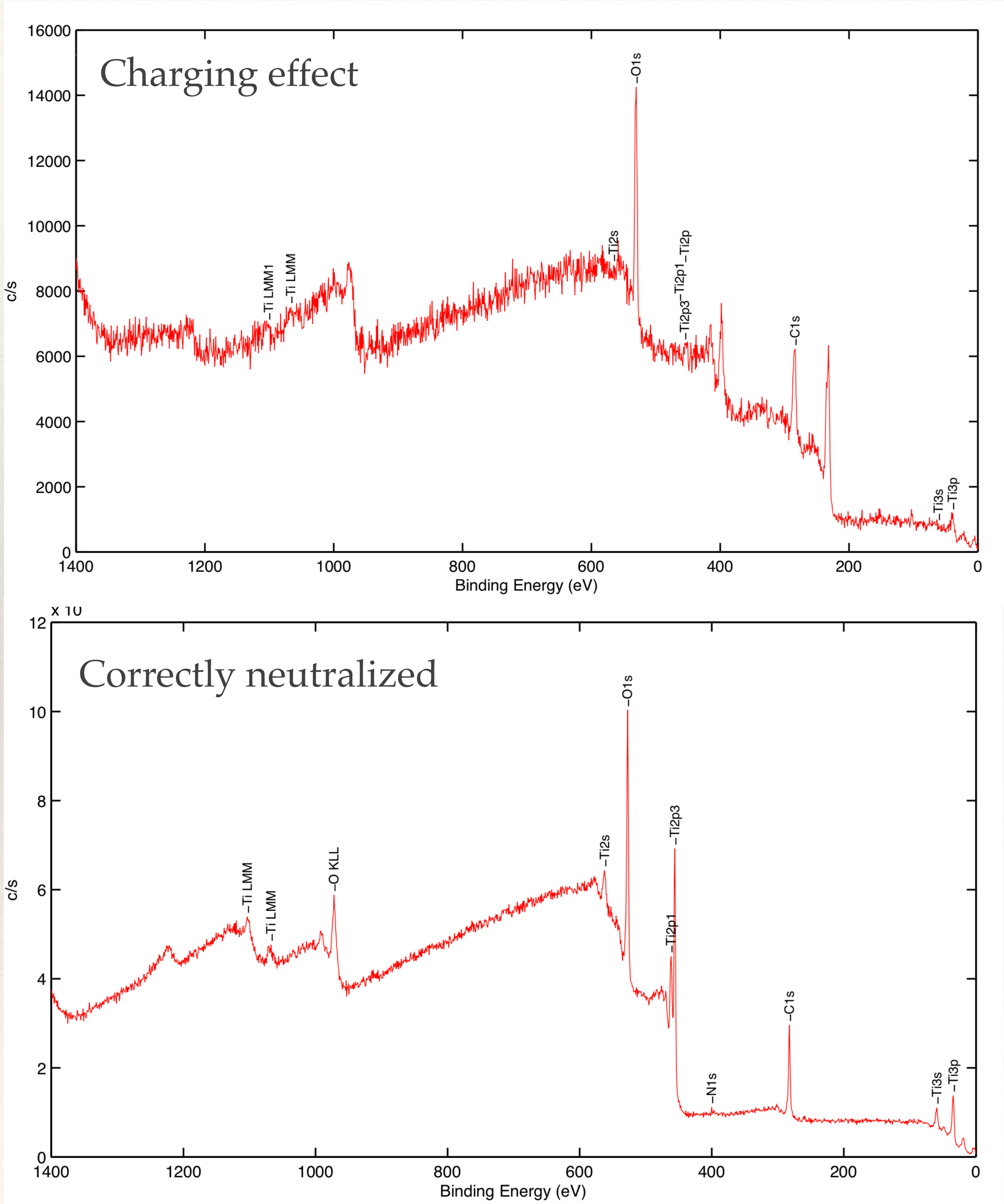
Insulating Samples

For dielectric samples, care has to be taken to avoid sample charging. Build up of charges at the surface might deform the spectra through

- Peak broadening
- Peak deformation



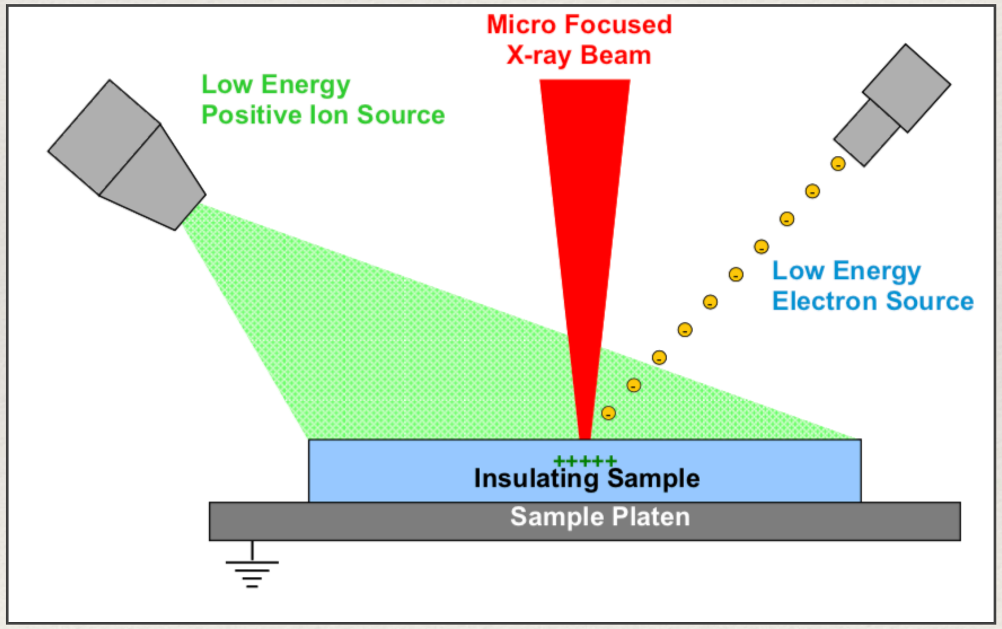
The samples are grounded, however, insulating sample exhibit some strong charging effects



Charge Neutralisation

To limit charging effects on dielectric samples, charge compensation has to be used:

- Efficiently compensates for accumulation of charges on the surface
- At equilibrium , i.e. if the electron intensity is high enough, the surface potential will be equal to the electron energy

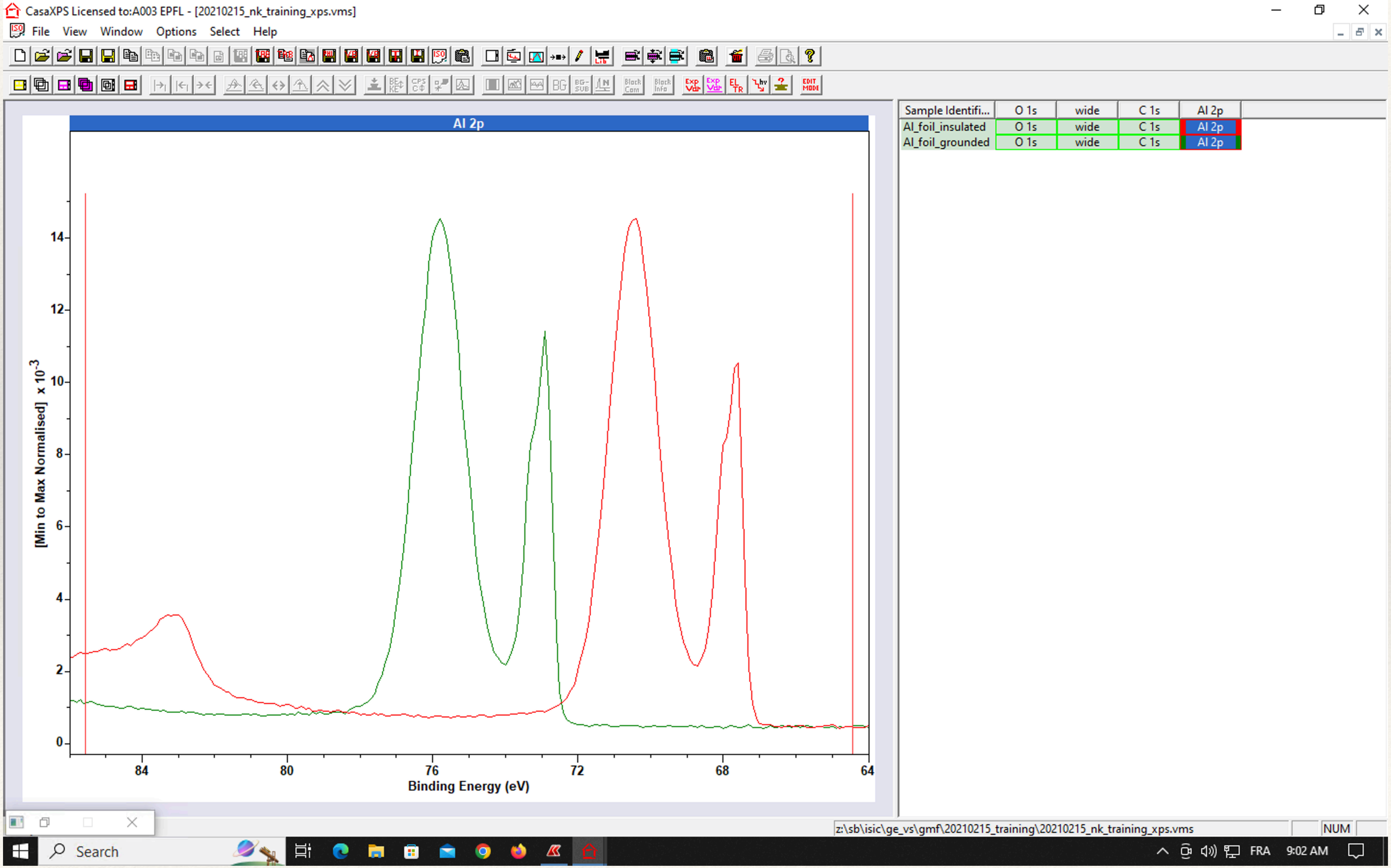


Dual charge compensation system
Source: Physical electronics

Typical systems:

- Electron flood gun (low energy electrons are ‘flooding’ the sample surface, efficiently neutralising positive charges
- Dual system, comprised of a low energy electron flood gun and a low energy ion gun

Energy ‘Referencing’



CasaXPS Licensed to:A003 EPFL - [20210215_nk_training_xps.vms]

Sample Identifi...	O 1s	wide	C 1s	Al 2p
Al_foil_insulated	O 1s	wide	C 1s	Al 2p
Al_foil_grounded	O 1s	wide	C 1s	Al 2p

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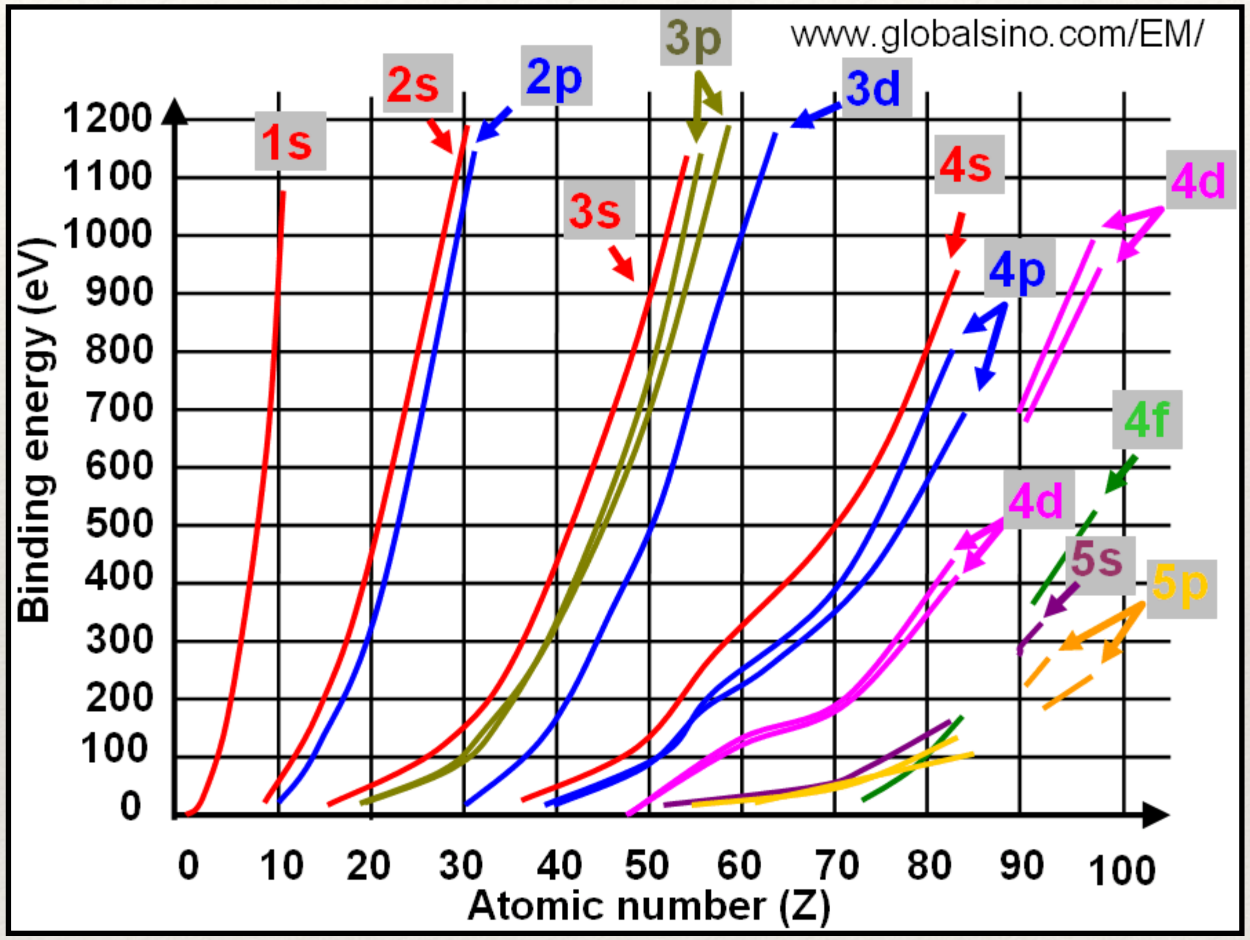
Istanbul Spices Market

‘Chemical Shift’

Origins and basic principle:
‘Flavours’ of an element

Binding Energy vs Z

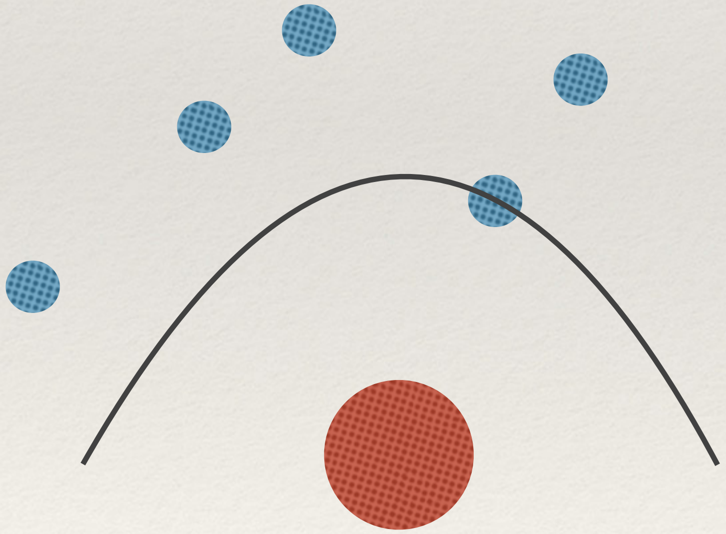
- Due to Coulombic attraction between the nucleus and the electronic orbitals, the BE increases with Z (for the same line of the periodic table)
- For the same reason the BE remains mostly unaffected by isotopes
- **But: Coulombic force is screened by valence electron, hence chemical shift**



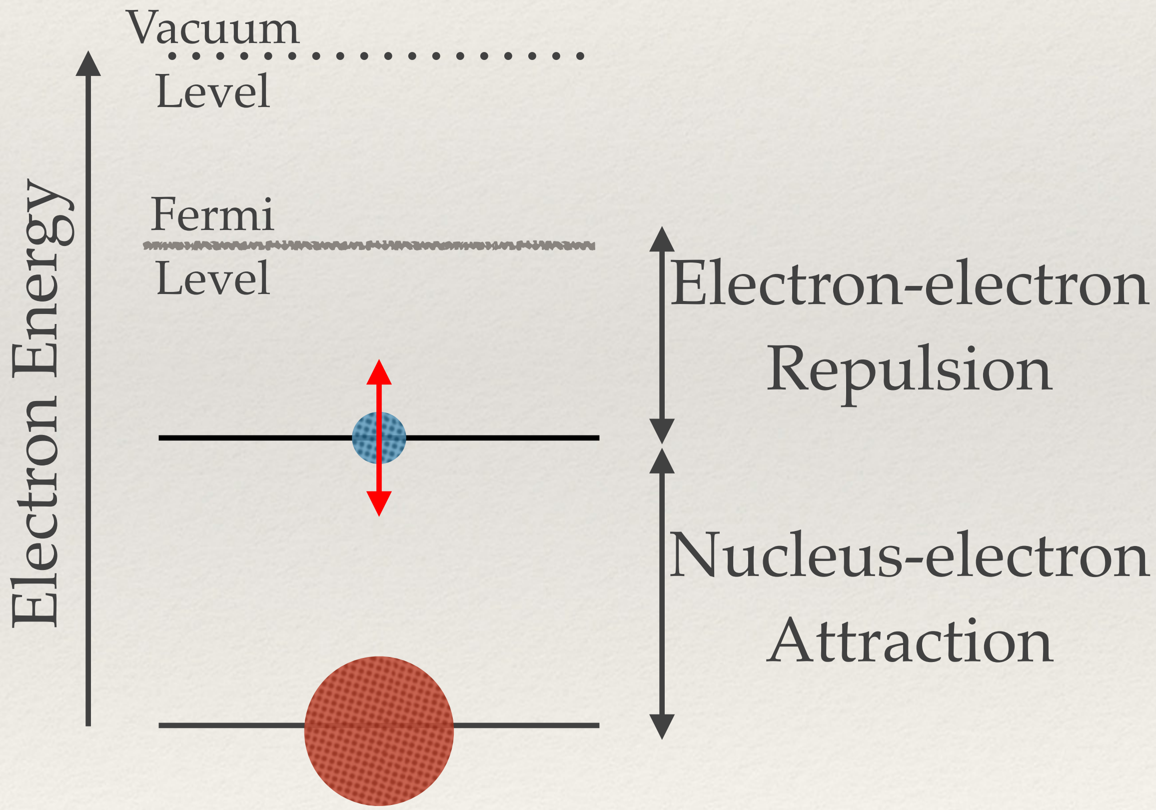
Electron binding energy vs atomic number Z, for low binding energies

XPS ‘vs’ ESCA: Chemical Shift

- Initially called Electron Spectroscopy for Chemical Analysis (ECSA) by K. Siegbahn, XPS reveals its full potential due to the **chemical shift**, i.e. BE shift, arising from the displacement of electronic orbitals upon changes in the atomic charge distribution
- K. Siegbahn showed that the chemical shift is a linear function of the net charge transfert in chemical bounding



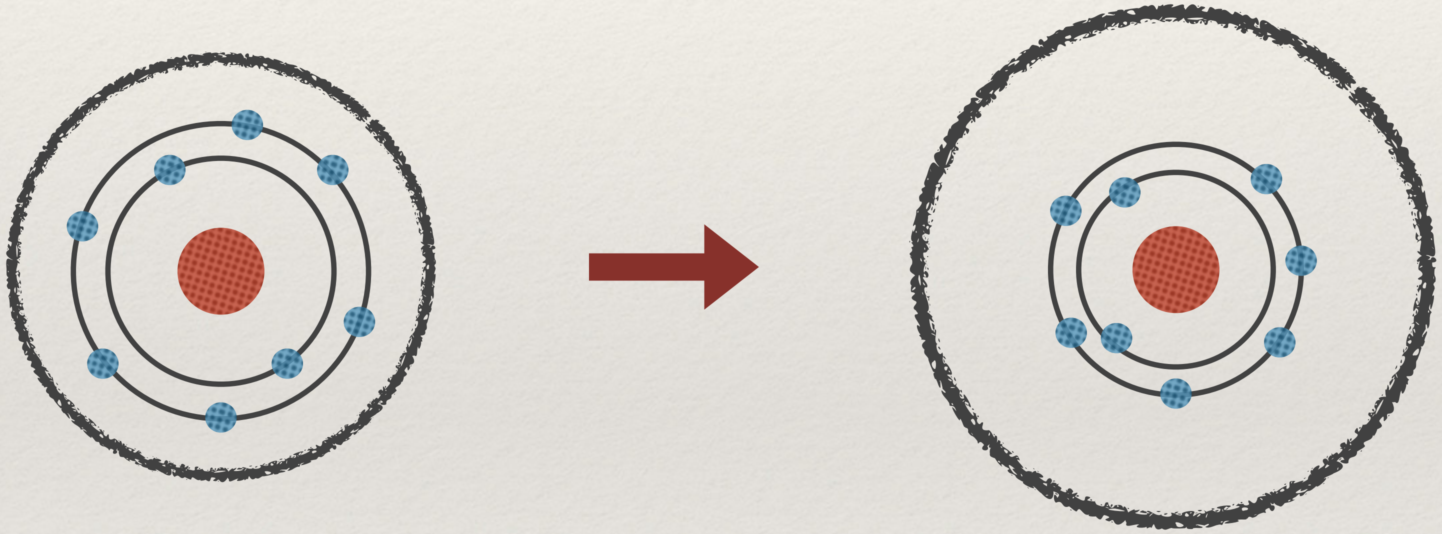
Atomic viewpoint



Energy viewpoint

Binding Energy vs Electronegativity

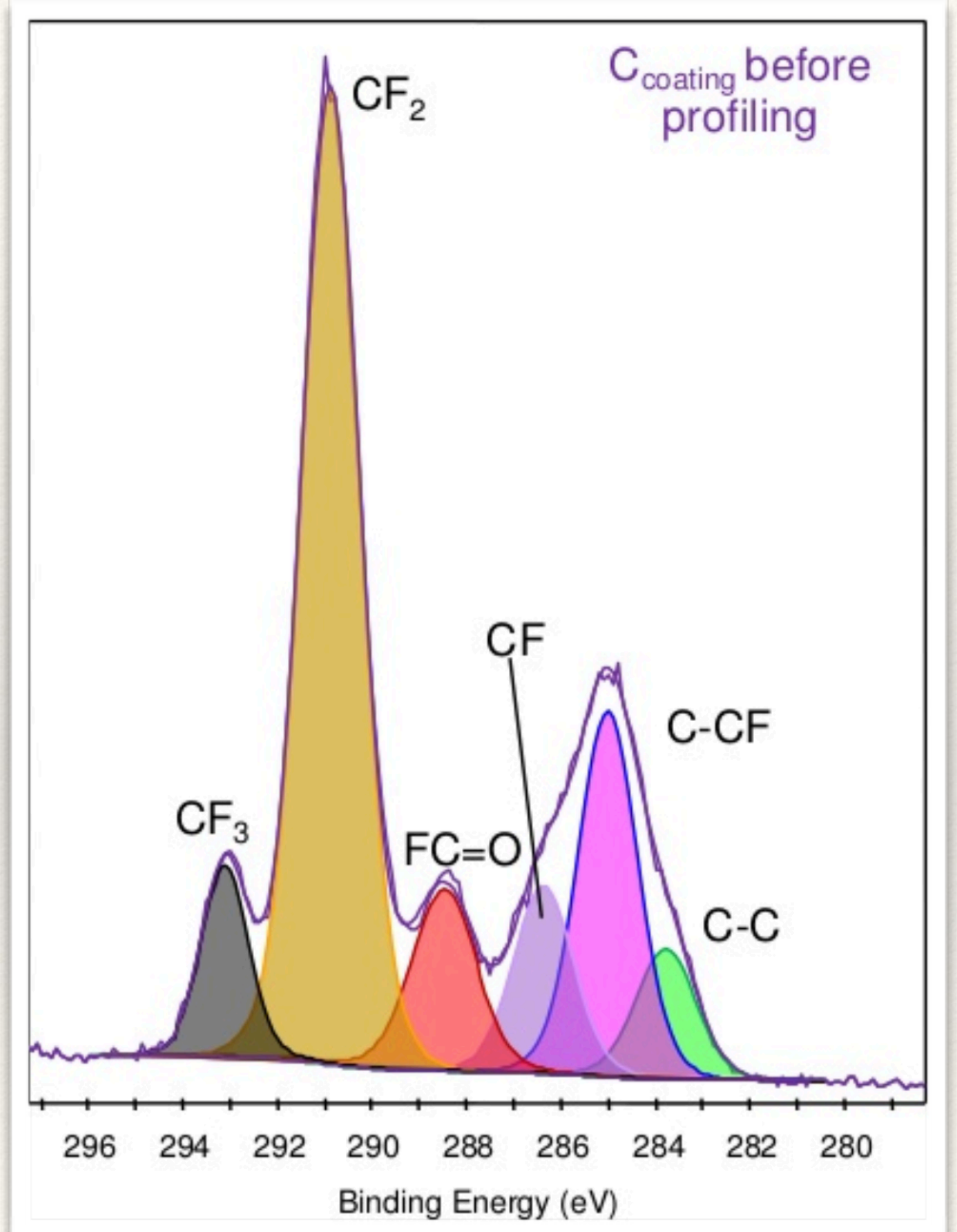
- When a covalent bond is created, electron density is increased at the more electronegative partner.
- The average radius of the valence band of the ‘donor partner’ increases
- Due to a decrease in the valence electrons screening, the core electrons are shifted towards the nucleus, and therefore increasing their binding energy, hence the ‘chemical shift’

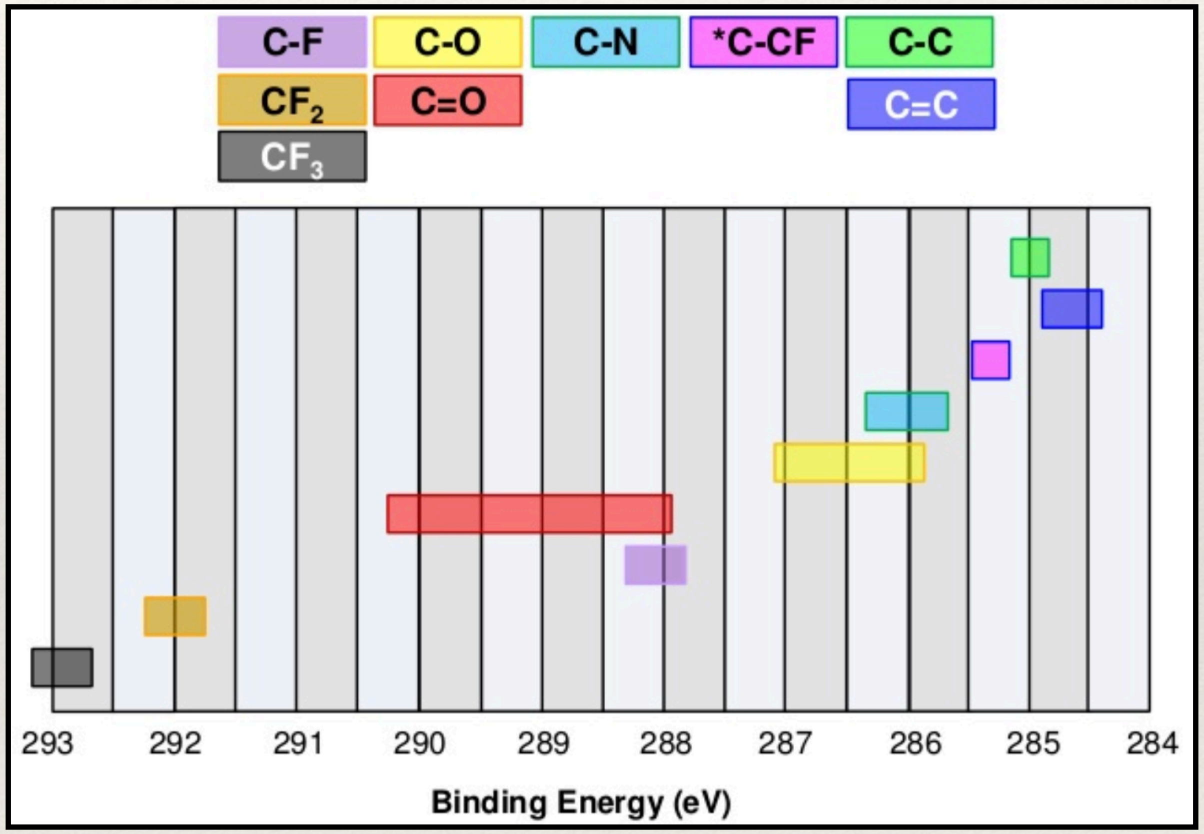


Group		BE eV
hydrocarbon	C-H, C-C	284-285
Amine	C-N	285.6
Alcool	C-O-H, C-O-C	286.5
Cl bound	C-Cl	287.0
F bound	C-F	287.8
Carbonyl	C=O	288.0

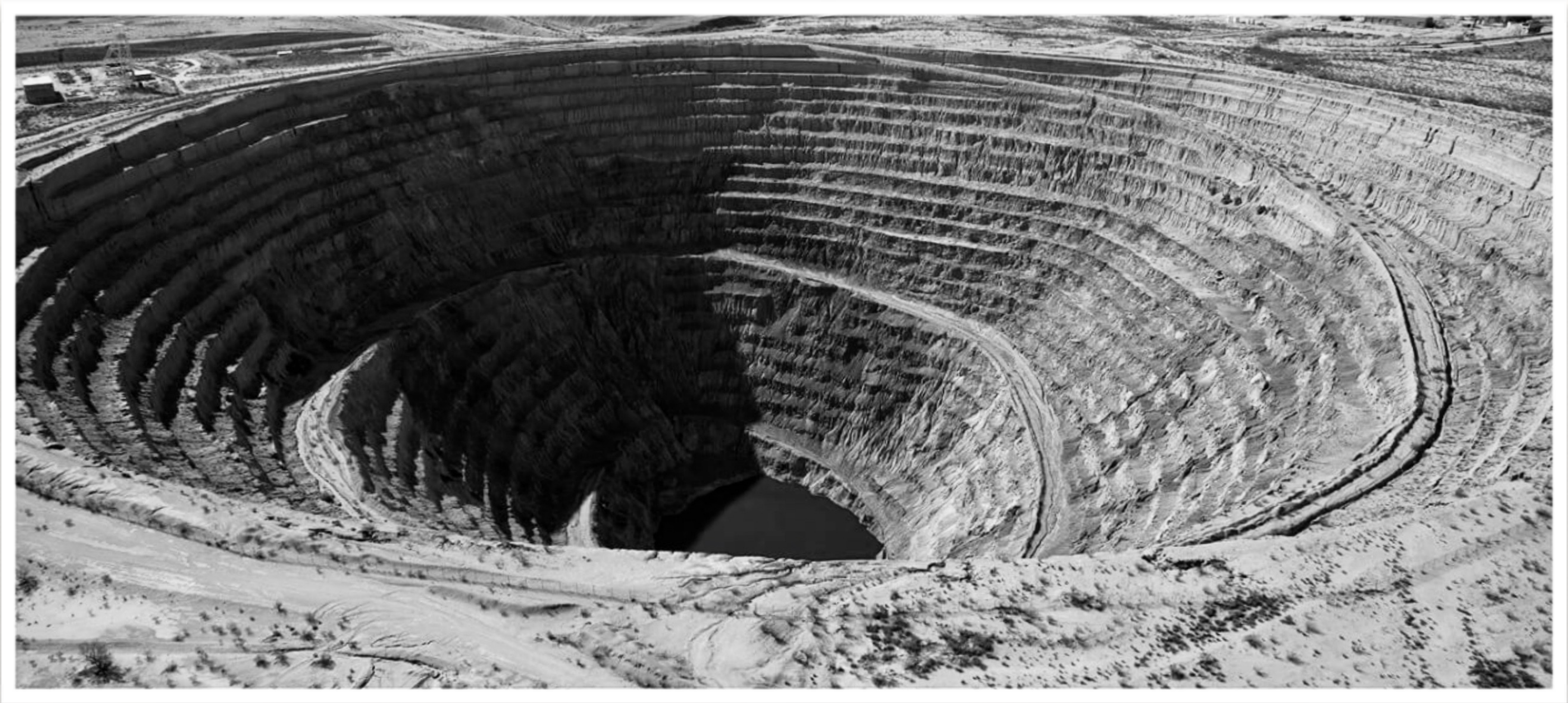
Electronegativity

Fluoropolymer C1s line





Source: Thermo-Fisher database



Copper Mine

Contamination & Beneath the Surface

Ar+ and GCIB for

- Surface cleaning
- Depth Profiling

Preparing and Mounting the Sample

In the majority of XPS applications, sample preparation and mounting are not critical. However, to ensure a clean working sample, several conditions have to meet. Aside from volatile material which are naturally removed by the UHV present in the analysis chamber.

- Abrasion (e.g. elimination of an oxide layer)
- Sputter etching (e.g. removal of organic contaminants)
- Fracturing (e.g. reveals a fresh surface)
- Ground to powders (mounted onto a vacuum compatible tape)

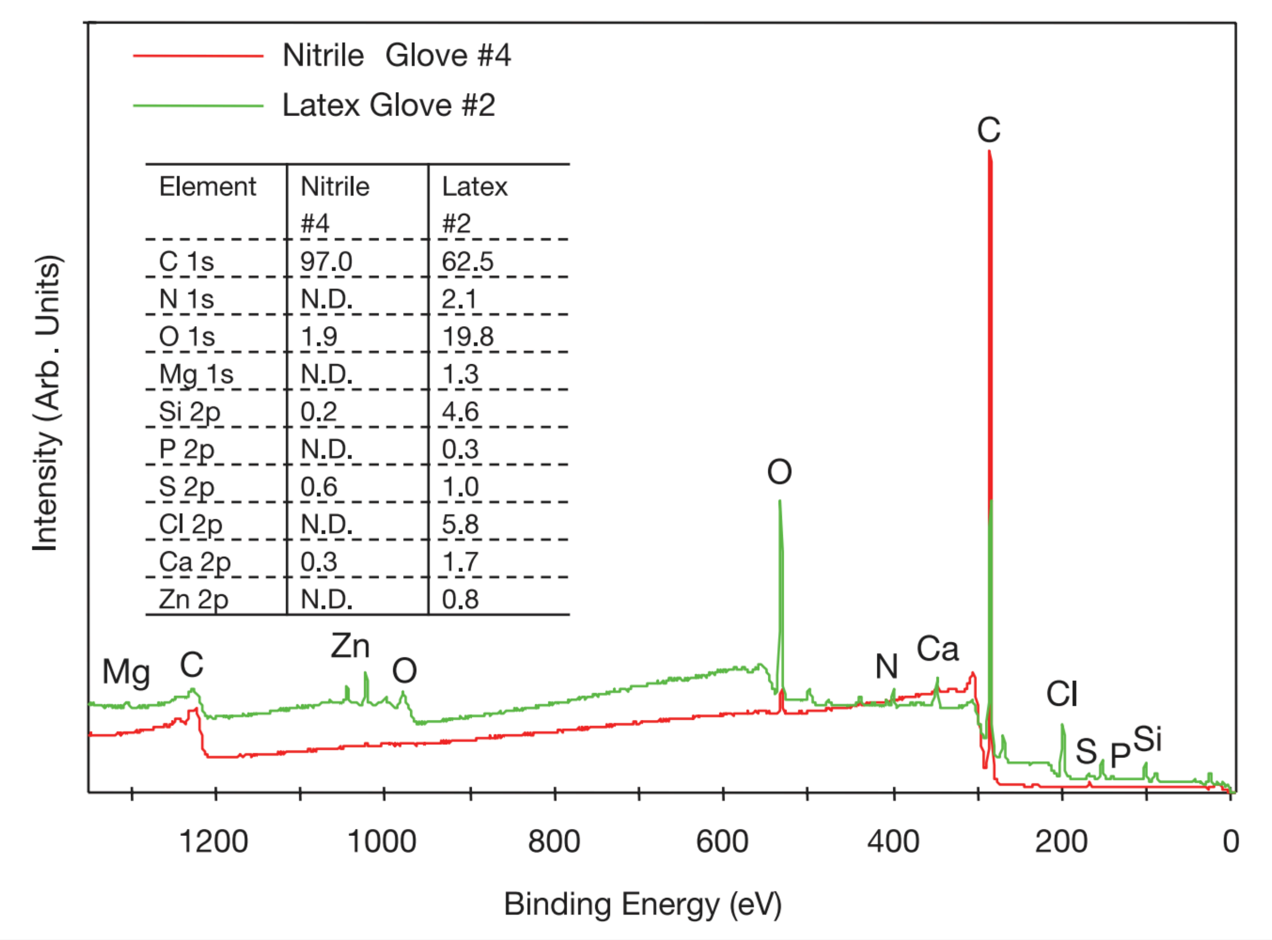
So…what can go wrong?

Study Case I: Clean Gloves?

15 different pairs of lab gloves have been measured by XPS. The results show that the surfaces composition can vary to a large degree.

Nitrile glove had only a small amount of oxygen present plus a few minor surface components (e.g., Si, S, and Ca).

Latex glove had much lower carbon and approximately ten times the oxygen present along with significant amounts of N, Mg, Si, S, Cl, and Ca, plus minor amounts of P and Zn.



Element	Nitrile #4	Latex #2
C 1s	97.0	62.5
N 1s	N.D.	2.1
O 1s	1.9	19.8
Mg 1s	N.D.	1.3
Si 2p	0.2	4.6
P 2p	N.D.	0.3
S 2p	0.6	1.0
Cl 2p	N.D.	5.8
Ca 2p	0.3	1.7
Zn 2p	N.D.	0.8

XPS survey spectra of the outer surfaces of nitrile and latex gloves and quantitative (atomic %) results

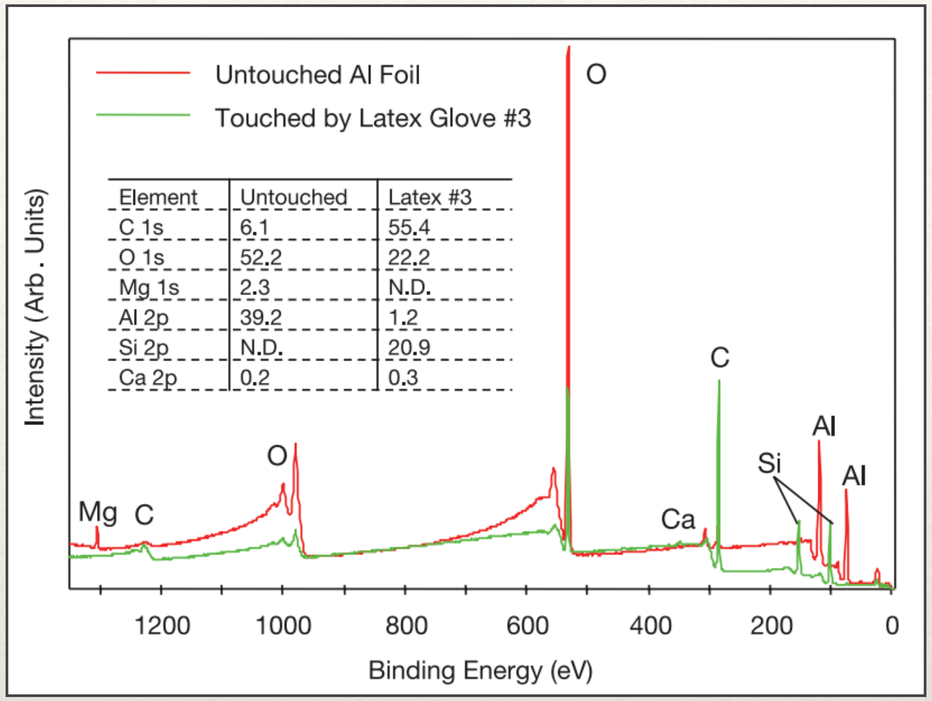
Full article from Thermo-Fisher: http://www.revbase.com/tt/sl.ashx?z=73090c66&dataid=433139&ft=1

Study Case I: Cross Contamination

What happens under contact between the gloves and a sample surface is much more interesting:

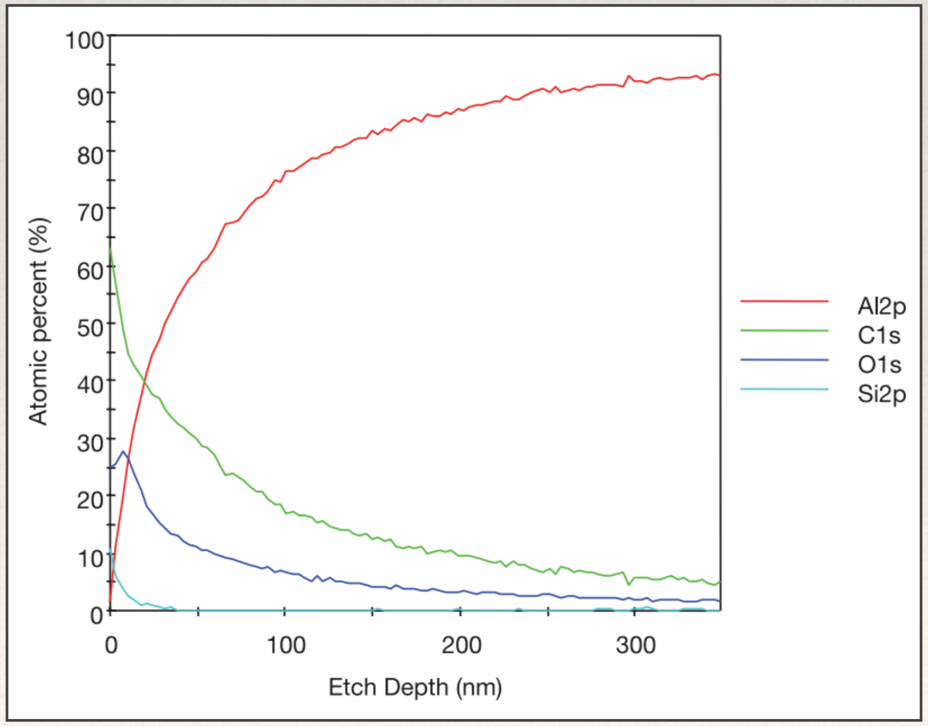
- The sample is covered by carbon!
- Additional contaminants are presents

When handling surface for surface analysis or where surface cleanliness is a priority, **clean** handling tools should be used. Never gloves



Element	Untouched	Latex #3
C 1s	6.1	55.4
O 1s	52.2	22.2
Mg 1s	2.3	N.D.
Al 2p	39.2	1.2
Si 2p	N.D.	20.9
Ca 2p	0.2	0.3

Survey spectra

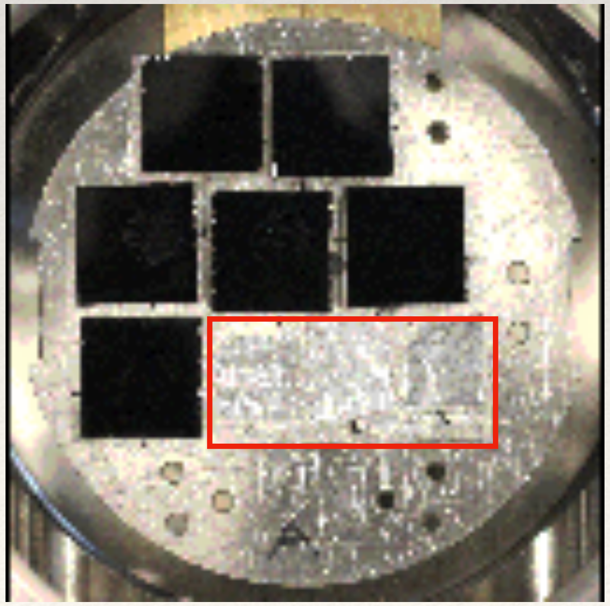


Depth Profile

Sample Mismanipulation

An Aluminium foil is used as a clean sample for the evaluation of the sensitivity of surface preparation in view of XPS measurements. Three samples are prepared as follow:

- Sample 1: Clean sample manipulated exclusively with metallic tweezer and stored wrapped in a clean Al foil
- Sample 2: Clean sample mis-manipulated by touching with gloves
- Sample 3: Clean sample mistreated by touching with bare fingers

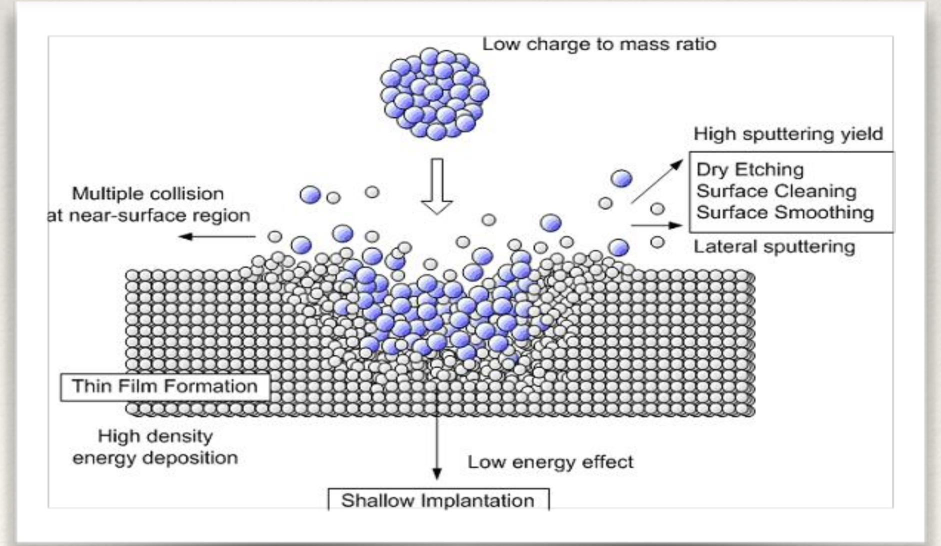


Sample stage with our 3 samples mounted on an insulating, vacuum compatible, double sided tape

Surface Contamination

When handling surface for surface analysis, where surface cleanliness is a priority, **clean handling tools should be used**. Never gloves.

But ok…the contaminant is there…so let's try to remove it!



Sputter tests on contaminated sample

- Use of an Ar+ sputtering
- Argon ion cluster sputtering

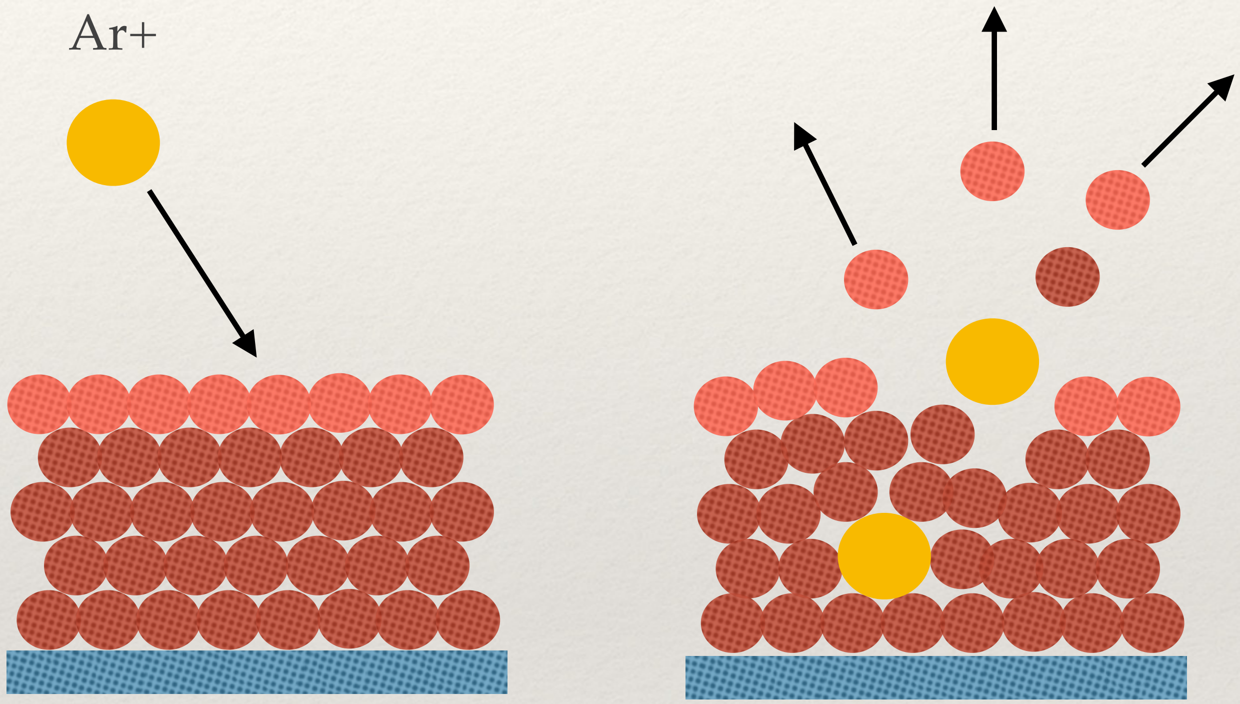
Surface Sputtering

Now that we have surface contaminated samples, either by adventitious atmospheric contamination, surface adsorption or simply by mismanipulation, what can we do?

- Sputter clean the surface: Argon ion / Gas cluster ion beam sputtering. But ion sputtering offers much more than surface cleaning!
- Measure beneath the surface: High energy XPS and ARXPS (next course)

Argon Ion Sputtering Principle

Argon ions are accelerated (typically 0.1– 10 keV), towards the surface of the sample, efficiently sputtering the surface, removing contamination, but also creating damages on the surface.



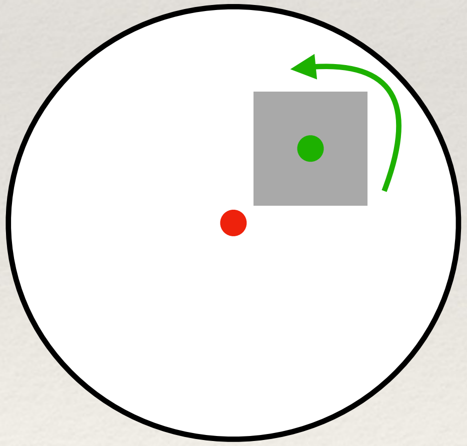
Sputtering, surface cleaning…and damages

Surface Cleaning Limitations

The efficiency and feasibility of organic contaminants removal largely depends on:

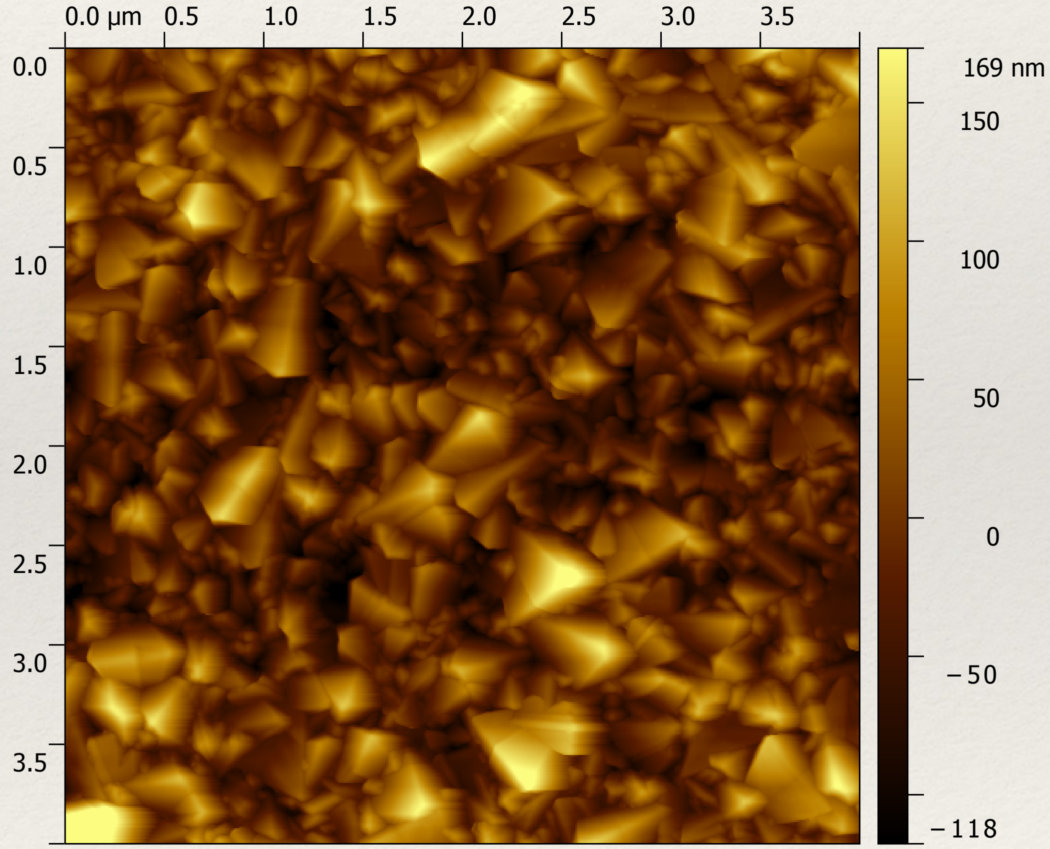
- The sample material: Organic contaminants could be easily cleaned-out from metallic surfaces leaving the main material virtually undamaged

- The sample topography/structure: Sharp angles prevent the ion beam to efficiently sputter the whole sample surface. compucentric/Zalar rotation might be use.



Rotation axis intersects
The sputter spot,
and not the center
of the sample stage

Schematics of a
compucentric rotation

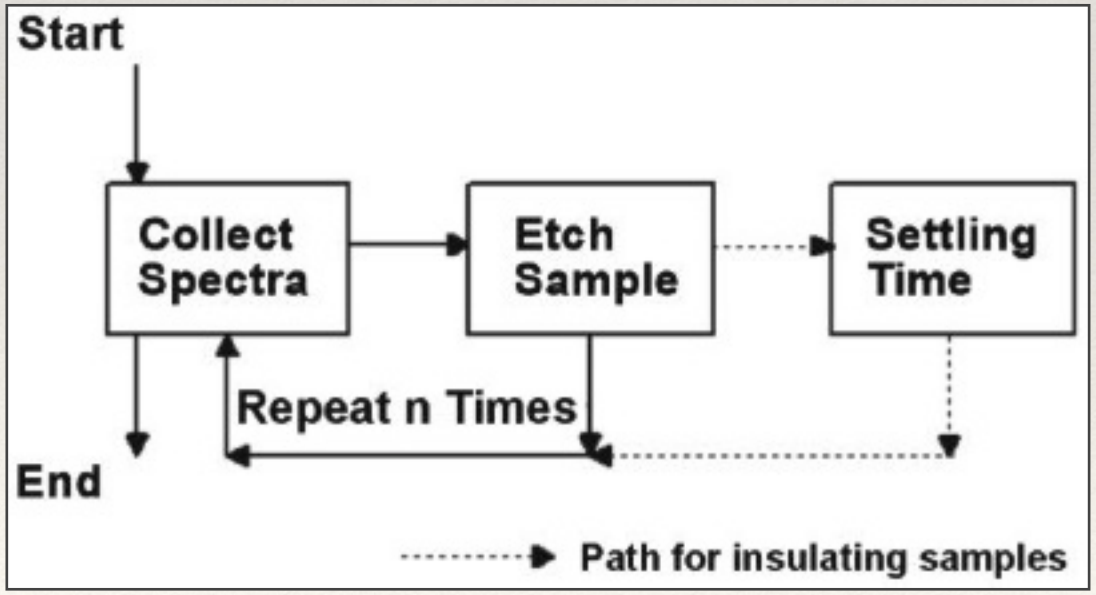


Topography of a typical FTO surface. Due to the surface roughness, ion sputtering would prove relatively inefficient

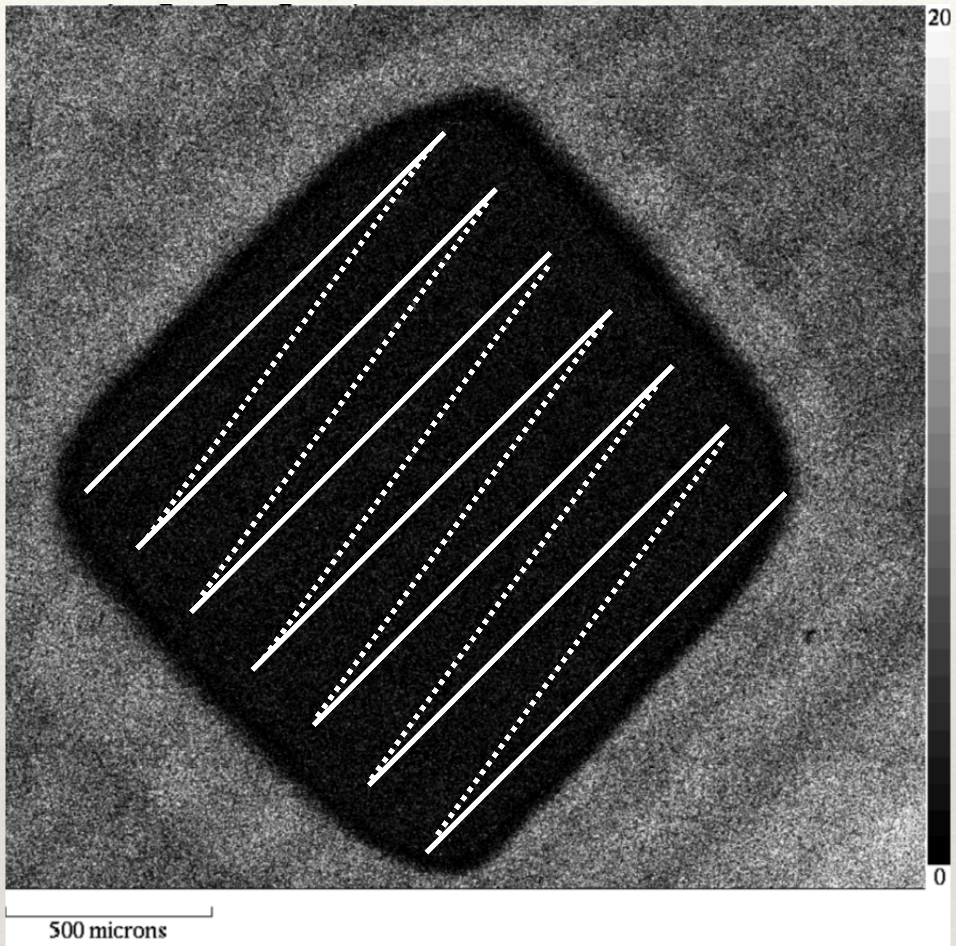
Depth Profiling

Depth profile is acquired using experimental loop (Zalar rotation possible):

1. A spectra is collected (survey or multiplex)
2. The surface is sputtered



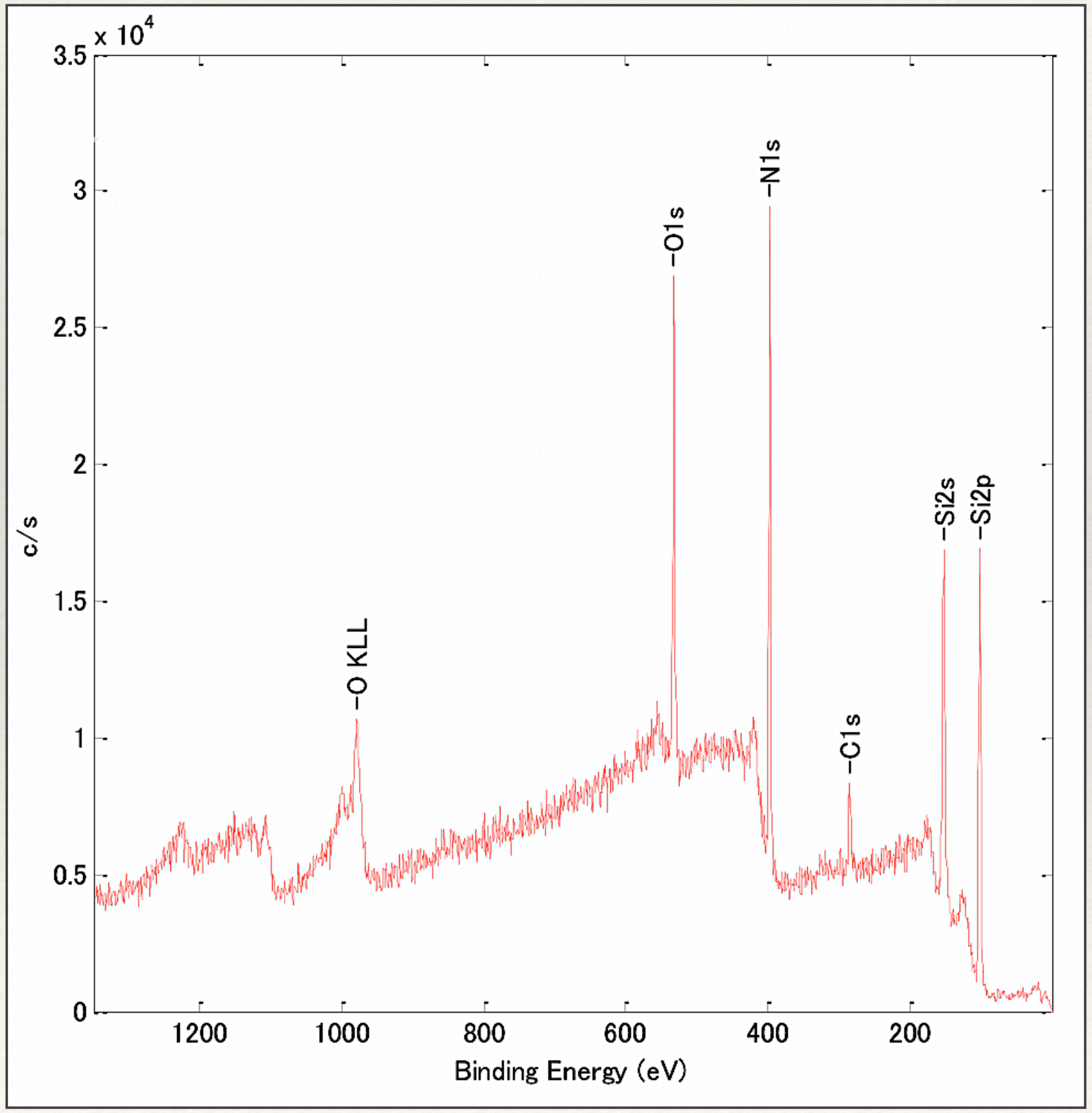
Typical cycle used for depth profiling

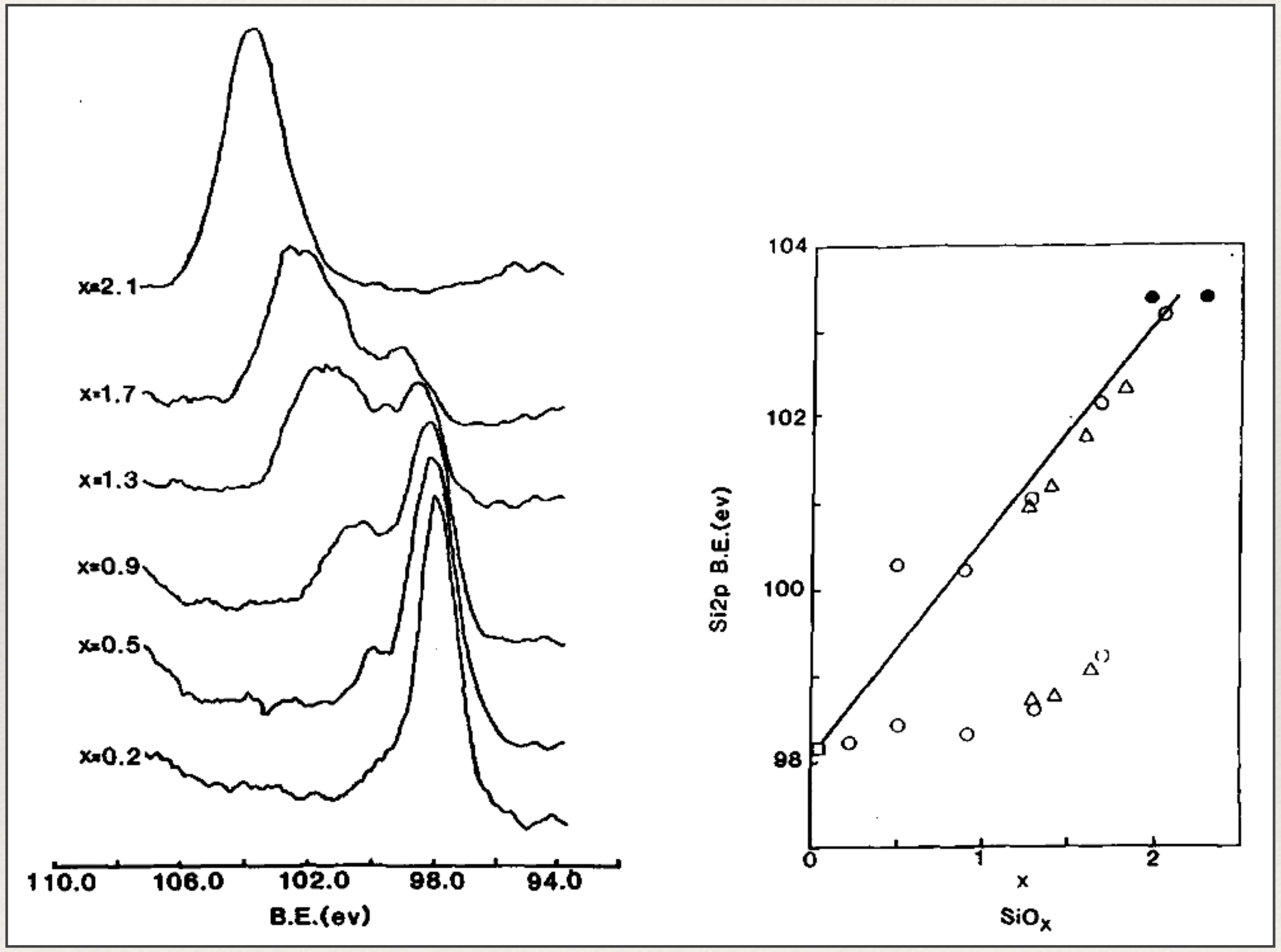


The ion beam is typical focused to a spot of 100um, and raster scanned, creating a sharp edged created

Si_3N_4 on Si

Surface properties: the top surface presents C, O, N and Si. A detailed analysis of the binding energy of Si, shows a some SiO_x, which is could be explained by surface modification after the deposition

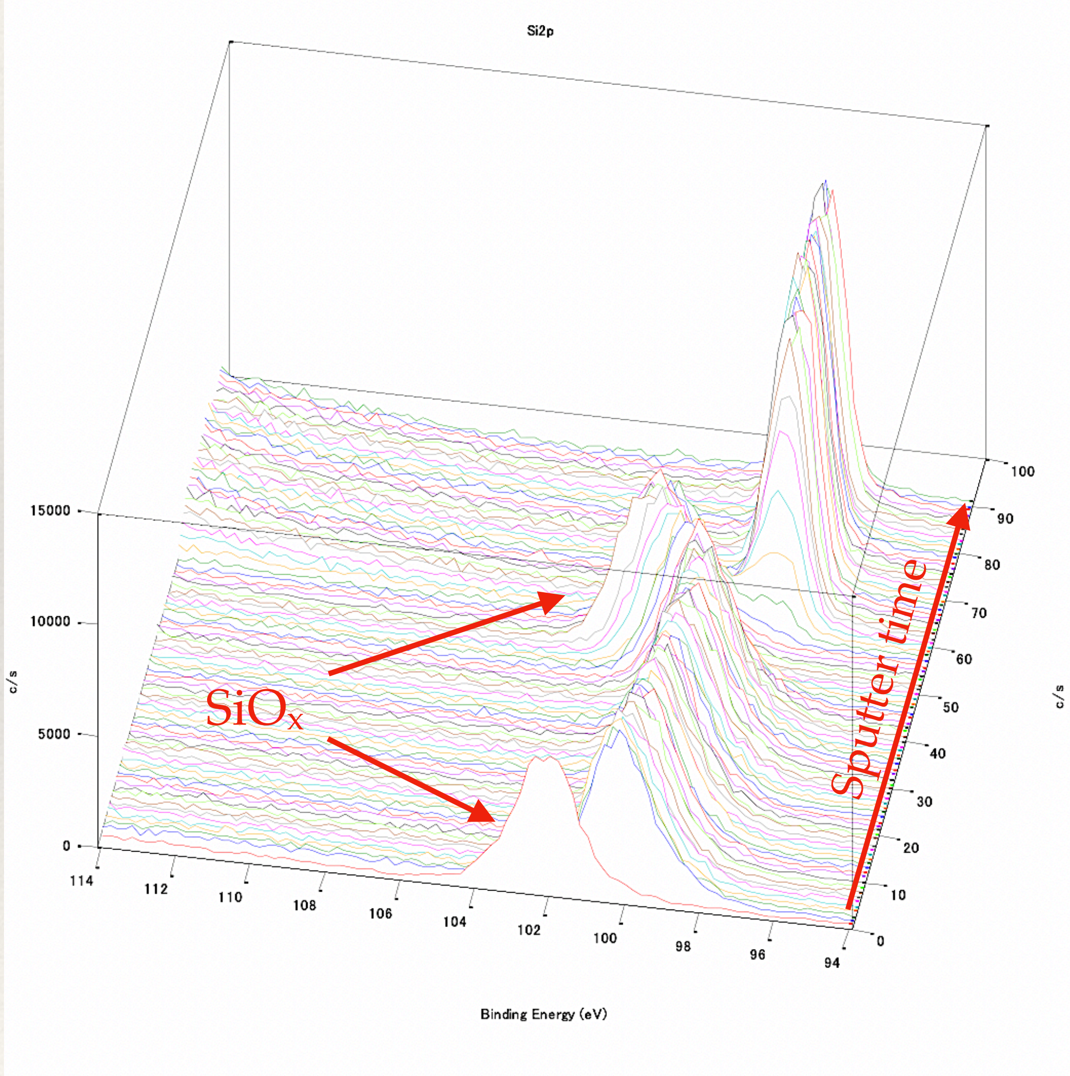




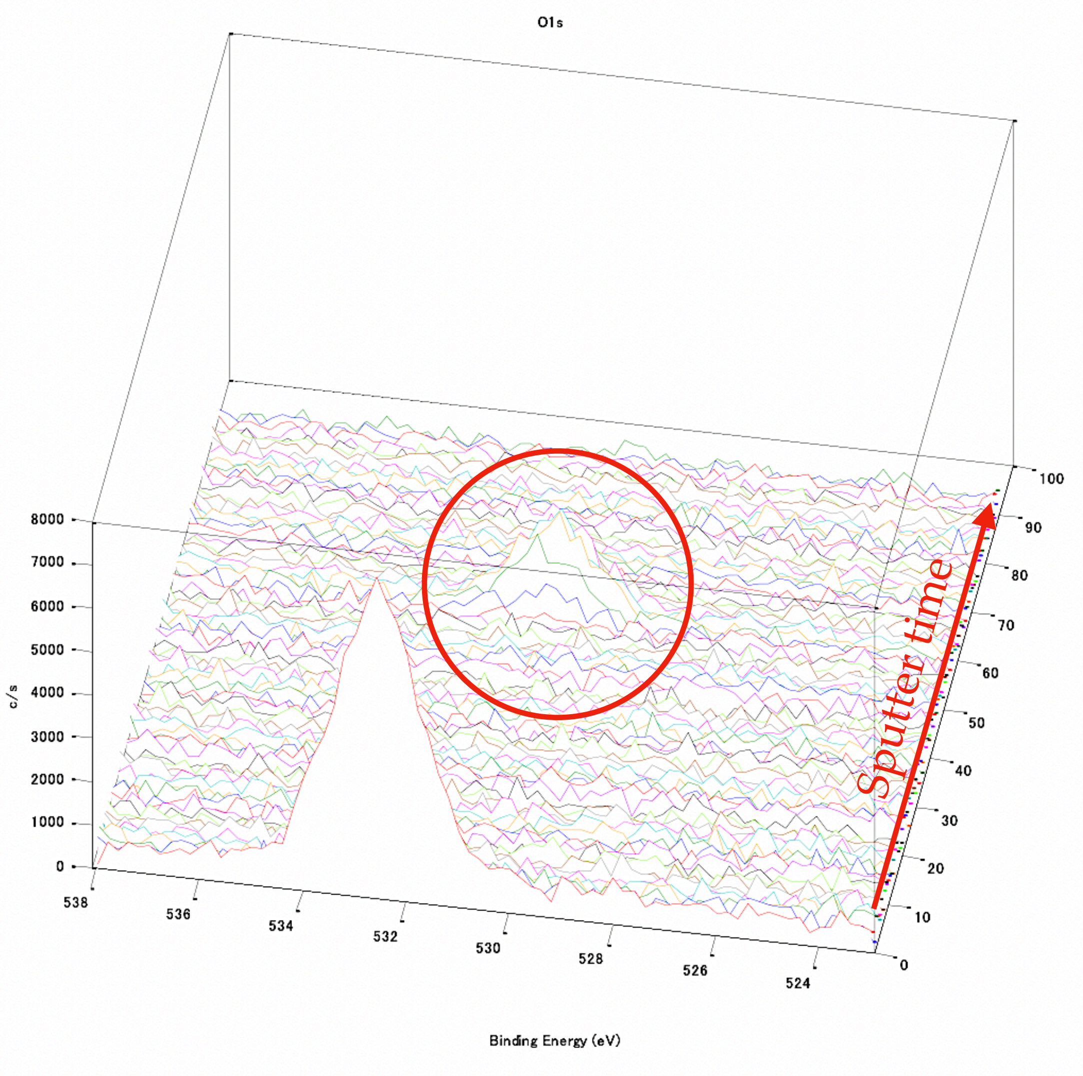
Y. N. SUN et al. *X-Ray photoelectron spectroscopy of O1s and Si2p lines in films of SiO_x formed by electron beam evaporation.* Thin Solid Films, 157 (1988) 351-360

Si_3N_4 on Si: Depth Profiling

- The depth profile shows an excess of oxygen at ~60min of sputtering, along with a strong shift in the BE position of the Si 2p line, revealing an SiO_x interfacial layer



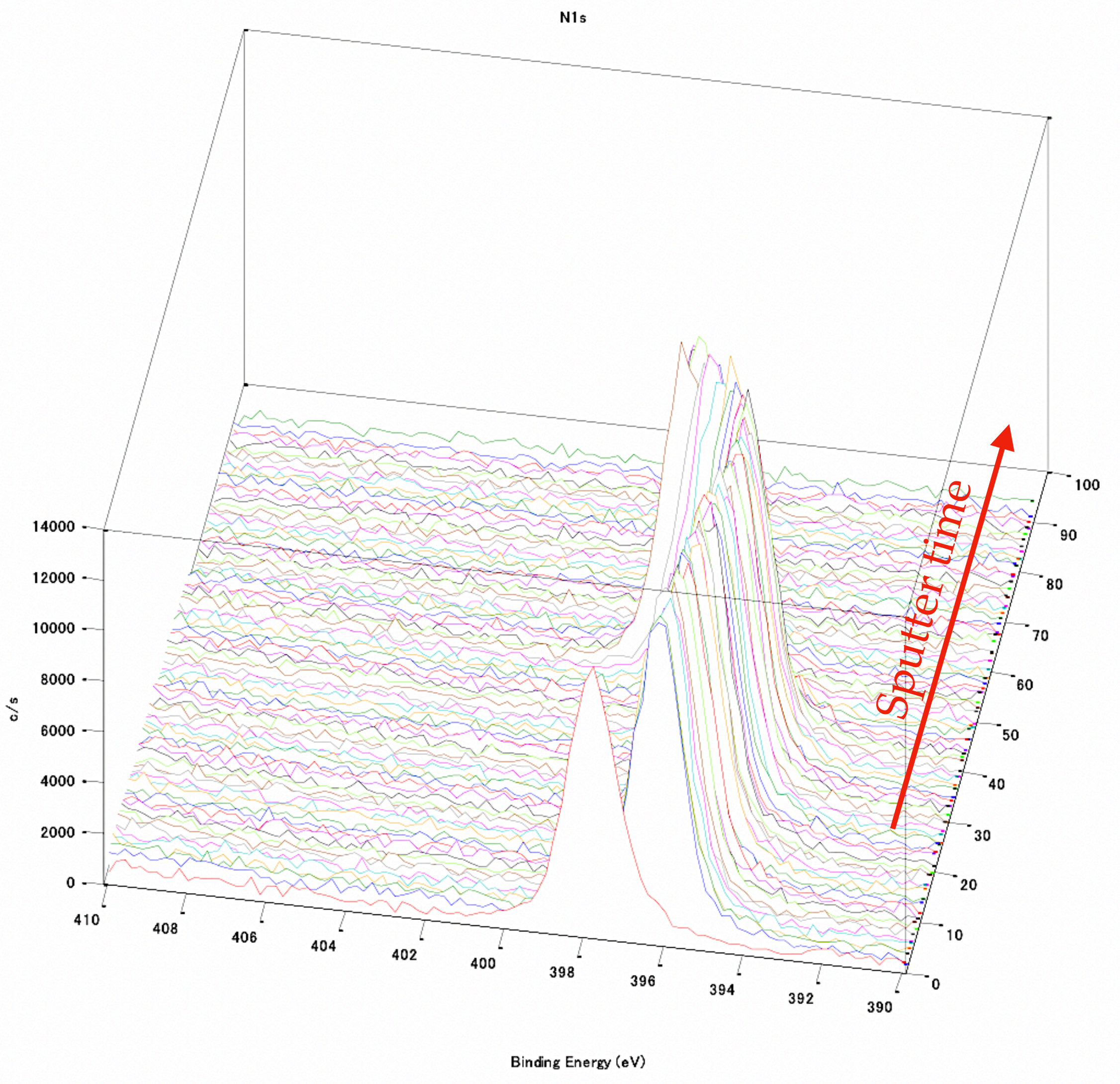
S2p line



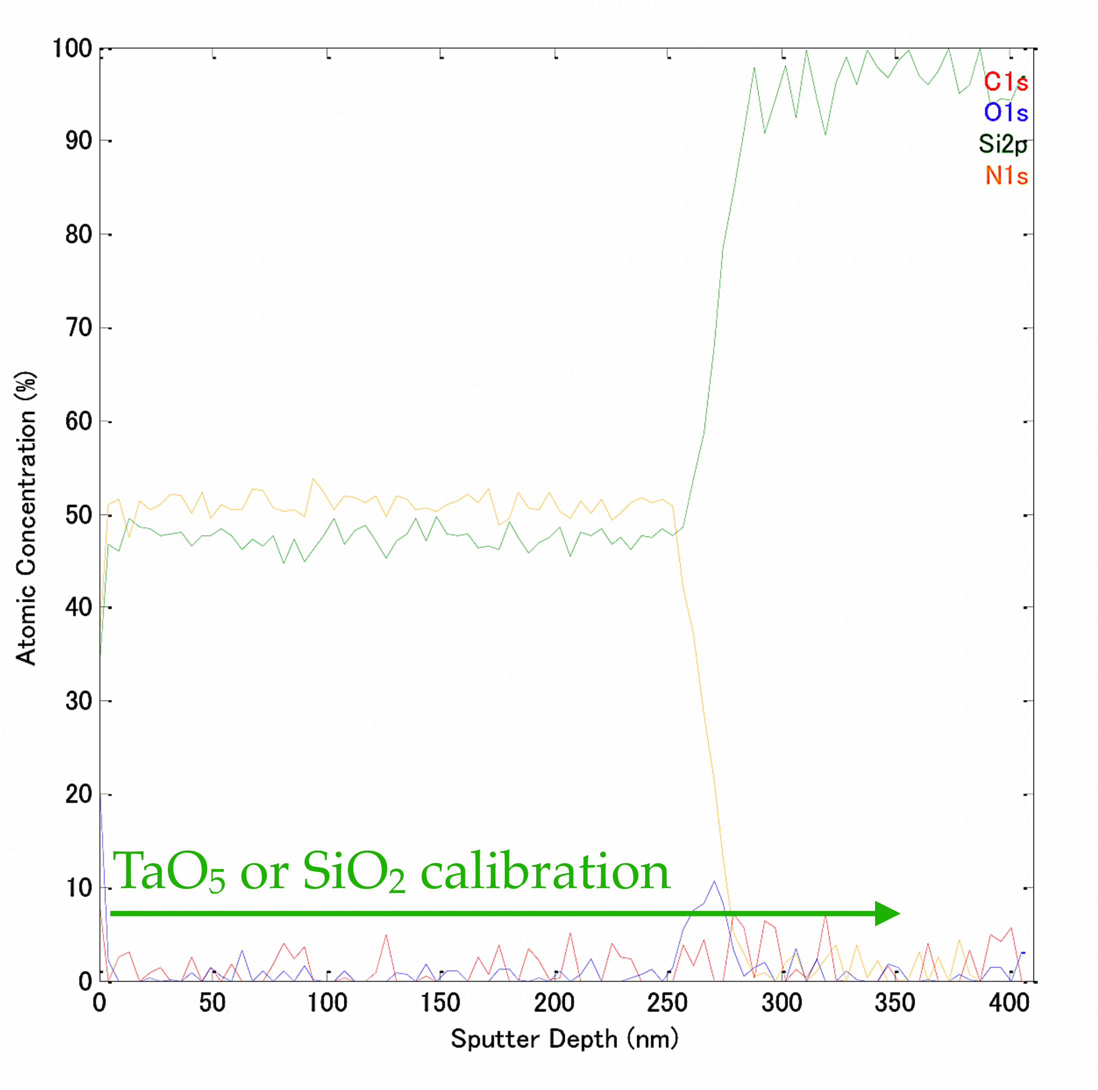
O1s line

Si_3N_4 on Si: Depth Profiling

- Concomitantly, the N1s line presents similar features (left)
- Integrating the peak area, the depth profile plot is traced (right). It presents the relative surface atomic concentration of each element from the surface to the sputtered depth



N1s line

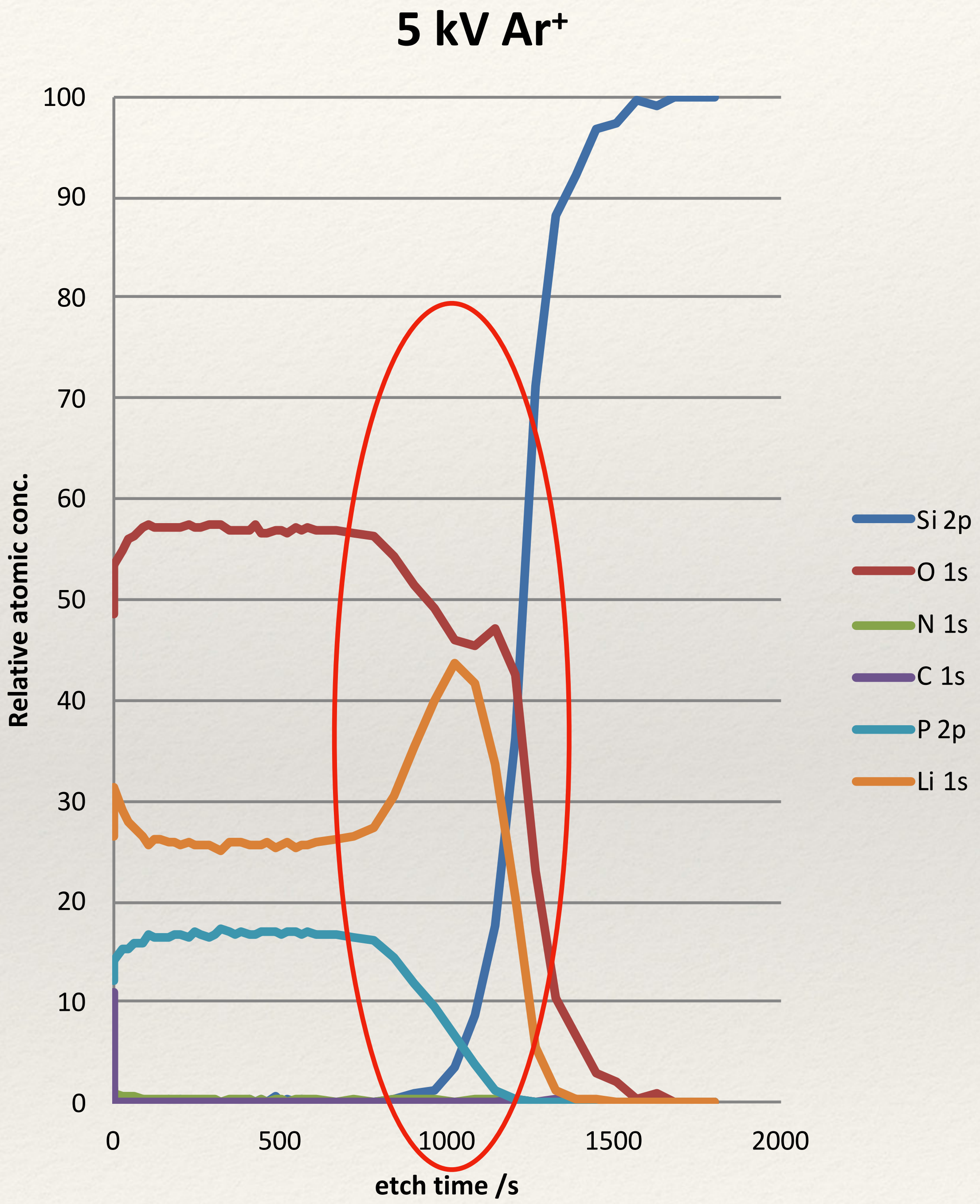


Depth profile at%

Depth Profile: Implantation and Migration

Conventional monatomic depth profiling is susceptible to produce spurious results regarding both elemental concentration and chemical state identification as it triggers:

- Differential sputtering
- Implantation
- Migration
- Chemical modification



Migration of Li under the sputter.
The chemistry is also affected

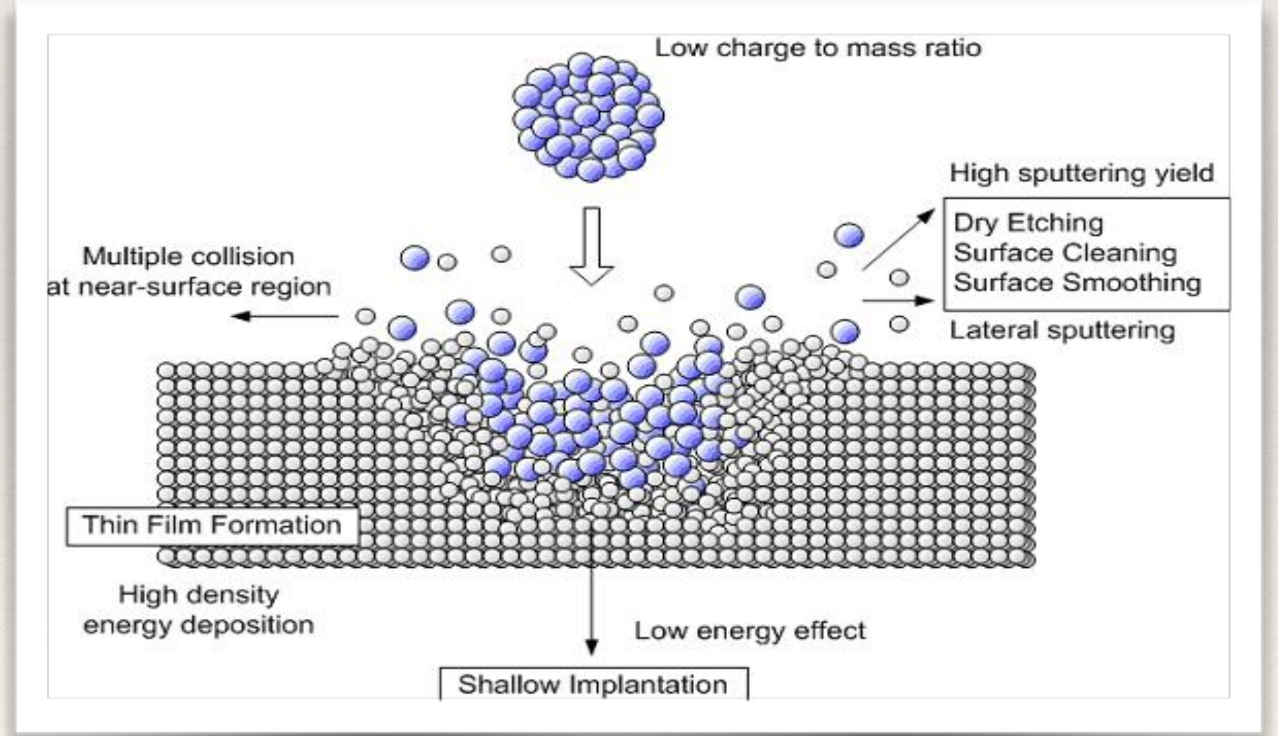
Argon Cluster Sputter Gun

Large clusters up to 5000 atoms are created and accelerated towards the surface with energy ~0.2-20keV

Low energy clusters are inefficient in sputtering inorganic material, i.e. ideal for surface cleaning

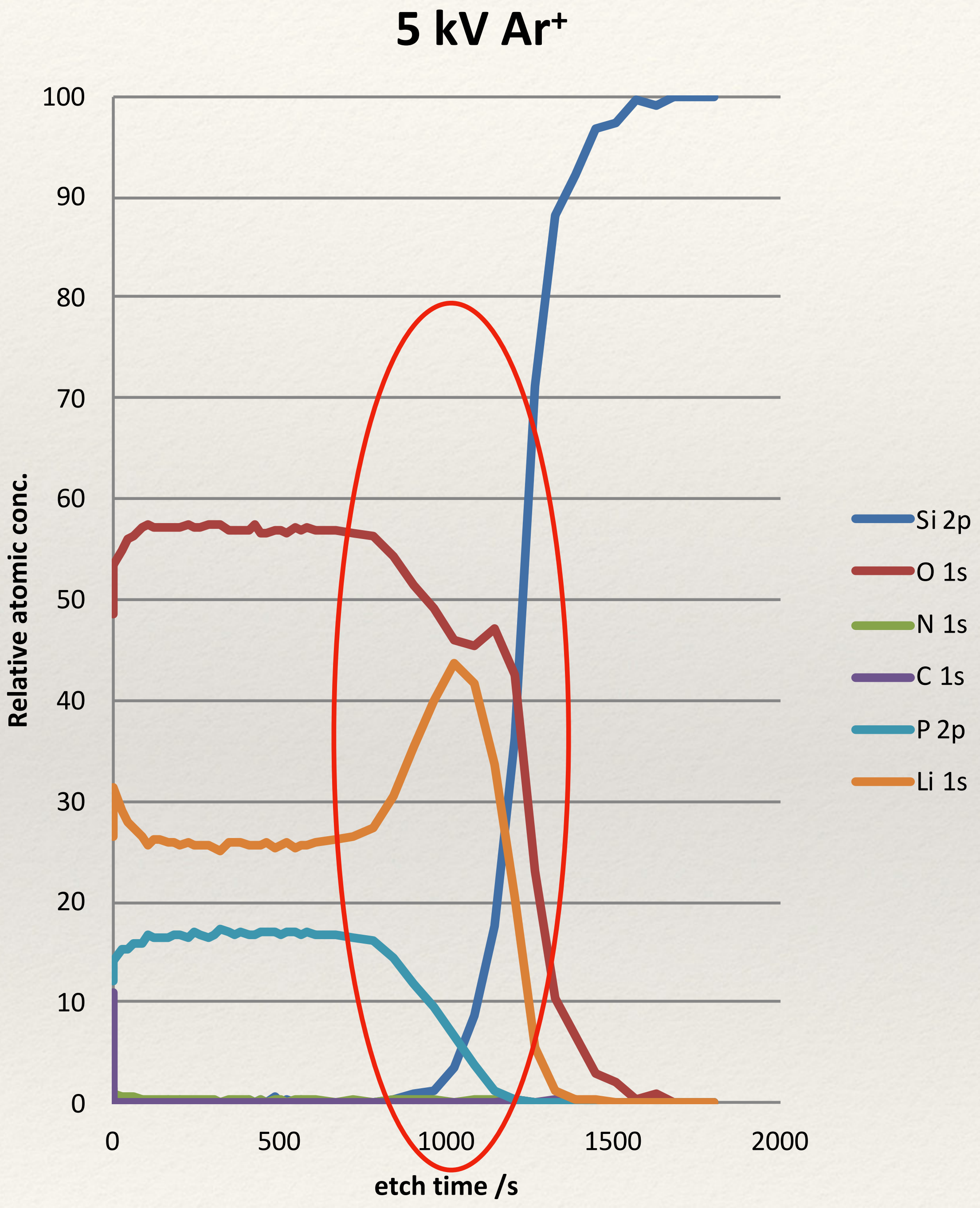
High energy cluster have a reasonable sputter rate for both organics and inorganic and allow:

- Reduction in light ion mobility
- Greater confidence in chemical state assignment

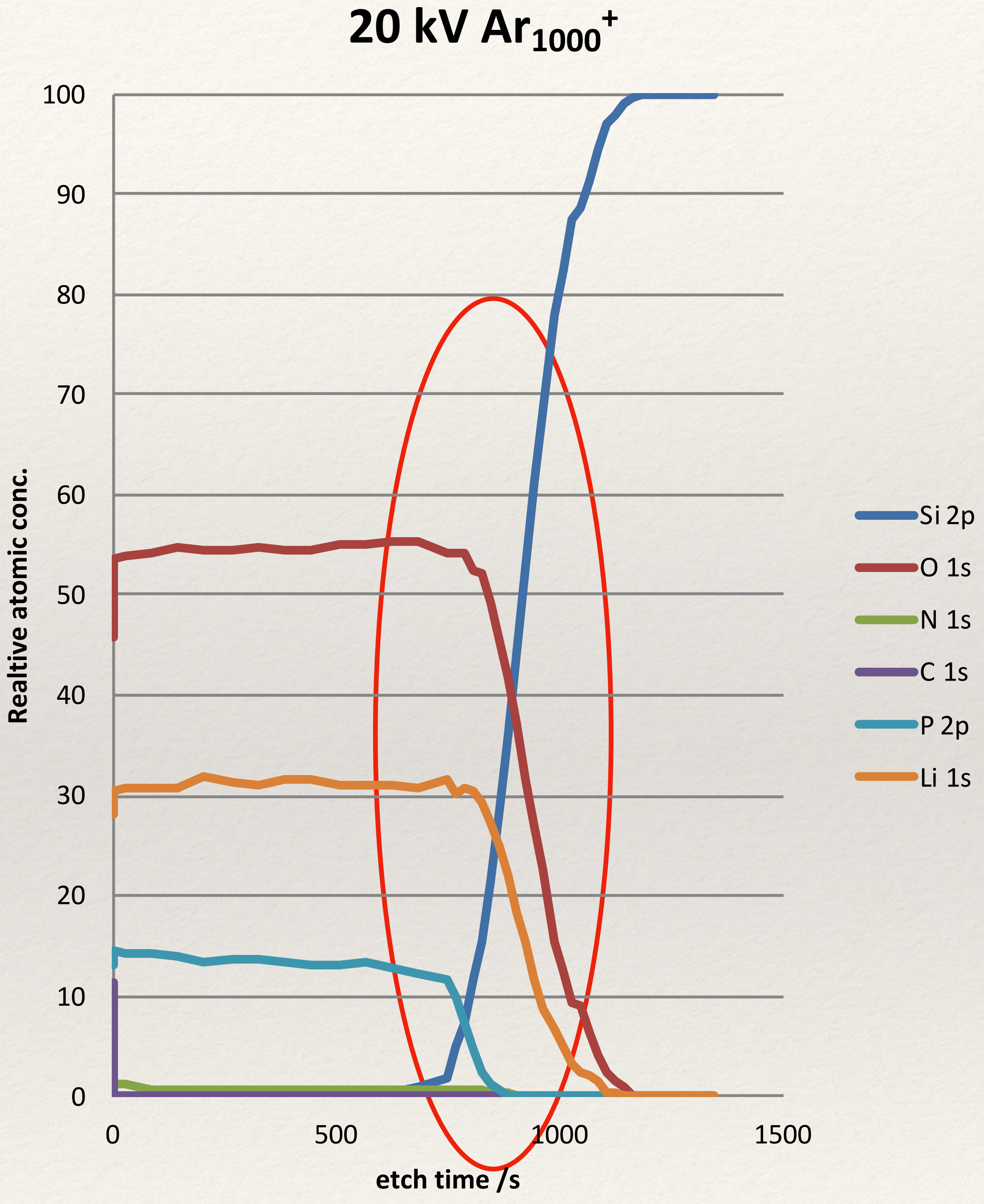


Sputtering with a Gas Cluster Ion Beam (/source): GCIB (/GCIS)

Ar+ vs CGIB


5 kV Ar^+

Migration of Li under sputtering.
The chemistry is also affected


20 kV Ar_{1000}^+

Mitigated migration of Li under sputtering.
The chemistry remains mostly unaffected

Ar+ vs CGIB

Ar+

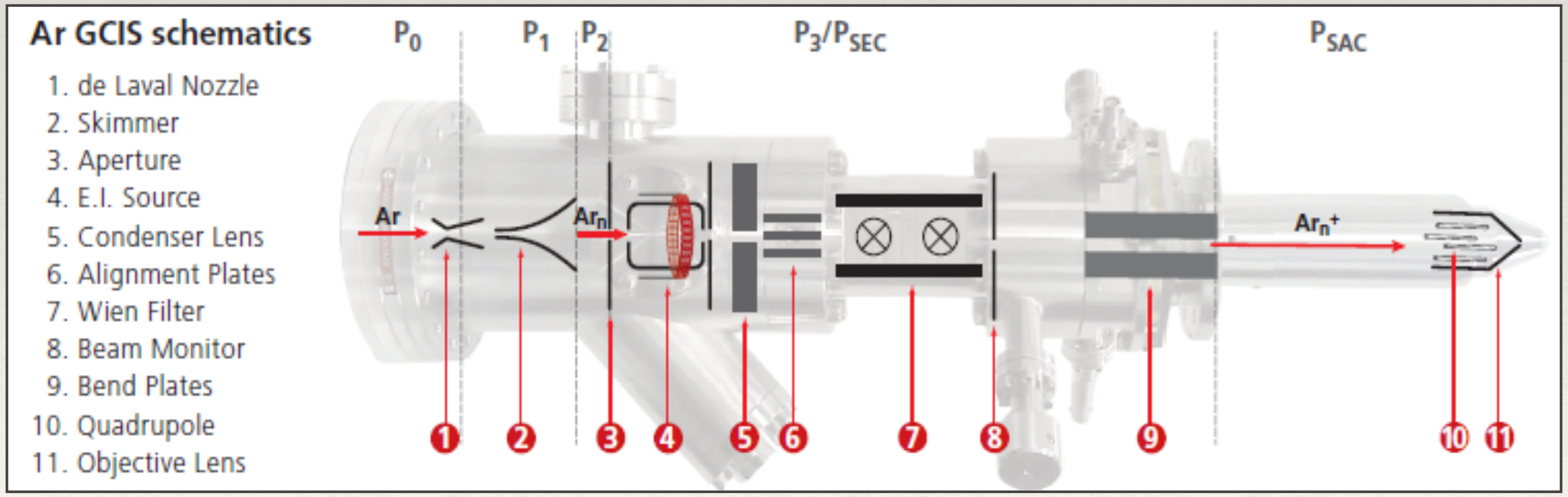
- Easily calibrated sputtering rates
- Steady state in depth profile

- Preferential sputtering (ion beam induced oxides reduction) -> modification of the chemical structure
- Implantation

GCIB

- Excellent for surface cleaning of organics
- Mitigation of ion beam induced oxide reduction

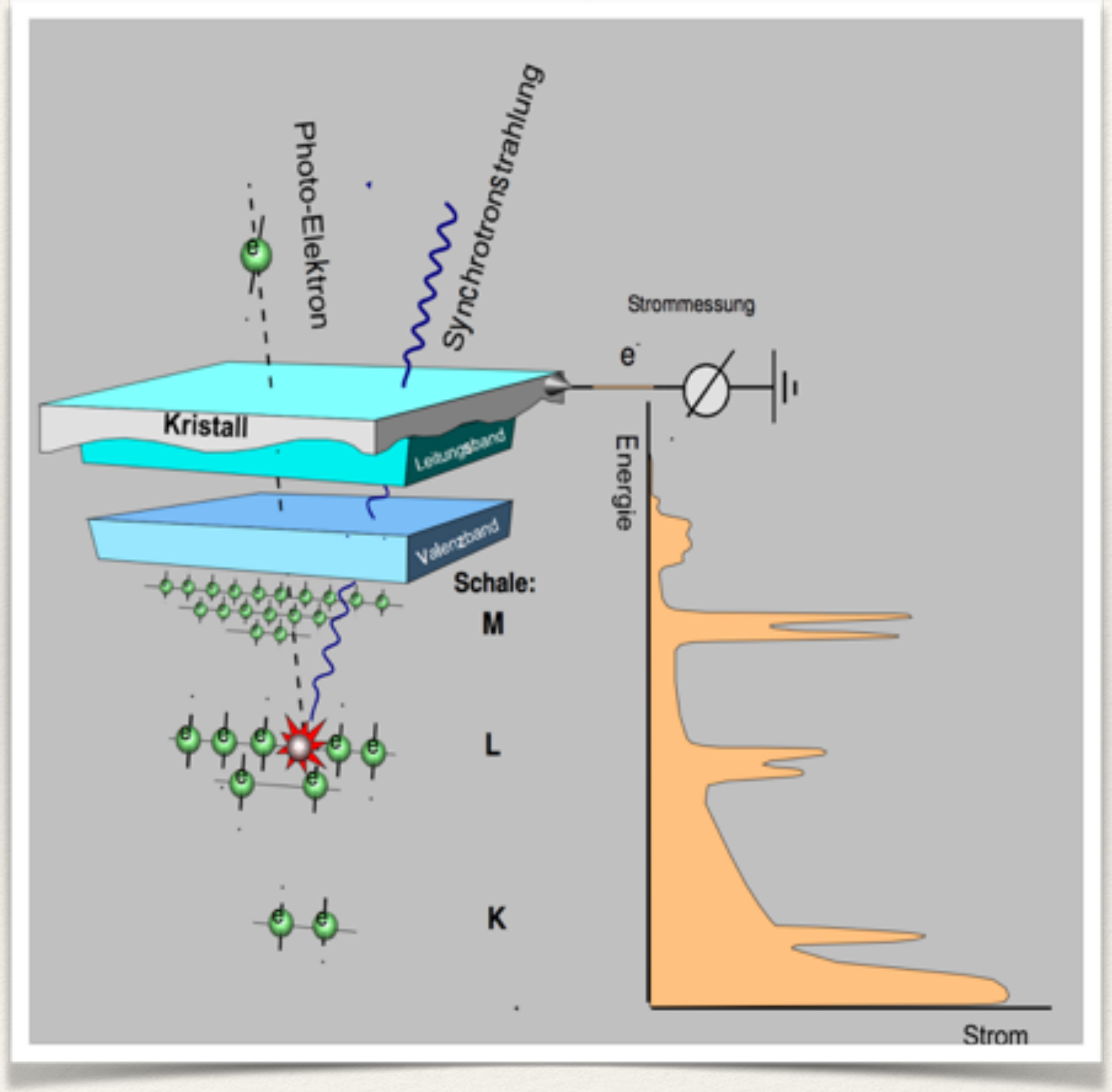
- Lower relative level of preferential sputtering in organics. However, 'doesn't' sputter away metals!
- A lack of "steady state" is observed in gas cluster ion beam depth profiles



Schematics of Kratos GCIB

Further reading: R.Simpson et al. *XPS investigation of monatomic and cluster argon ion sputtering of tantalum pentoxide.* Applied Surf. Sci. 405, 2017

Summary



- Identification of the different lines composing an XPS spectrum: A complete XPS spectrum can easily be decomposed into it essential contributions, giving a full overview of the measured material
- Identification of the measurements artefact and secondary features
- Sputtering allows for both
  - Surface preparation (removal of atmospheric organic contamination)
  - Depth profiling

Thank you!

Next course

- Chemical State analysis in details
- Quantification
- Study case II: Fitting 'real-world' complex data
- Non-destructive depth profiles: ARXPS

References

- Briggs et al. *Practical surface analysis*, Wiley, 1990
- Moulder et al. *Handbook of X-ray Photoelectron Spectroscopy*. Perkin-Elmer, 1992
- IMFP calculations: Cumpon and Seah, Surf. Interface Anal. 25 (1997), 430
- Thermo-Fisher XPS webpage:

  https://xpssimplified.com/whatisxps.php

  Gloves case: http://www.revbase.com/tt/sl.ashx?z=73090c66&dataid=433139&ft=1