

Familiarization with XPS method and technique

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The scope of lecture:

1. **What is inside XPS physics ?** (*the description of physical phenomena used in XPS*)
2. **Why X-ray Photoelectron Spectroscopy ?** (*a brief review of XPS method features*)
3. **XPS Instrumentation** (*main parts and XPS tricks for XPS beginners*)
4. **UPS technique** (*UPS method features and examples*)

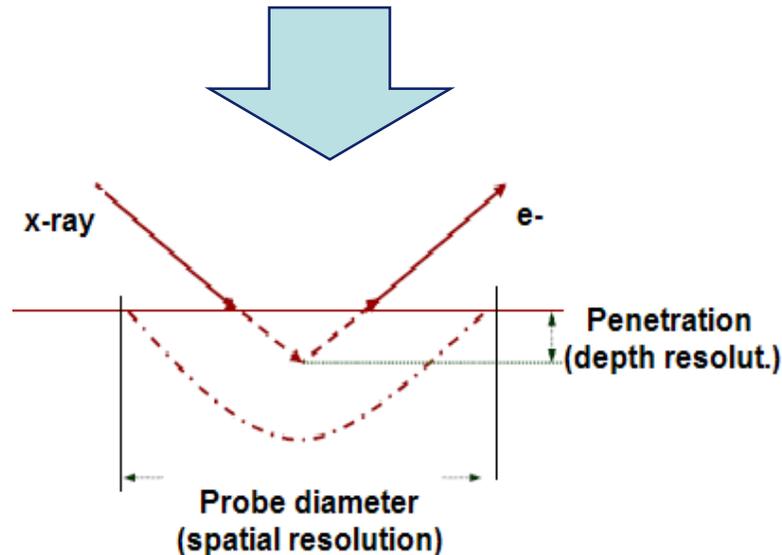
Part 1. What is inside XPS physics ?

1-1. What is inside XPS physics ?

UPS : Ultraviolet Photoelectron Spectroscopy

XPS : X-ray Photoelectron Spectroscopy

AES : Auger Electron Spectroscopy



”Core-hole creation” techniques

X-ray Photoelectron Spectroscopy (XPS)
X-ray Absorption Spectroscopy (XAS)

- **UPS-XPS-AES-XES**, LEED and LEELS ... – are the material science techniques which belong to the **Electron Spectroscopy Techniques Group** → *electrons are carrying the information about the material under study* ;

- **XPS** is a technique that's applying an X-rays in the range of about 150 – 2000 eV in order to examine solids* ;

* Rigaku Pat. Pended **UltraCarry™** and **MiniCarry™** sample probes allow to study liquids in vacuum media

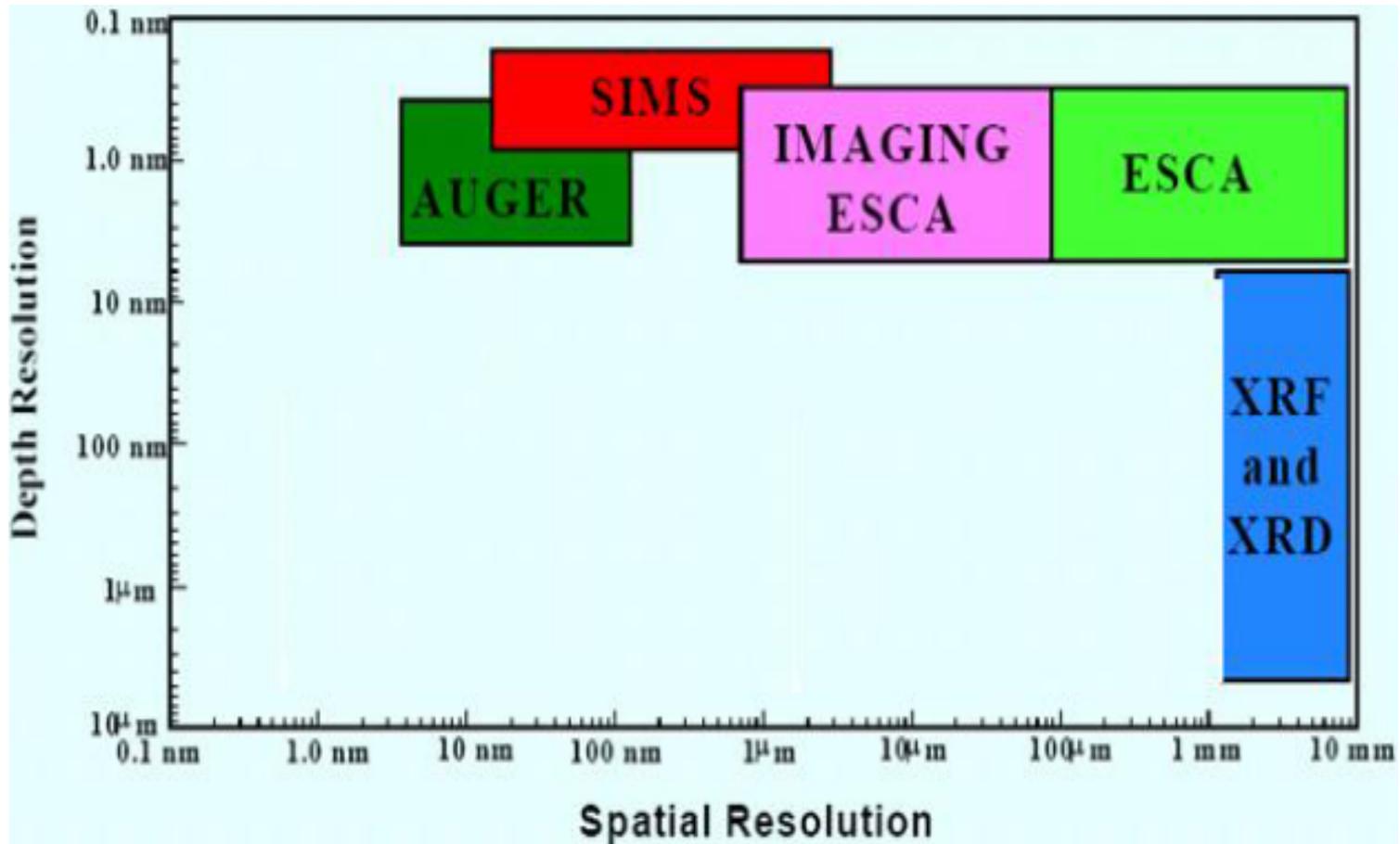
Why a lot of ”similar” spectroscopies are used?

- Because of **spatial** and **depth resolution** as well as **signal-to-noise ratio** (depends on the type of Spectroscopy and Spectrometer construction) and **type of physical process**

”Core-hole decay” techniques:

Auger Electron Spectroscopy (AES)
X-ray Emission Spectroscopy (XES)

1-2. What is inside XPS physics ?



XPS Spatial and Depth resolution* according to ThermoFisher Scientific Data
(reproduced from ThermoFisher Web Site © ThermoFisher Scientific)

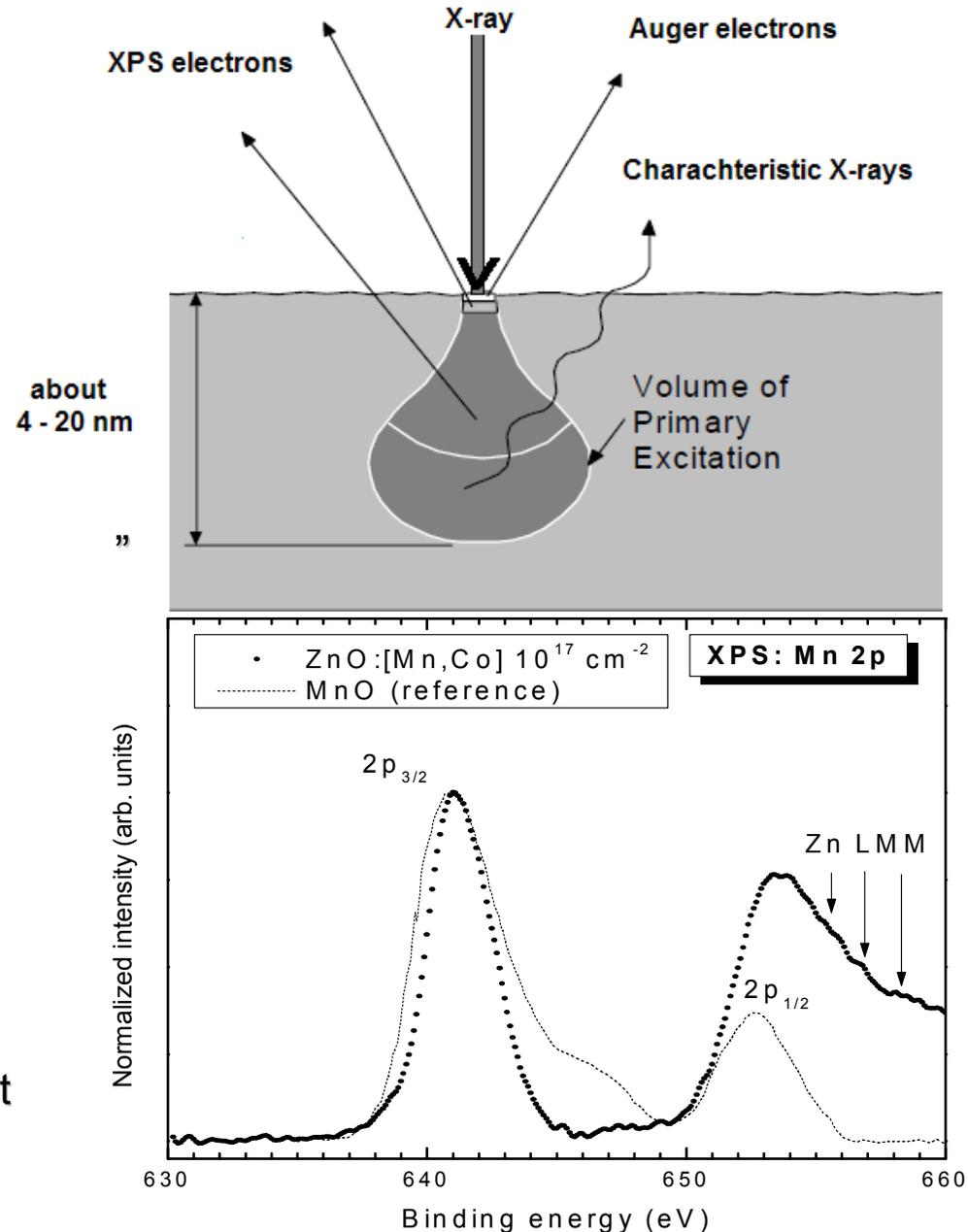
* XPS Systems of the Year 2011 have spatial resolution of 4 μm

1-3. What is inside XPS physics ?

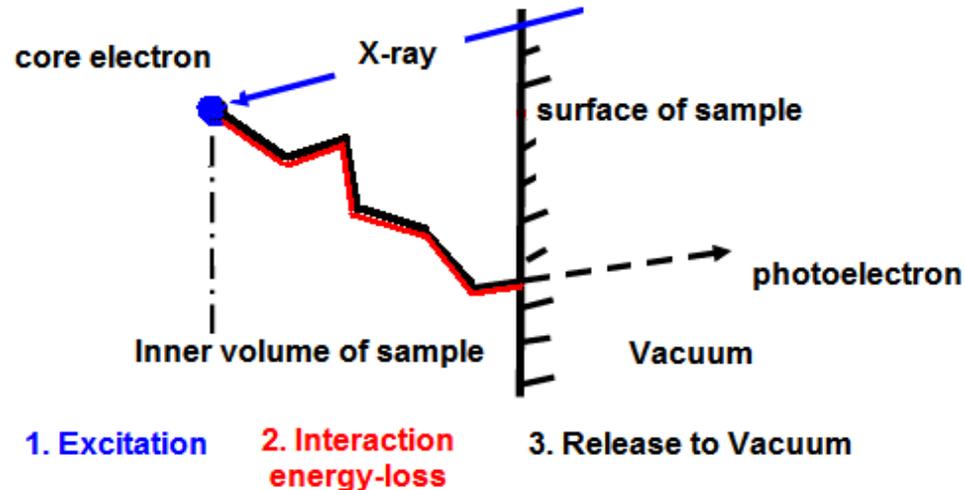
"Underwater rocks" in XPS :

- A lot of **side-effects** occur while the sample is excited by primary X-ray beam under **XPS** study → strongly affect the **spectrometer resolution** and **signal-to-noise ratio** ;
- Auger side-process becomes a problem in some cases due to **side-overlapping** with some XPS lines → the need to use another X-ray source (i.e. Mg K α instead of Al K α)
- Local X-ray overheating of the sample → **XPS signal drop-out**

The spectra were obtained by author at ULVAC-PHI XPS Versaprobe 500



1-4. What is inside XPS physics ?



In the frame of this model, the XPS intensity at a normal incidence is:

$$I(\theta) \propto \frac{\sigma_{tot}}{4} \quad \text{where} \quad \sigma_{tot} = \sum_{nl} \sigma_{nl}$$

because when more than one orbital is excited, then σ_{tot} **is just the summation of partial photoionization cross-sections σ_{nl}**

Actually, an ionization cross-section σ is **the probability per unit area and per unit time that a photon of a given energy can be absorbed by an atom to excite the photoelectrons.**

$$\sigma(h\nu) = \frac{P(h\nu)}{I(h\nu)} \quad \text{here } P \text{ – are the } \underline{\text{absorbed}} \text{ photons per unit time and } I \text{ – are the } \underline{\text{incident}} \text{ photons}$$

Gelius molecular orbital rule (by K.M.Siegbahn and Gelius): the cross-sections for MO are influenced by the nature of atomic orbital, from which this MO is „constructed”.

1-5. What is inside XPS physics ?

XPS process

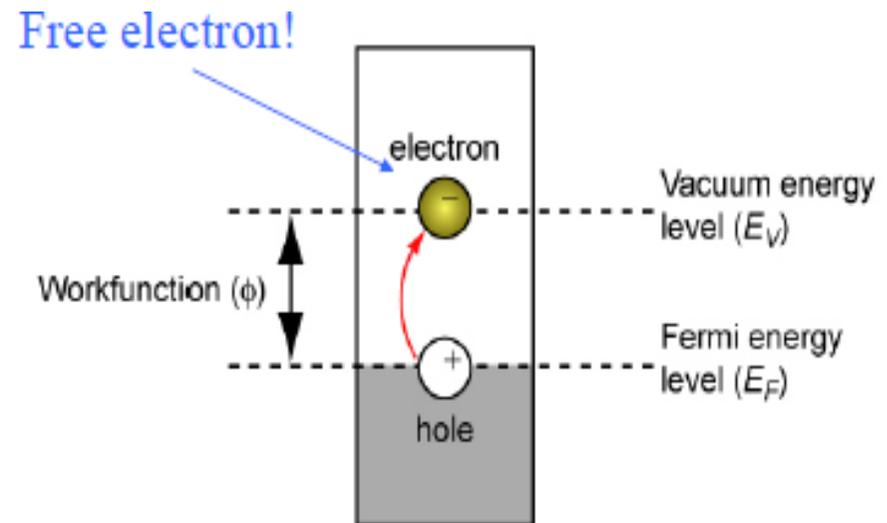
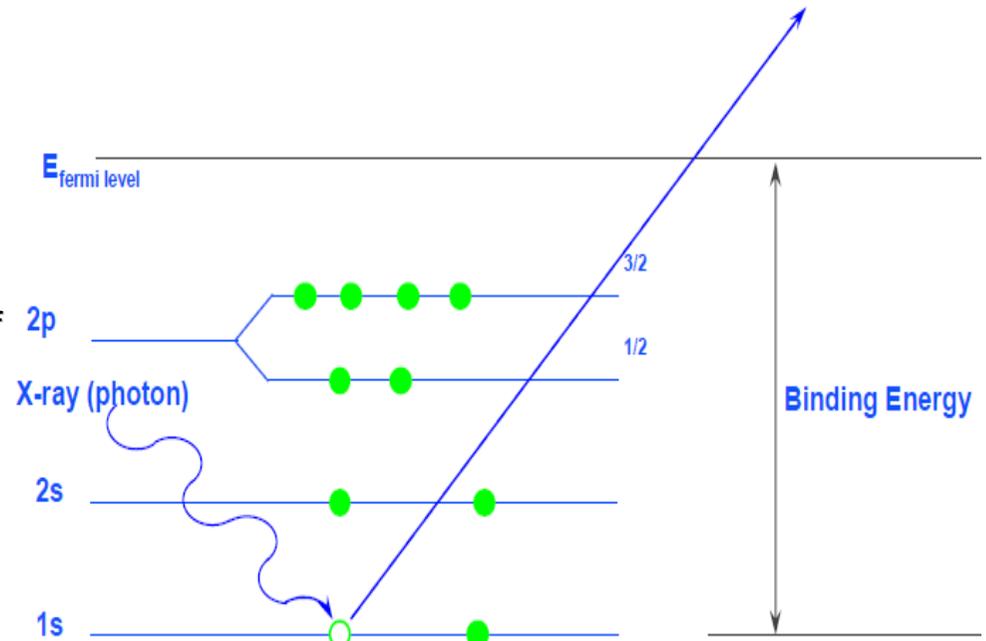
➤ $E_{\text{binding}} = E_{\text{photon}} - E_{\text{kinetic}} - \phi$,

where ϕ is a work-function of XPS spectrometer (usually this correction is made at the factory and used automatically, the value of ϕ is in the range of 2 - 5 eV and varies for different type of XPS systems) ;

$E_{\text{binding}} < E_{\text{photon}}$ (XPS excitation rule)

- **Binding Energies (BE)** usually are measured with respect to Fermi-level rather than to the *level of free electron ("Vacuum" level) – zero point for the energy scale calibration of XPS spectrometer* : $\phi = E_F - E_V$;

- Thus only E_{kinetic} value is measured directly in order to detect E_{binding} , because E_{photon} and ϕ are known



1-6. What is inside XPS physics ?

Particular values of work-function for different materials (according to data of Advanced Photonics Laboratory © 2004, Chang Gung University)

Material	Crystal State	Workfunction (eV)
Na	polycrystalline	2.4
Cu	polycrystalline	4.4
Ag	polycrystalline	4.3
Au	polycrystalline	4.3
Pt	polycrystalline	5.3
W	polycrystalline	4.5
W(111)	single crystal	4.39
W(100)	single crystal	4.56
W(110)	single crystal	4.68
W(112)	single crystal	4.69

Physical meaning: it is a potential "barrier" for electron emission

(**Note:** in the most modern XPS spectrometers it is selected automatically by Central XPS Data Processing Unit while the test-spectrum acquiring is performed before "clean" measurements)

1-7. What is inside XPS physics ?

XPS spectra – why Auger appears ?

➤ **Core-lines**: of relatively narrow shape, results from 1s (*K*-shell), 2s (L_1 -shell), 2p ($L_{2,3}$ -shell).

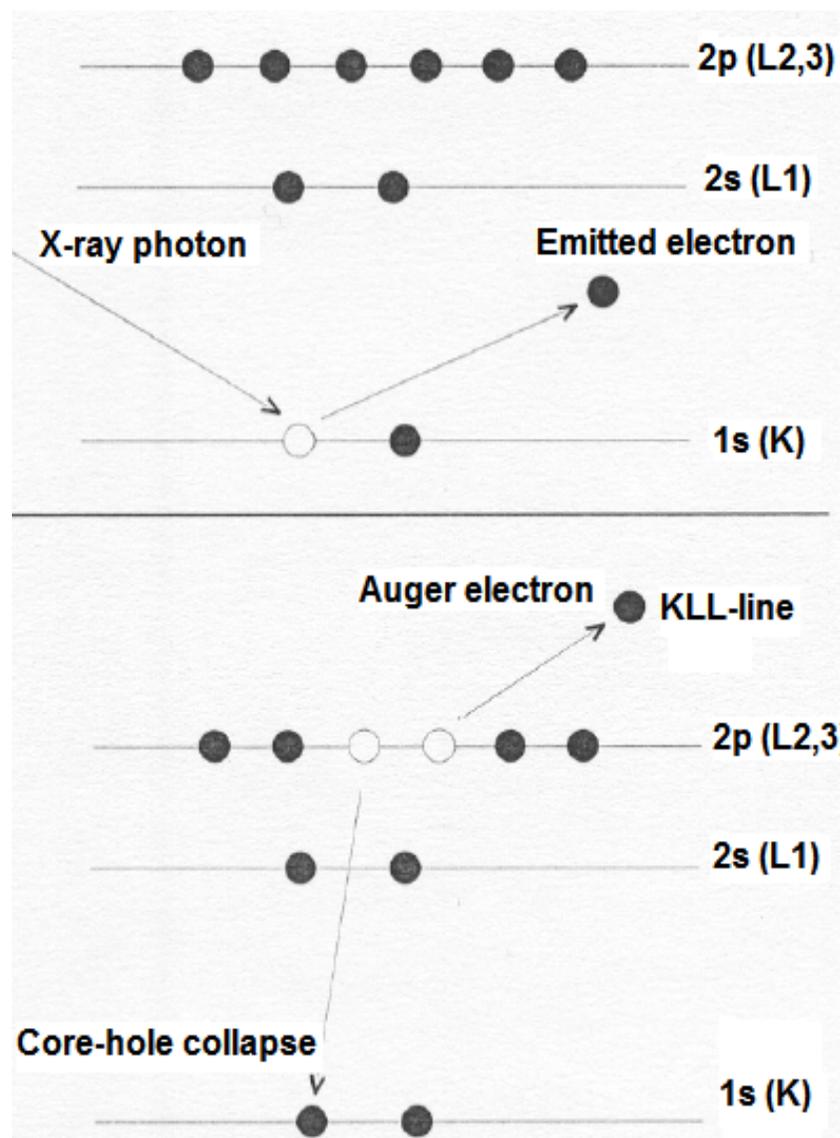
➤ **Valence-band**: much broader, usually represents the total DOS near the Fermi level energy region

Some of their spectral parameters (**but not the BE position**) are affected by the X-ray source energy !

➤ **Auger-lines**: Actually the kinetic energy of electron should not be affected by the incident x-ray photon energy – it should be as a "fingerprint" of a concrete part of electronic structure of material under study.

BUT (!), the energy positions of Auger peaks in the BE scale depend on incident x-ray photon energy due to simultaneous coulombic re-arrangement of electrons in the final state →

→ we can avoid Auger overlapping with XPS peaks by **CHANGING THE X-RAY SOURCE ENERGY !**

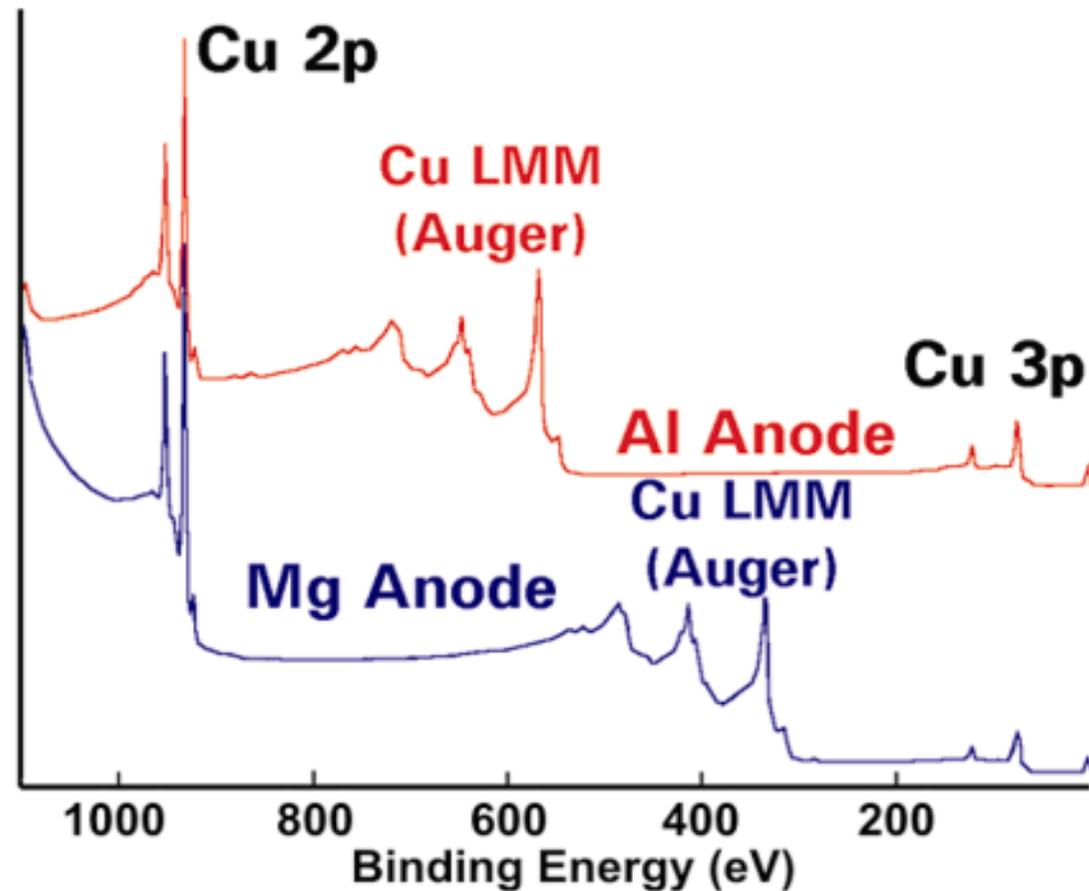


1-8. What is inside XPS physics ?

How it looks actually:

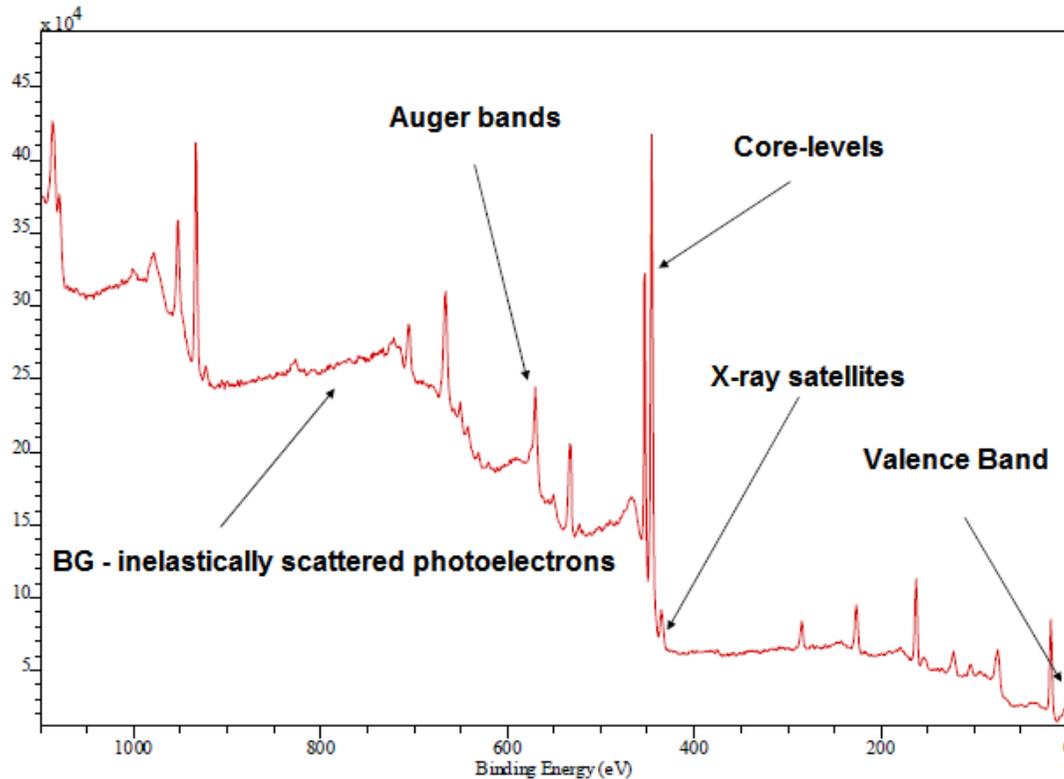
An example of XPS Survey recorded under different X-ray excitation sources – Al K α and Mg K α .

Recorded at ThermoFisher XPS
EscaLab 250 Xi by ThermoFisher
analytical scientists © 2010



1-9. What is inside XPS physics ?

Typical structure of XPS Survey



VB (0 eV – 35 eV region):

Electron states that are participated in chemical bonding of a material

X-ray satellites:

Fixed BE-positions, low intensities

Core-level XPS:

"Fingerprint" of material under study

Auger Bands:

Much broader than core-levels, has a complicated shape

BG :

Bremsstrahlung-excited electrons (right side of XPS peak) and inelastically scattered electrons (left)

1-10. What is inside XPS physics ?

XPS spectra – why chemical shift appears ?

Point Charge Model:

$$E_B = E_i^0 + kq_i + \sum q_j/r_{ij}$$

E_i^0 in atom i in given reference state. It considered to E_b for the neutral atom
 Weighted charge of i
 Potential at i due to surrounding charges
 Related to electro-negativity
 Such as valence change
 Relaxation in the final state, lattice change

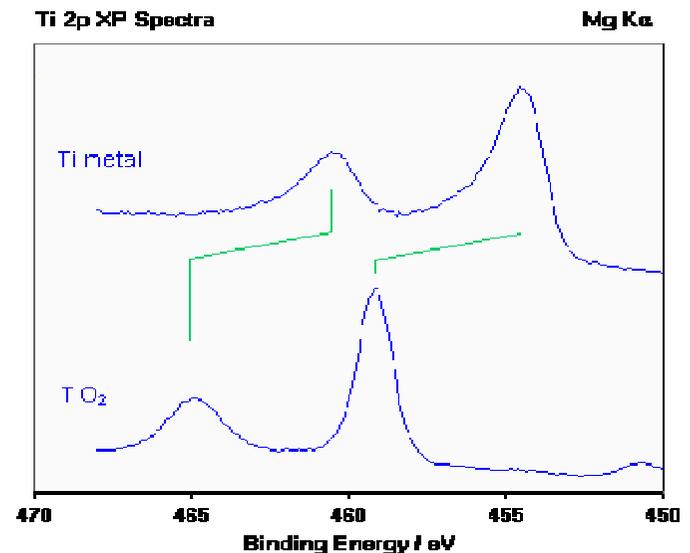
Thus, for compounds with the dissimilar bonding majority comparing to reference, the XPS peak position will be also different → it is a "fingerprint" of chemical bonding type

Example : XPS Si 2p peak in "pure" Si wafer BE = 99 eV, but (sic!)

XPS Si 2p peak in SiO₂ BE = 102.3 eV

Withdrawal of valence electron charge → increase in BE (oxidation)

Addition of valence electron charge → decrease in BE

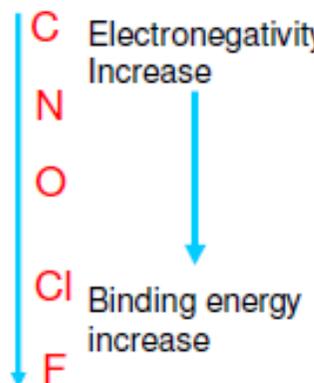


1-11. What is inside XPS physics ?

XPS spectra – any other reasons for chemical shift ?

Chemical Shift due to Electronegativity Effects

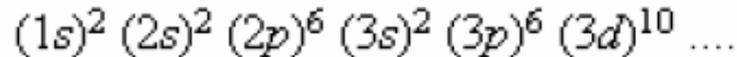
Atoms of a higher positive oxidation state exhibit a higher binding energy due to the **extra coulombic interaction** between the photo-emitted electron and the ion core. **This ability to discriminate between different oxidation states and chemical environments** is one of the major strengths of the XPS technique

<i>Functional Group</i>		<i>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	

1-12. What is inside XPS physics ?

Why we obtain sometimes single XPS peak and in other - double XPS peaks ?

XPS peak is originated from the photoelectrons in the core-levels and valence band.
For example. The inner core electronic configuration of the initial state of the Pd is :



In the quantum mechanics, the nonmenclature for a core level is nlj :

n is the principle quantum number;

l is the orbit angular momentum quantum number;

j is the total angular momentum quantum number;

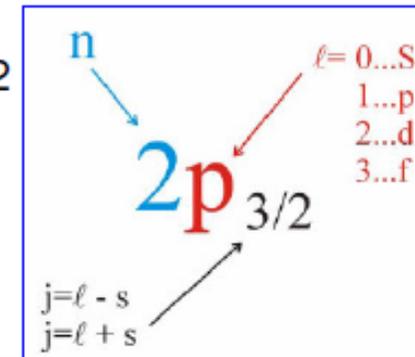
$$j = l + s$$

s is the spin angular momentum quantum number, $s = \pm 1/2$

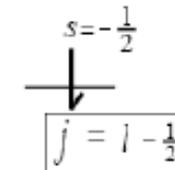
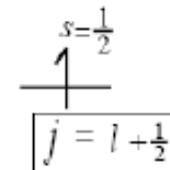
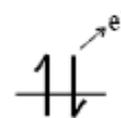
If $l=0$, giving a singlet XPS peak;

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

Subshell	l values	j values	Peak area ratio
s	0	1/2	--
p	0, 1	1/2, 3/2	1:2
d	1, 2	3/2, 5/2	2:3
f	2, 3	5/2, 7/2	3:4



L-S Coupling ($j = l \pm s$)



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