Graduate Program
Department of Physics
Materials Characterization Techniques

X-ray photoelectron spectroscopy (XPS)

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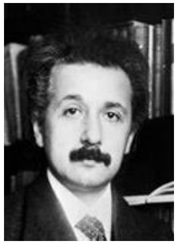
A. Introduction

Photoelectron spectroscopy is based on the photoelectric effect, which was first observed by Hertz in 1887 and interpreted by Einstein in 1905.

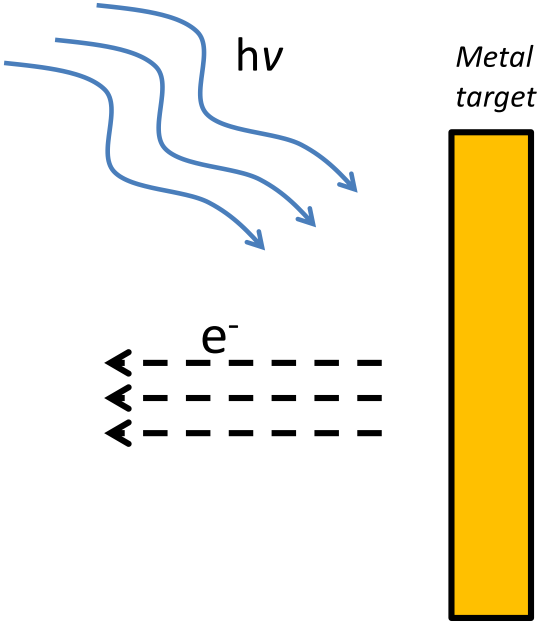
Hertz



Einstein

- The number of emitted photoelectrons depends on the intensity of the light.

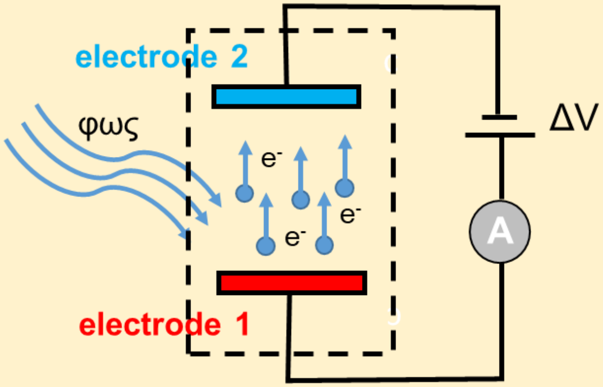
- The energy of the photoelectrons depends on the wavelength of the light.



A. Introduction

The experimental setup in the figure was used to study the photoelectric effect. Electrode 1 is illuminated with ultraviolet light of wavelength 240 nm, and the electrons emitted cross the vacuum and strike electrode 2, causing a current to flow through the wire connecting them. By gradually increasing the voltage between the two electrodes using the potentiometric device, it is observed that the current in the microammeter becomes zero when the voltage reaches 1.40 V.

(a) What is the energy of the photons in eV?
(b) What is the maximum kinetic energy of the emitted electrons, in eV?
(c) What is the work function of electrode 1 in eV?
(d) What is the maximum wavelength that would cause the emission of electrons from electrode 1?
(e) In which region of the electromagnetic spectrum does the wavelength calculated in (d) belong?



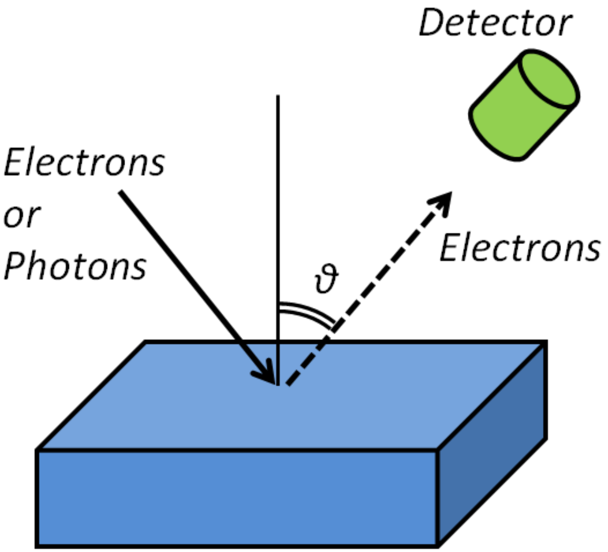
DESCRIPTION OF THE SETUP:

The setup consists of a high-vacuum tube in which two metal electrodes are placed. The first electrode (electrode 1) serves as the cathode, and when it is illuminated it emits electrons. These electrons are collected by the second electrode (electrode 2), the anode. With the help of a potentiometric device, we can vary the voltage applied to the electrodes. Finally, using a microammeter inserted into the circuit, we can measure the current due to the electrons emitted by the illuminated cathode.

A. Introduction

- In general, in electron spectroscopies, photons or electrons are used to excite and emit electrons.

- The energy — and very often the angular distribution — of the emitted electrons is analyzed.



Depending on the excitation source

- ➢ **X-ray photoelectron spectroscopy (XPS)**
- ➢ **Ultraviolet photoelectron spectroscopy (UPS)**
- ➢ **Auger electron spectroscopy (AES)** — may use either electrons or photons.

*XPS is often called Electron spectroscopy for chemical analysis (ESCA)

A. Introduction

Technique	Excitation source	***Detected particle***	***Information***
XPS	*Photon*	*Electron*	*Core levels*
UPS	*Photon*	*Electron*	*Valence band*
AES	*Photon / Eectron*	*Electron*	*Core levels / Valence band*

Note:

[1] UPS and XPS are often referred to as photoemission spectroscopies or simply photoelectron spectroscopies.

[2] When AES is performed using X-rays as the excitation source, the technique is often called X-ray excited Auger electron spectroscopy (XAES).

A. Introduction

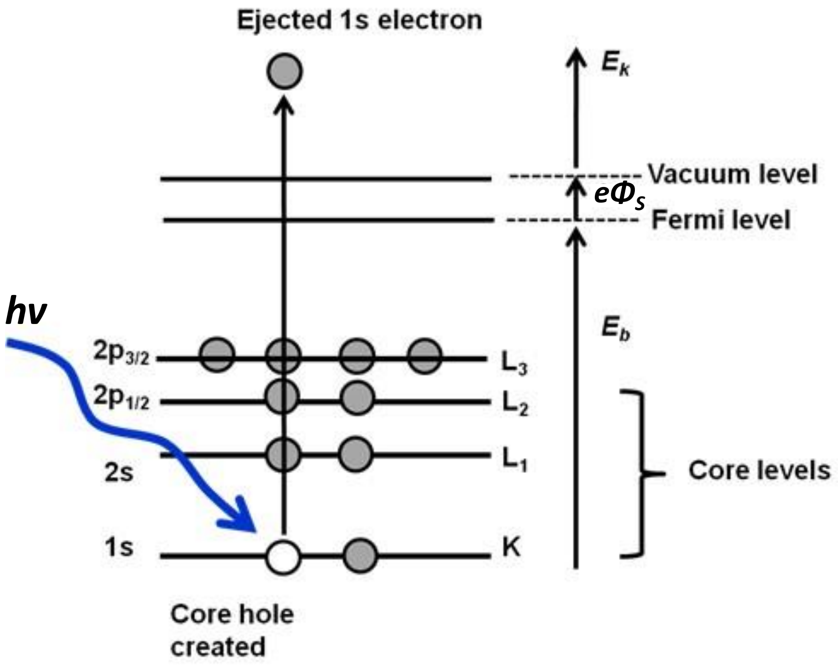
X-RAY PHOTOELECTRON SPECTROSCOPY (XPS)

XPS is widely used in heterogeneous catalysis research and, more generally, in materials science

- elemental composition of solids
- oxidation state of the elements
- dispersion of one phase relative to another
- chemical composition of multilayer samples as a function of depth

B. Physical explanation of XPS

When an atom in a solid absorbs a photon of energy hv (greater than the work function of the solid $e\Phi_S$), an electron (a photoelectron) with binding energy E_B is emitted with kinetic energy E_K.



Διατήρηση της ενέργειας:

$$E_K = hv - E_B - e\Phi_S$$

- E_K photoelectron kinetic energy
- ***h*** Planck constant
- ***v*** is the frequency of the excitation radiation
- E_B is the binding energy (measured relative to the Fermi level of the sample)
- $e\Phi_s$ is the work function of the sample (this is the minimum energy required to move an electron from the highest occupied energy level of the solid (the Fermi level) to the vacuum level).

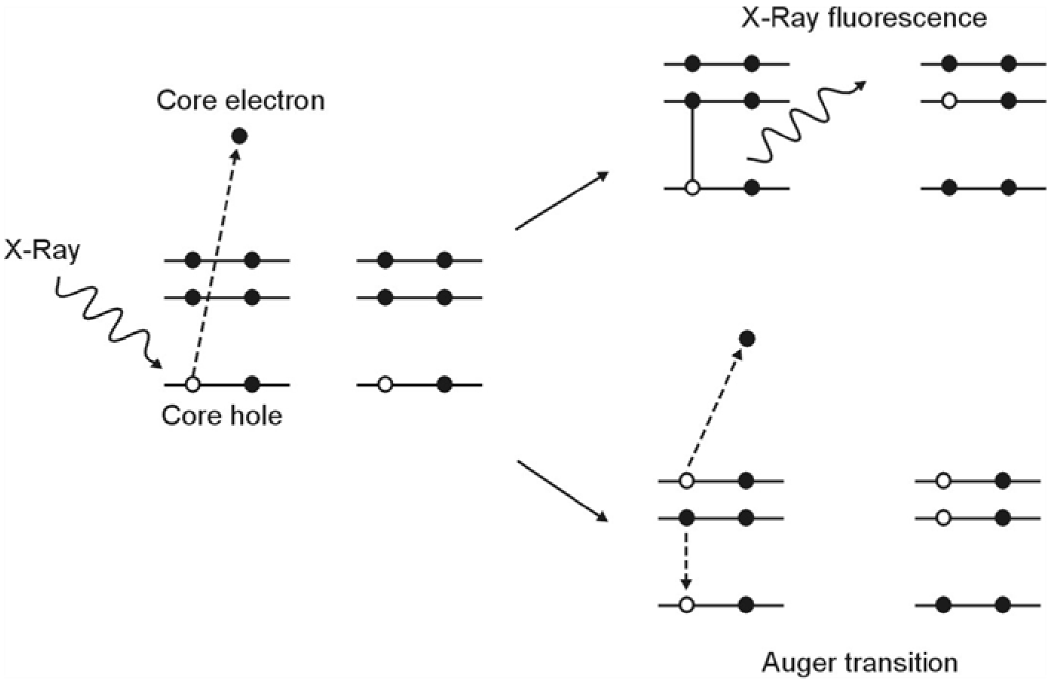
The XPS technique focuses mainly on detecting electrons that originate from the core energy levels of solids.

B. Physical explanation of XPS

Core hole

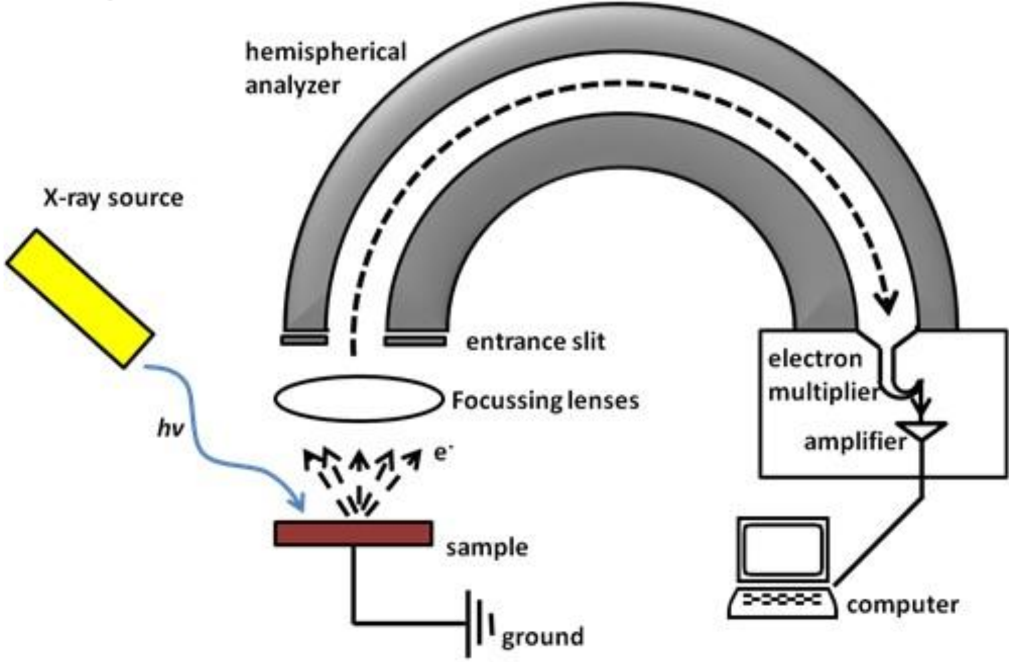
(a) X-ray fluorescence. Release of energy through the emission of an X-ray photon.

(b) Auger electron emission. Release of energy through the emission of an Auger electron.



<u>Auger electrons appear in the XPS spectrum and provide important information about the sample.</u>

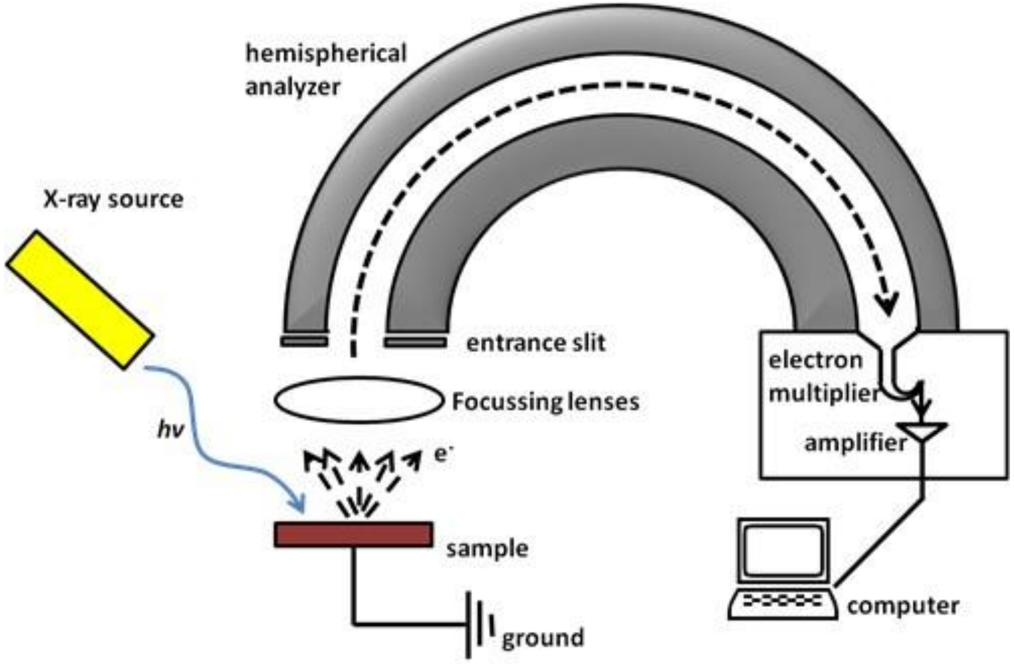
C. Experimental setup



- X-ray source. The X-rays are often monochromatized. Laboratory sources or synchrotron radiation facilities are used. Common lab sources: Al Kα (1486.6 eV) and Mg Kα (1253.6 eV).
- Electron analyzer (most commonly a hemispherical analyzer).
- Detector, often a channeltron (electron multiplier).
- Sample.
- The experimental setup is housed in an ultra-high-vacuum chamber.

C. Experimental setup

2 A portion of these electrons is collected by the electron analyzer, separated according to their kinetic energy, and directed to the detector.



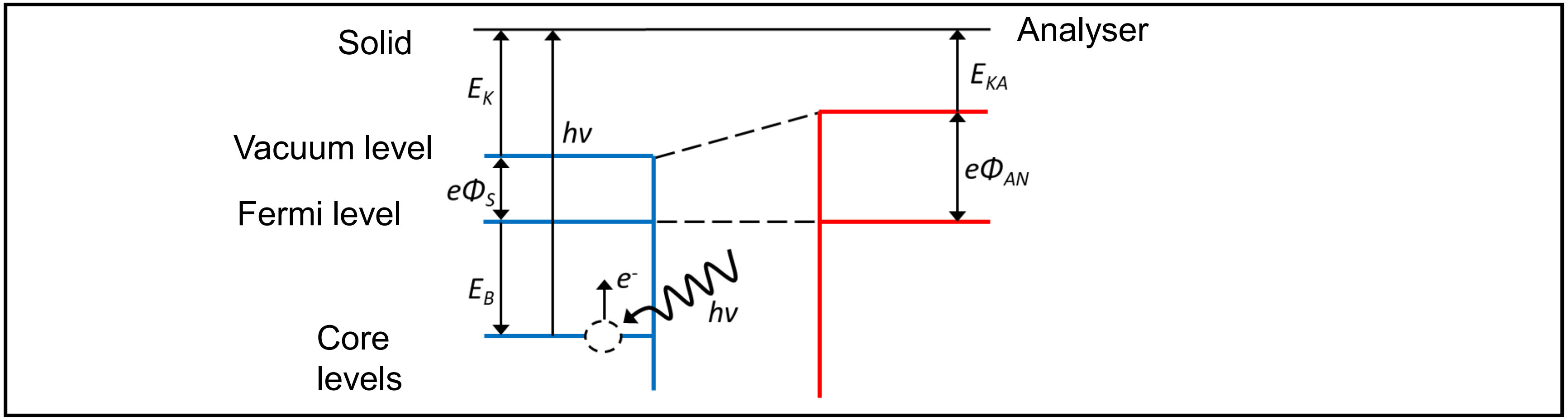
3 The detector produces an electrical signal proportional to the number of detected electrons for each value of kinetic energy.

1 The emitted electrons leave the surface in all directions.

4 This signal is converted into graphical form either analogically, using a recorder, or digitally, using a computer.

Note: The XPS spectrum expresses the number of generated photoelectrons as a function of their kinetic energy, E_K, as measured by the analyzer.

The sample is in ohmic contact with the analyzer, usually through a common ground, so that the Fermi levels of the two align



The kinetic energy of the electrons emitted from the surface is

$$\boldsymbol{E_K = h\nu - E_B - e\Phi_S}$$

For the electrons to reach the analyzer, they must overcome the energy barrier caused by the contact potential between the sample and the analyzer, $e\Delta V = e\Phi_{AN} - e\Phi_S$. Thus, the kinetic energy measured in the analyzer will be equal to

$E_{KA} = E_K - e\Delta V$

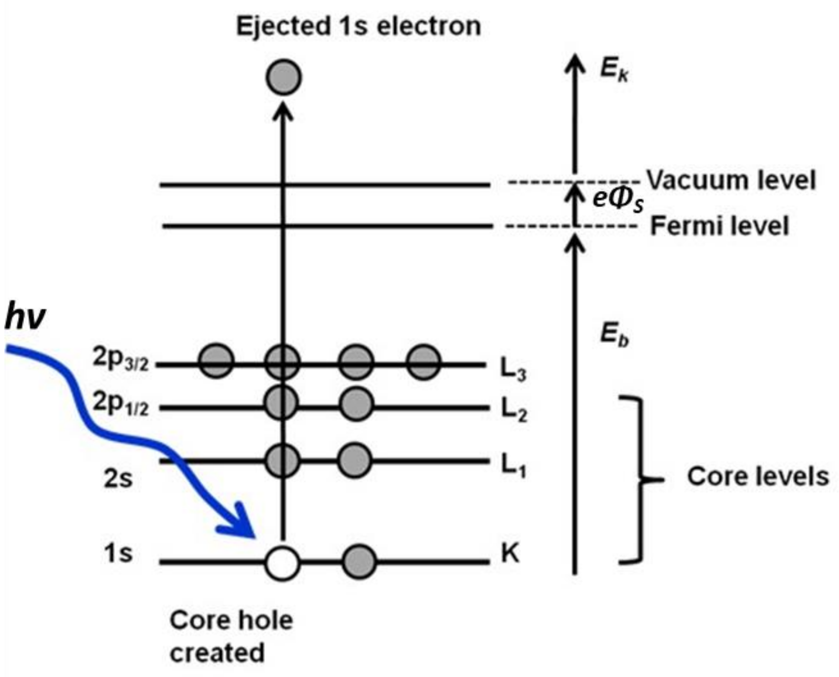
$E_{KA} = h\nu - EB - e\Phi_{AN}$

In practice, to simplify the above equations, a potential is applied to the analyzer $V = -\Phi_{AN}$ (therefore Φ_{AN} does not appear in the equation) → $\boldsymbol{E_{KA} = h\nu - E_B}$

D. Chemical identification

Electrons located in core electronic levels have energies characteristic of the type of atom.

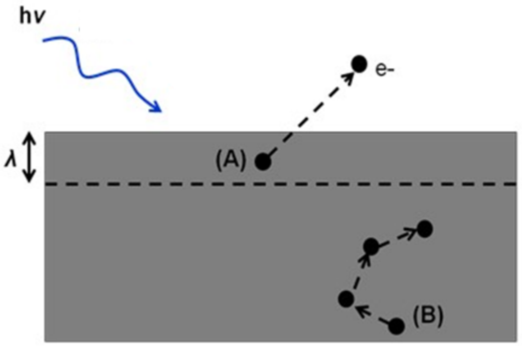
For a given photon energy, photoemission from an atom will lead to photoelectrons with specific kinetic energy values that vary systematically from element to element.



E. Surface sensitivity

XPS is a surface-sensitive technique. The detected electrons originate only from the first atomic layers of the solid.

The surface sensitivity arises from the fact that electrons in the energy range 5–2000 eV have a high probability of inelastic scattering.



(A) Electron escaping with low probability of energy loss

(B) Electron most likely will not escape due to high probability of energy loss

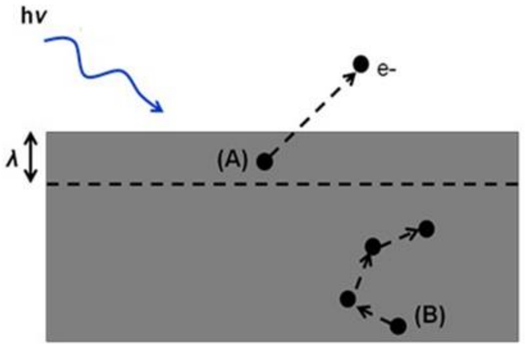
The surface sensitivity of these techniques depends on the probability that an electron can travel the distance from the emitting atom to the detector without losing energy in a random manner.

The quantity that characterizes the probability of inelastic scattering is the inelastic mean free path (IMFP), λ , of the electron within a solid.

The value λ depends

1. the kinetic energy of the electron
2. the type of solid

E. Surface sensitivity



(A) Electron escaping with low probability of energy loss

(B) Electron most likely will not escape due to high probability of energy loss

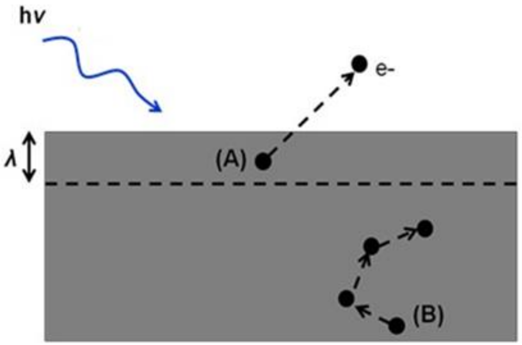
Inelastic scattering occurs due to a series of discrete events that lead to energy loss of the electron.

(i) Plasmon excitations. These are quantized oscillations of the electron density of the free-moving electrons in the valence band / conduction band of the solid. This type of excitation dominates at low energies (10–20 eV).

(ii) Electron–hole pair excitations — low-energy excitations that dominate at energies below ~10–20 eV.

(iii) Core-level ionisation events at energies greater than about 50 eV.

E. Surface sensitivity



(A) Electron escaping with low probability of energy loss

(B) Electron most likely will not escape due to high probability of energy loss

The probability, *P(d),* that an electron with kinetic energy *E* travels a distance dd inside a solid without losing energy is given by the relation

$$P(d) = e^{d/\lambda(\mathrm{E})}$$

The probability *P(d)* decreases very rapidly and is practically zero for distances *d>5λ*.

The depth distribution function of the detected electrons, that is, the frequency with which electrons originating from various depths *d* are detected, is directly proportional to the probability that an electron escapes from each depth, namely to *P(d)*.

$$f = \frac{\int_0^d P(x)dx}{\int_0^\infty P(x)dx} = 1 - P(d)$$

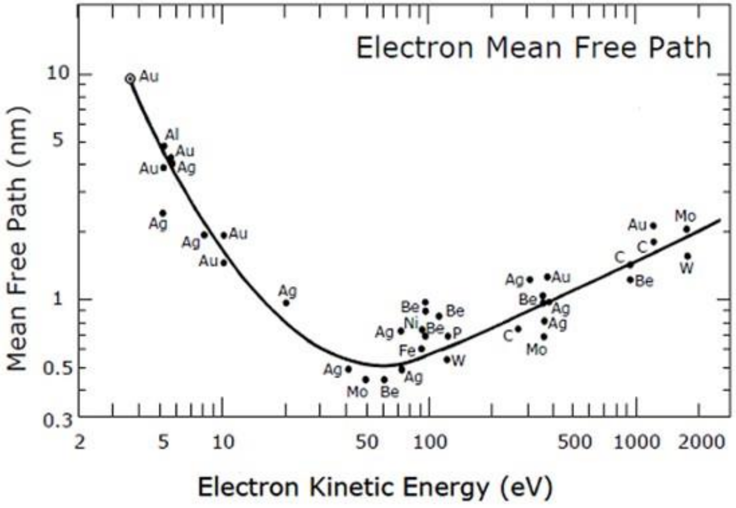
When *d=λ, f=0.63*, meaning that 63% of the electrons originate from one IMFP below the surface. For *d=3λ*, the corresponding fraction becomes greater than 95%.

E. Surface sensitivity

Universal curve of Inelastic Mean Free Path – IMFP, λ(E)

The IMFP for metals exhibits a minimum in the kinetic energy range of 50–100 eV, which is on the order of 0.6 nm.

The inelastic mean free path of electrons in metals is typically smaller than:1 nm for kinetic energies in the range 15 < E (eV) < 3502 nm for kinetic energies in the range 10 < E (eV) < 1400That is, the IMFP corresponds to only a few atomic monolayers for low-energy electrons.

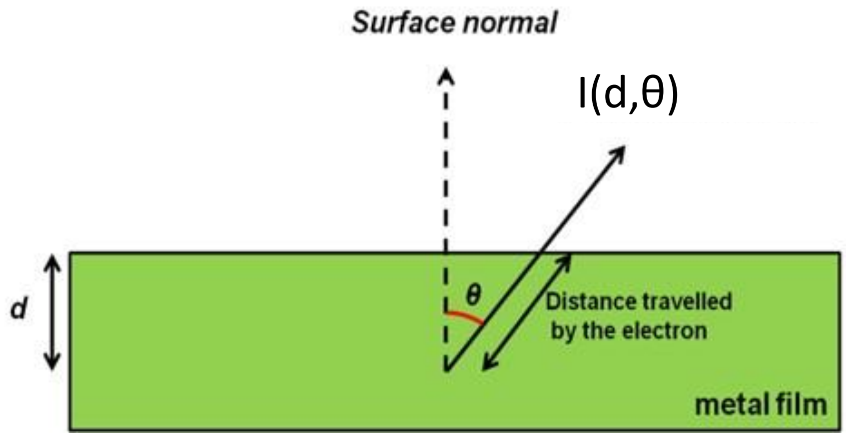


The fit has been performed using the Seah and Dench equation:

$$\frac{\lambda}{nm} = \frac{538\alpha}{E_{kin}^{2}} + 0.41\alpha^{3/2}\sqrt{E_{kin}}$$

E. Surface sensitivity

The emission of electrons with kinetic energy E_k from an atom at a depth d below the surface of the solid generates, within the solid, a signal of intensity I_0 directed toward the external detector.



where θ is the angle between the line connecting the detector to the emitting atom and the surface normal of the sample.

The attenuation of the intensity I_d of electrons with initial intensity I_o ,after traveling through a material depth d, can be calculated using:

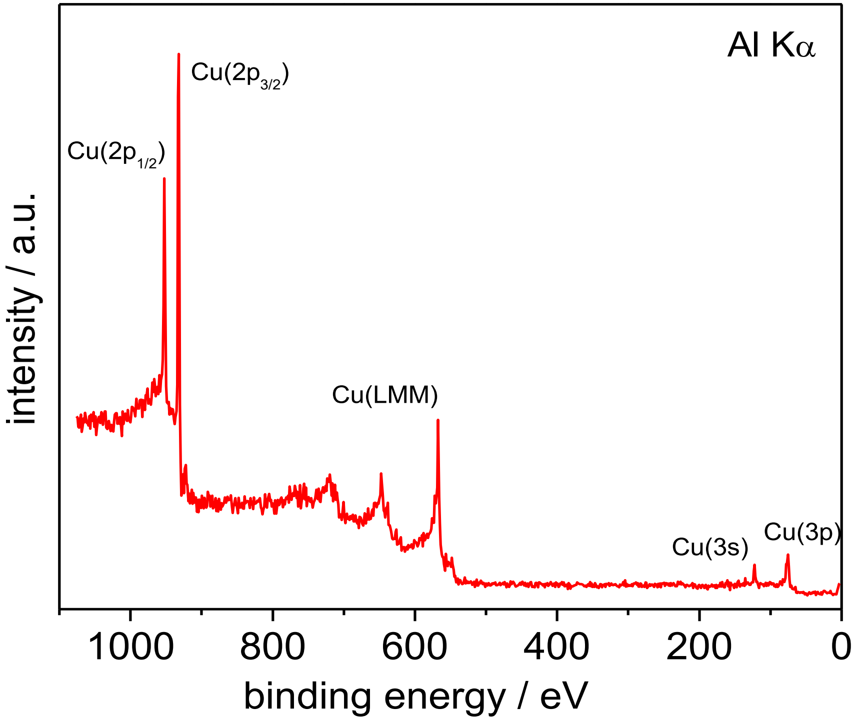
$$\mathrm{I}(d,\theta) = \mathrm{I}_0 e^{-\mathrm{d}/\lambda(\mathrm{E})\cos\theta}$$

The surface sensitivity can be enhanced by adjusting the detection geometry (by increasing the angle θ)

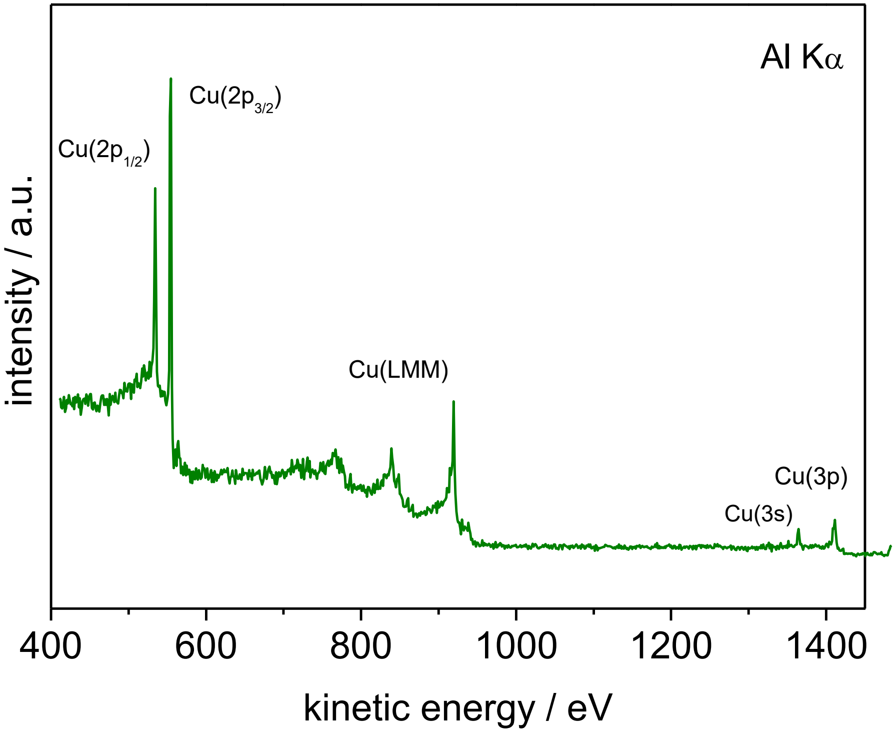
The larger the emission angle, the longer the path length the electron must travel within the solid, and therefore the greater the probability of energy loss.

F. Typical XPS spectra

XPS of clean Cu
As a function of **binding energy**.



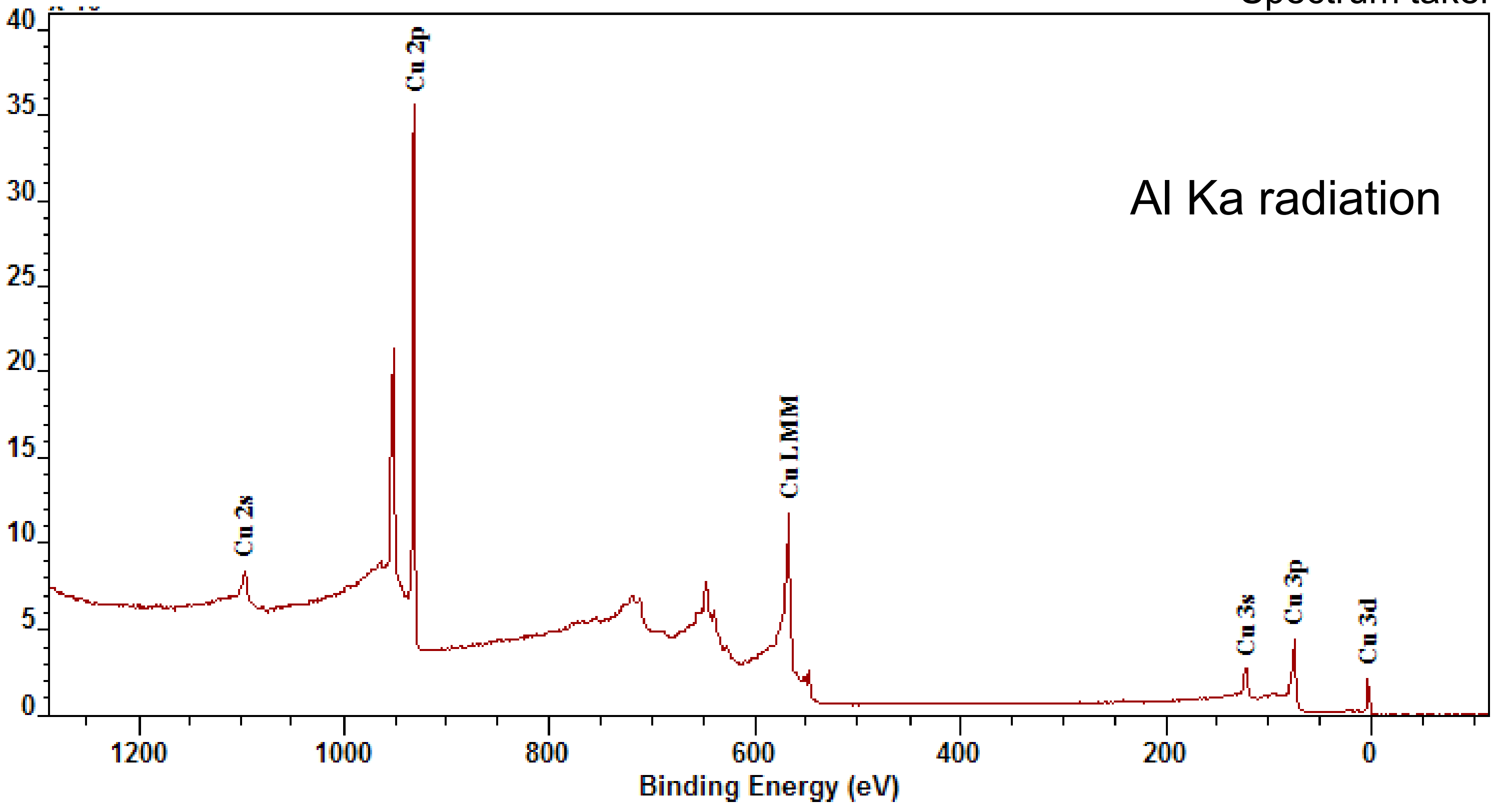
As a function of **kinetic energy**.
Kinetic and binding energy as correlated by:
$E_k = h\nu - E_b - \Phi$



F. Typical XPS spectra

XPS spectrum of clean Cu foil

Spectrum taken from casa-xps

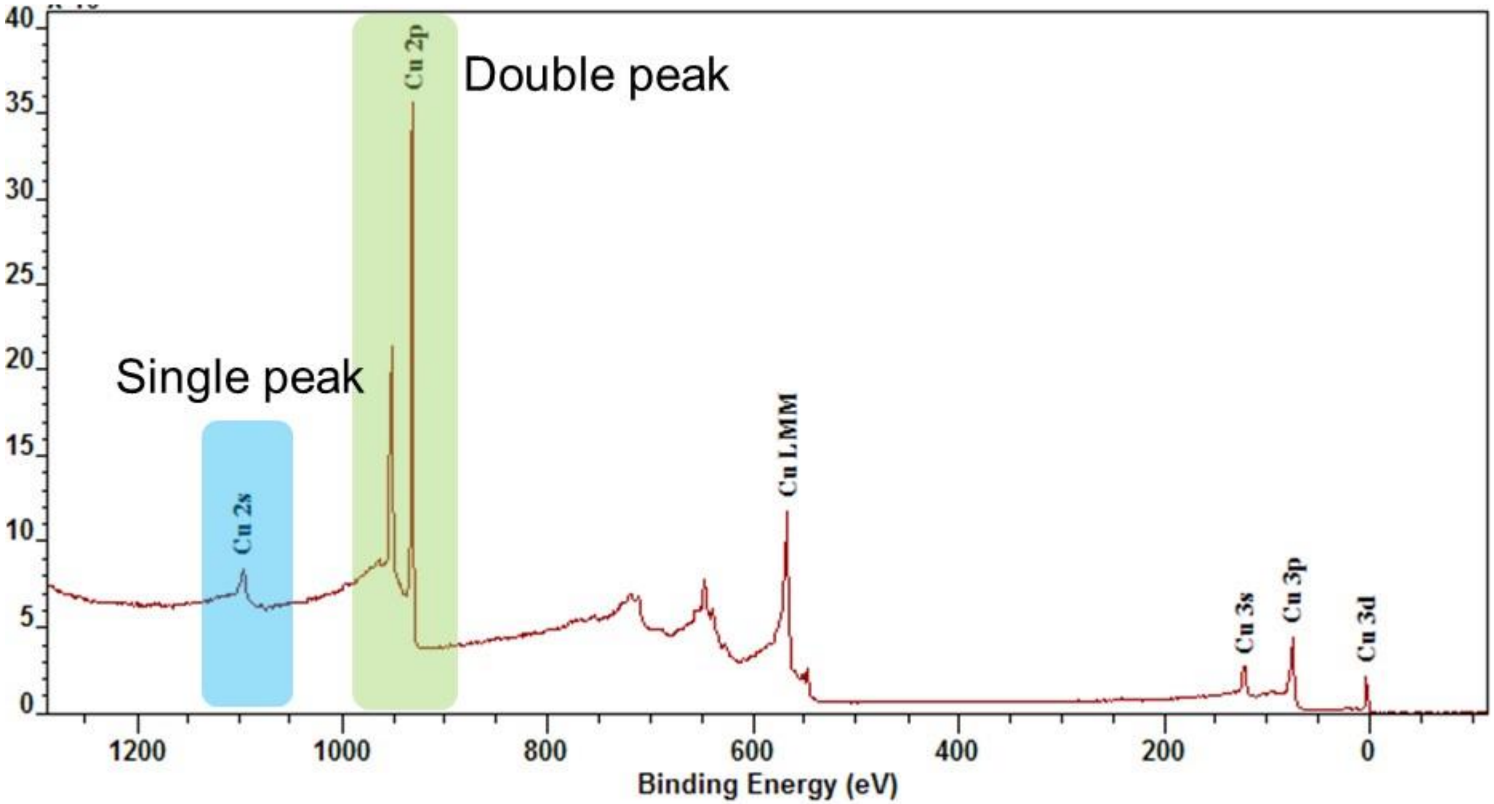


Note that X-rays excite electrons both from the core levels and from the valence band. However, XPS is mainly used to detect electrons originating from the core levels of the solid. Electrons emitted from the valence band will appear with low intensity in the low–binding-energy region (high–kinetic-energy region) of the spectrum.

F. Typical XPS spectra

1. Naming of peaks in XPS

The peaks in the spectrum appear at discrete binding energies. Both single peaks and double peaks (doublets) are observed.



F. Typical XPS spectra

1. Naming of peaks in XPS

The peaks are identified on the basis of the quantum numbers associated with the origin of the photoelectron

n l j

•***n*** is the principal quantum number. *The value of n take integer numbers* 1, 2, 3 etc.

•***l*** is the azimuthal (orbital angular momentum) quantum number. Its value can take integer numbers0, 1, 2,...,(n-1)

Τιμή l	***Τροχιακό***
0	*s*
1	*p*
2	*d*
3	*f*

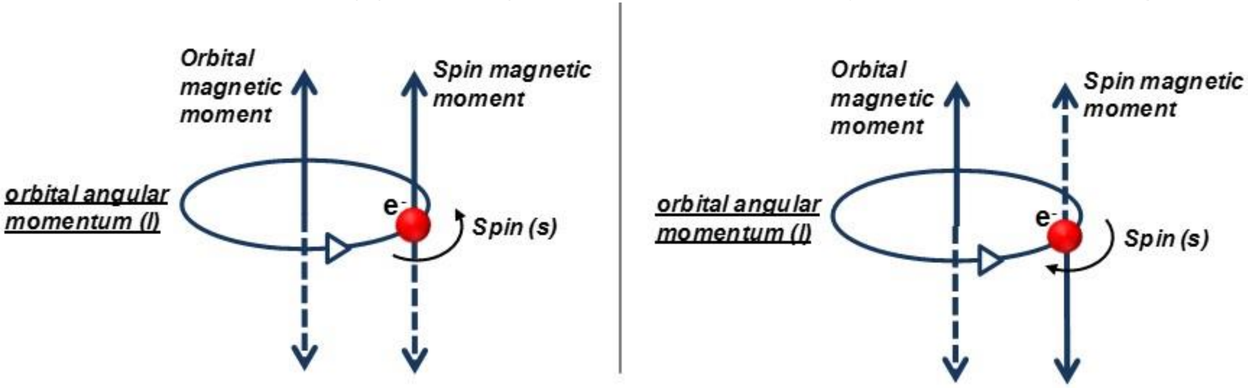
F. Typical XPS spectra

1. Naming of peaks in XPS

- ***j*** is the total angular momentum, given by *j = |l + s|*

The presence of doublets and singlet peaks occurs due to the value of *j*

The value of j arises from the so-called spin–orbit coupling.



j = |*l* + s|

j = l + 1/2

j = l – 1/2

When photoemission occurs from a level with a non-zero azimuthal (orbital angular momentum) quantum number (i.e. *l = 1, 2, 3 ...*), the uncoupled electron spin can combine with the orbital angular momentum, giving rise to two states (a doublet). Each state can be described by its total angular momentum *j*.

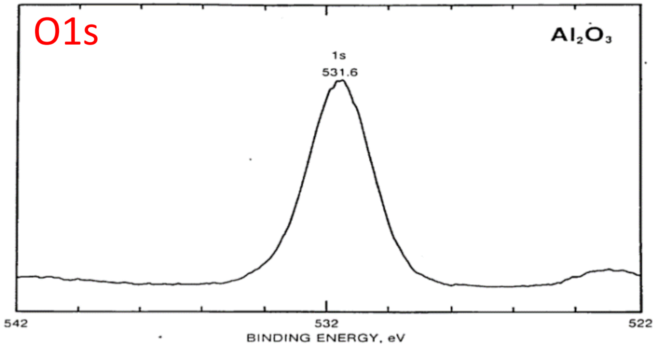
F. Typical XPS spectra

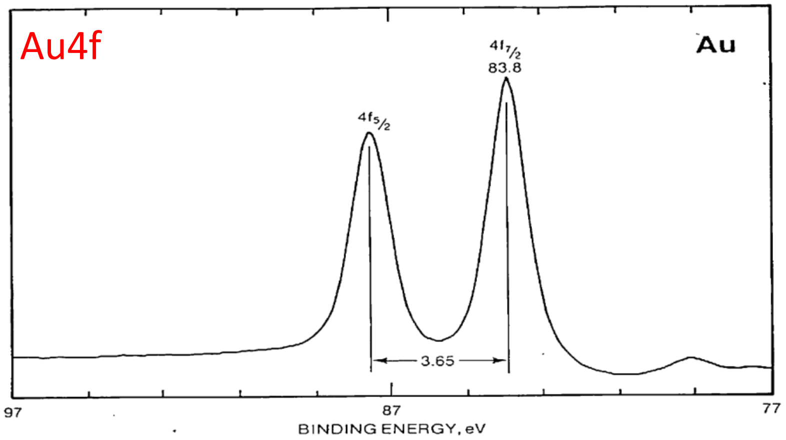
1. Naming of peaks in XPS

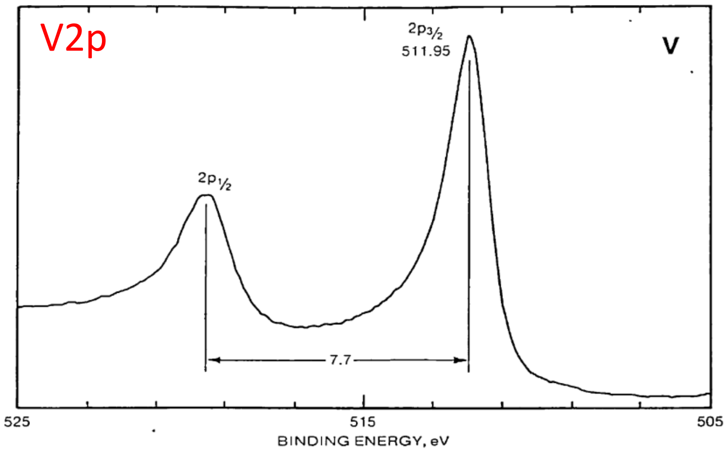
The relative intensity of the two states

The relative intensity of the two states is determined by their degeneracy $\boldsymbol{g_j = 2j+1}$

Τροχιακό	$j = \lvert l + s \rvert$		*Expected ratio* $(2j_1+1) : (2j_2+1)$
	$j_1\ (s = -1/2)$	$j_2\ (s = +1/2)$	
s	-	-	-
p	1/2	3/2	1 : 2
d	3/2	5/2	2 : 3
f	5/2	7/2	3 : 4







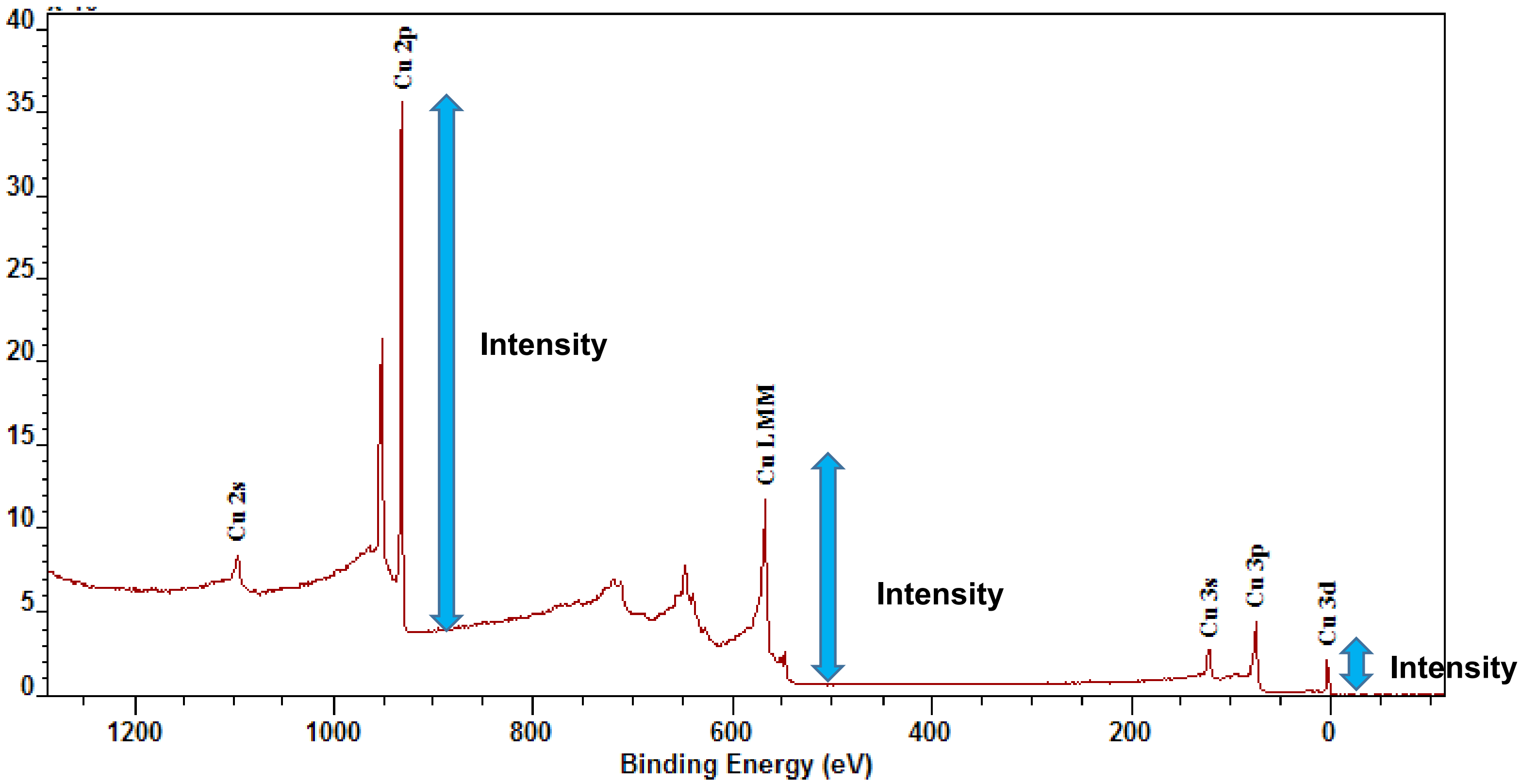
F. Typical XPS spectra

1. Naming of peaks in XPS

Quantum numbers				**Notation**	
n	***l***	***s***	***j***	**X-Ray level (most common in AES)**	**electron level (most common in XPS)**
1	0	±1/2	1/2	K	1s
2	0	±1/2	1/2	L_1	2s
2	1	+1/2	3/2	L_2	$2p_{3/2}$
2	1	-1/2	1/2	L_3	$2p_{1/2}$
3	0	±1/2	1/2	M_1	3s
3	1	+1/2	3/2	M_2	$3p_{3/2}$
3	1	-1/2	½	M_3	$3p_{1/2}$
3	2	+1/2	5/2	M_4	$3d_{5/2}$
3	2	-1/2	3/2	M_5	$3d_{3/2}$
4	3	+1/2	7/2	N_6	$4f_{7/2}$
4	3	-1/2	5/2	N_7	$4f_{5/2}$
etc….					

F. Typical XPS spectra

2. Peak intensity

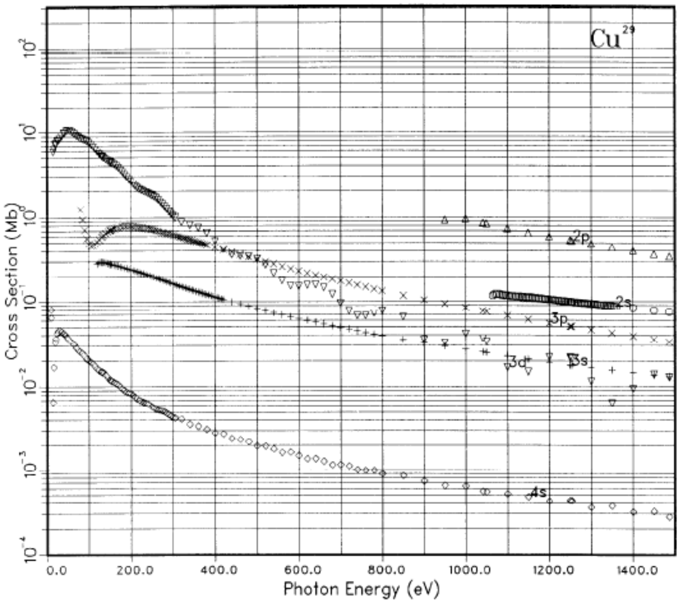


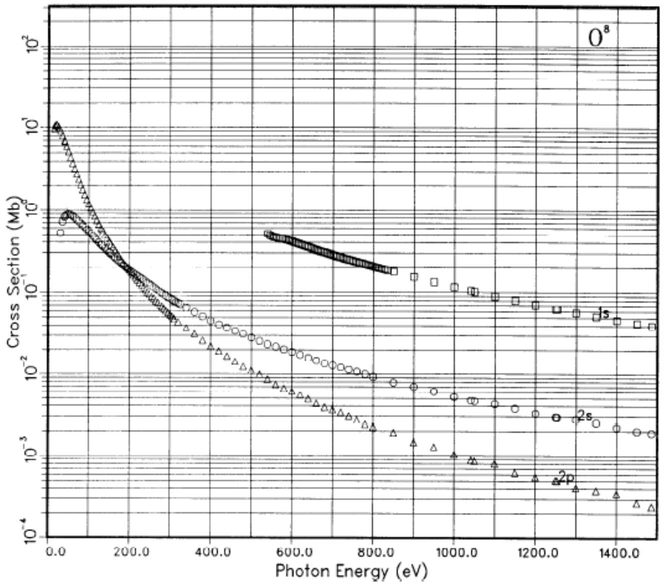
F. Typical XPS spectra

This is mainly due to the different ionization cross sections of the various electronic levels of the solid during the photoionization process (i.e., the probability that a given level will be ionized when irradiated by a photon).

The ionization cross section depends both on the type of orbital and on the photon energy.

e.g. Variation of the ionization cross section of copper and oxygen as a function of photon energy.

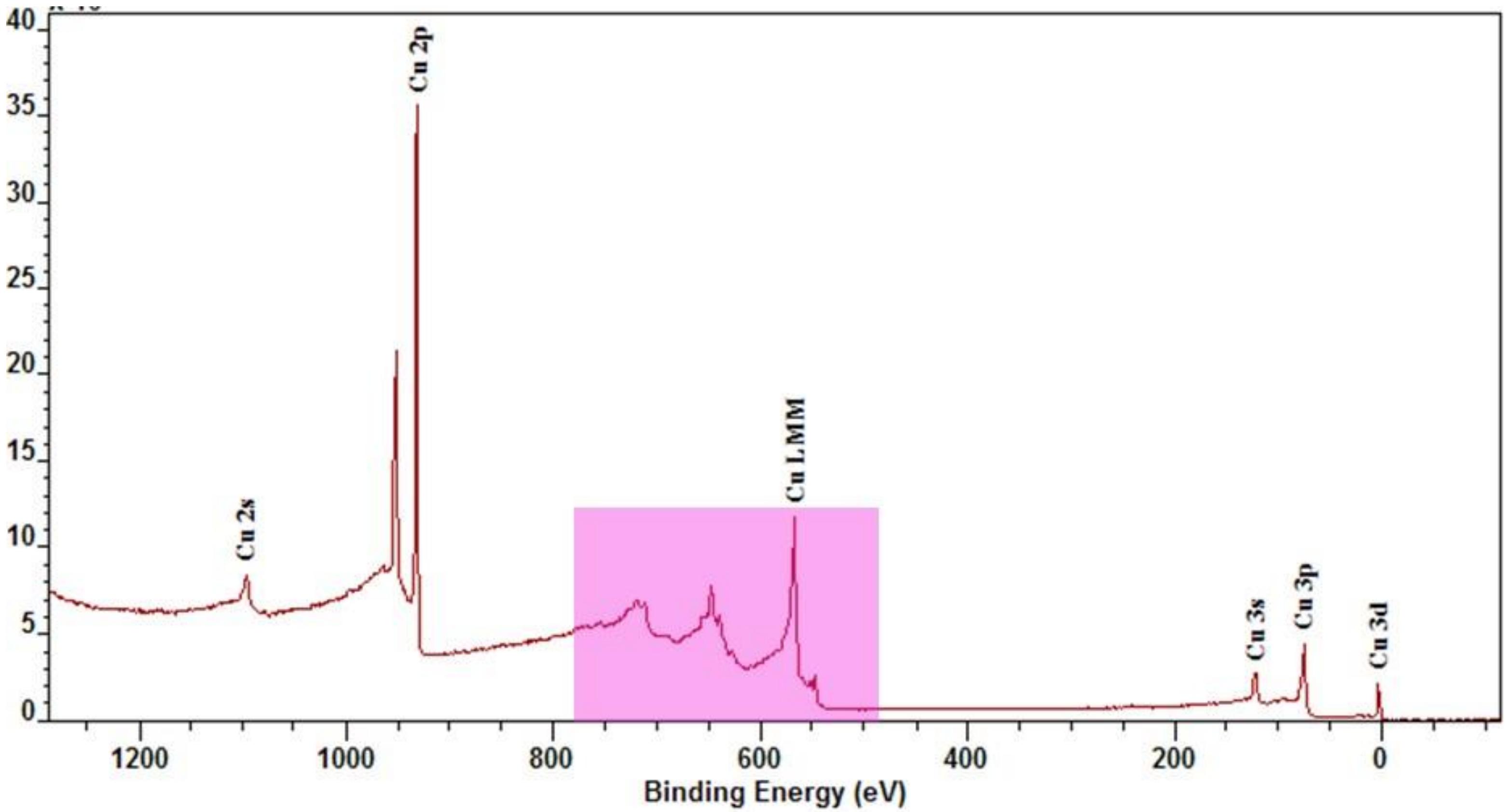




Ionization cross sections are particularly important when XPS is performed using synchrotron light sources.

F. Typical XPS spectra

3. Auger electron emission



F. Typical XPS spectra

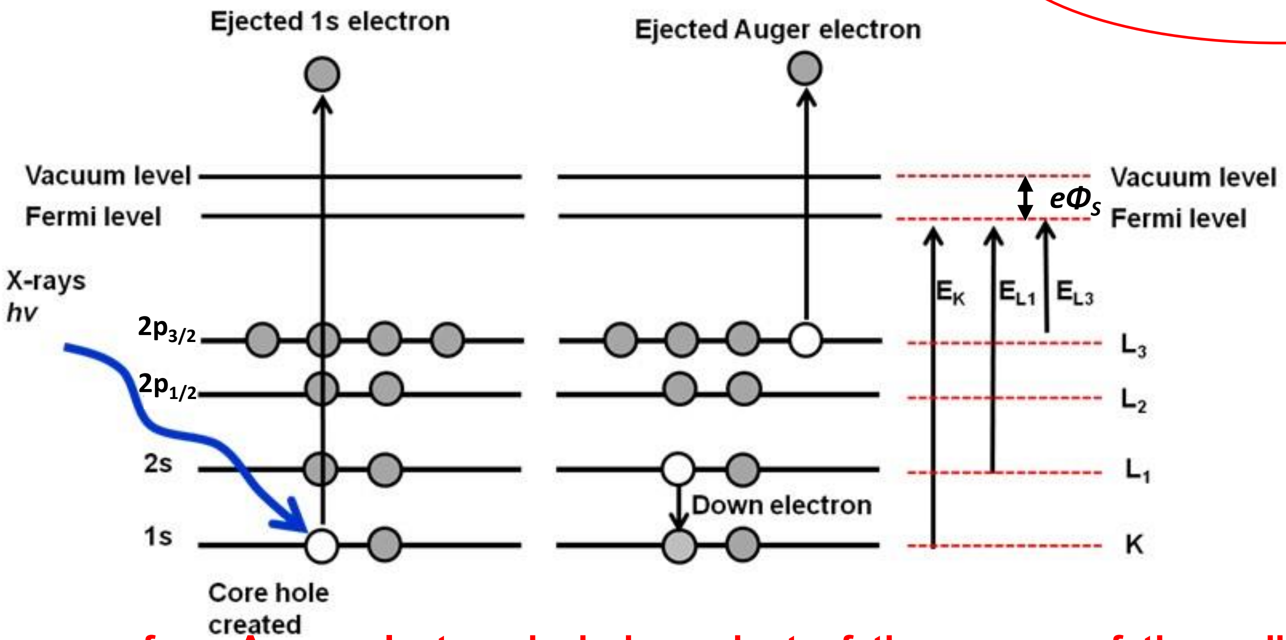
X-ray excited Auger electron spectroscopy (AES)

XPS:

$$E_{kin} = h\nu - E_b - e\Phi_s$$

AES :

$$E_{kin} = E_K - E_{L1} - E_{L3} - e\Phi_s$$



- **The kinetic energy of an Auger electron is independent of the energy of the radiation used for excitation.**

$$E_{kin} = E_K - E_{L1} - E_{L3} - \Phi$$

- **The kinetic energy of the emitted photoelectrons will increase with increasing hv and will decrease with decreasing *hv***

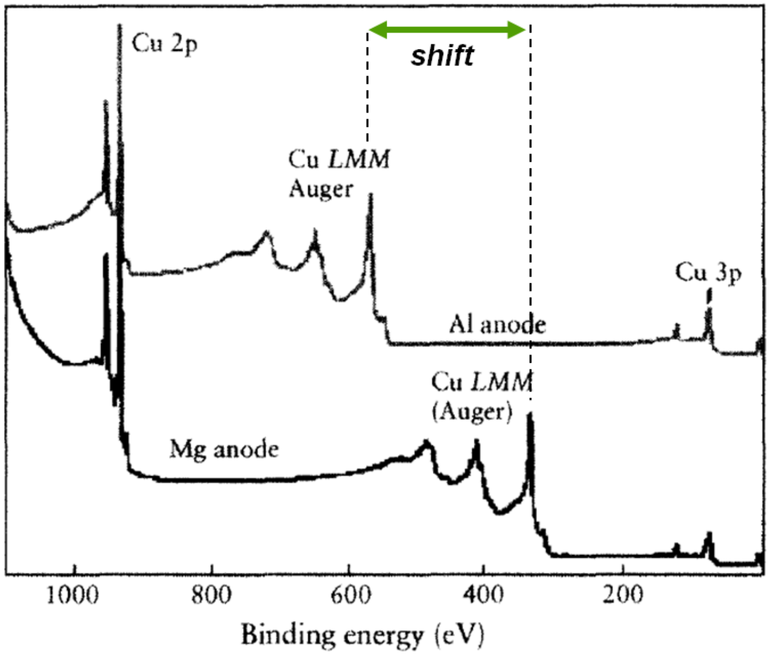
$$E_{kin} = h\nu - E_b - \Phi$$

F. Typical XPS spectra

3. Auger electron emission

The kinetic energy of an Auger electron is independent of the energy of the radiation used for excitation. This is a very useful property, especially when Auger peaks overlap with photoelectron peaks.

Laboratory X-ray sources commonly use anodes that can produce either *Mg Kα* radiation (1253.6 eV) or *Al Kα* radiation (1486.6 eV). Switching from an Mg anode to an Al anode (or vice versa) will shift the Auger peaks (on the binding-energy scale), and therefore any overlap can be avoided.



This is due to the fact that the *kinetic energy* of Auger electrons does *not* depend on *hv*, whereas the *kinetic energy* of photoelectrons *does* depend on *hv*.

XPS wide scan of a clean Cu sample

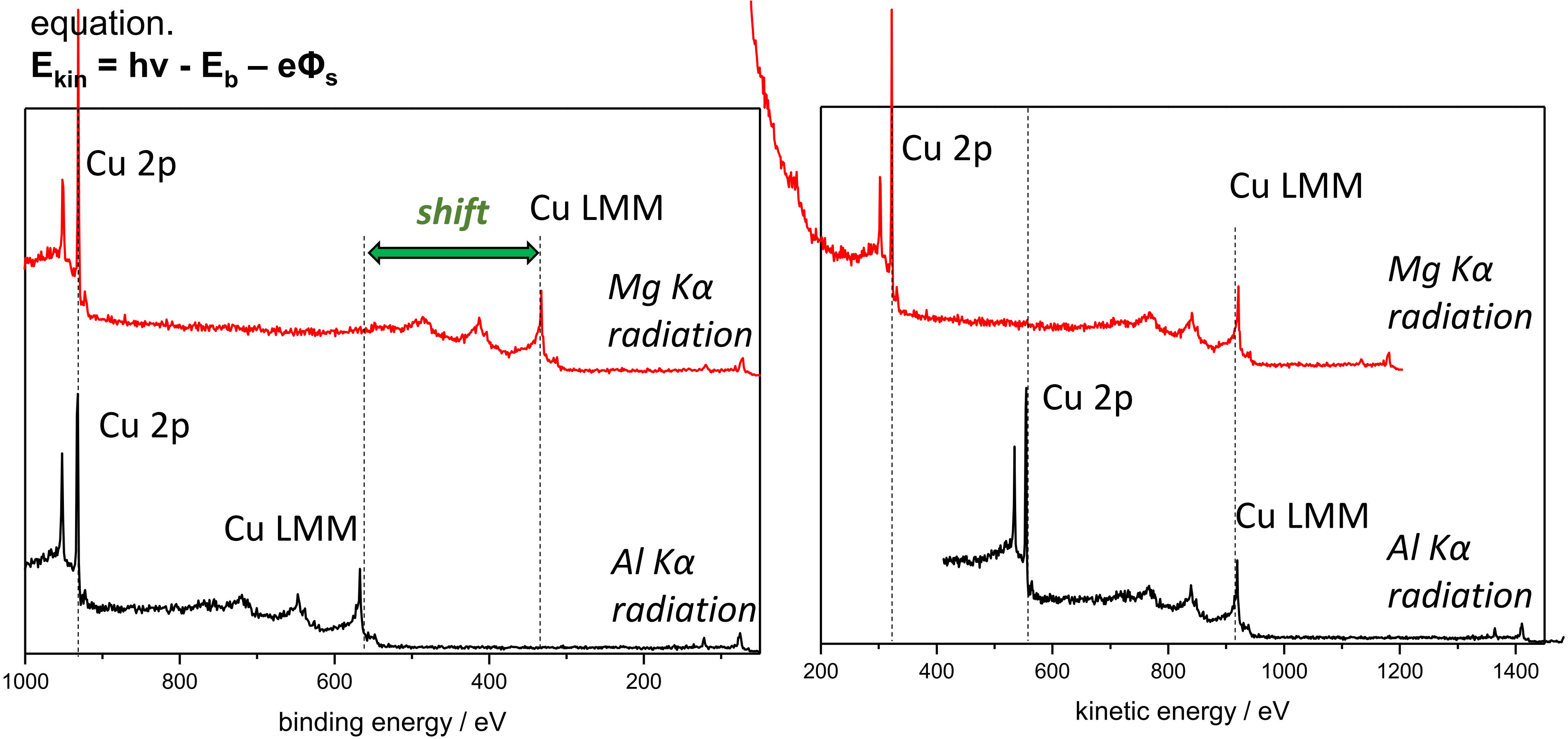
F. Typical XPS spectra

3. Auger electron emission

Scanning a copper-foil sample using Al Kα and Mg Kα radiation. The data are displayed both on a binding-energy scale (left graph) and on a kinetic-energy scale (right graph).

The conversion from a kinetic-energy scale to a binding-energy scale is done using the XPS equation.

$$\mathbf{E_{kin} = h\nu - E_b - e\Phi_s}$$



F. Typical XPS spectra

Peak positions: initial-state and final-state effects

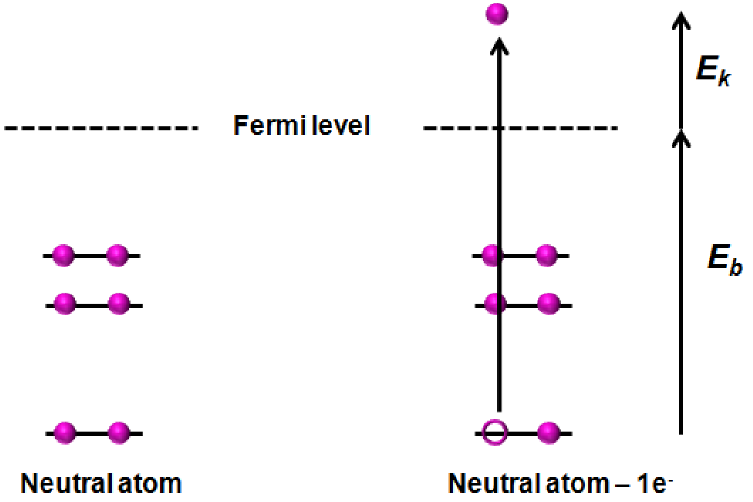
Sudden approximation (or frozen orbital approximation)

For practical reasons, it is often assumed that no relaxation of the atom occurs after the emission of the electron.

In other words, the orbital energies are assumed not to change during ionization. This means that the binding energy E_B, of the photoelectron is equal to the negative value of the orbital energy, $-\varepsilon$.

$$E_B = -\varepsilon$$

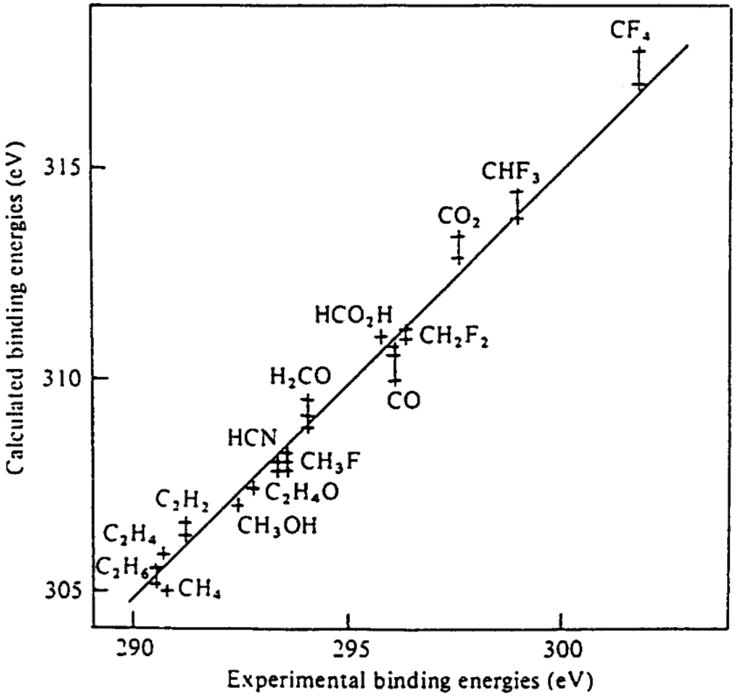
This approximation is known as Koopmans' theorem.



F. Typical XPS spectra

Peak positions: initial-state and final-state effects

However, the measured binding energies and the calculated orbital energies differ by more than 10–30 eV



This discrepancy is due to both initial-state and final-state effects of the atom.

→ **Calculated and experimentally measured binding energies for organic molecules**

In reality, Koopmans' theorem does not hold because of the "relaxation" of the electronic structure (redistribution) that occurs after ionization.

When a core-level hole is created in the solid, the electrons "relax" in order to lower the total energy and partially screen the hole.

F. Typical XPS spectra

Peak positions: initial-state and final-state effects

The binding energy, E_B , of a photoelectron, and therefore the position of a peak in the X-ray photoelectron spectrum, depends on:

1. **The initial state of the atom** (i.e., the state of the atom before ionization)
2. **The final state of the atom** (i.e., the state of the atom after ionization)

$$E_B = E_f - E_i$$

Therefore, the shift in the position of a peak in a photoelectron spectrum may arise from both initial-state and final-state effects of the atom.

F. Typical XPS spectra

Peak positions: initial-state and final-state effects

Initial-state effects are associated with changes in the electronic environment of an atom (such as changes in its oxidation state), or more generally with modifications in the local chemical environment of the atom.

When electrons are withdrawn from an atom due to chemical bonding (i.e., an increase in its oxidation state), the electronic environment of the atom is altered.

Consequently, the binding energy $\mathbf{E_B}$ of its electrons will appear shifted in the X-ray photoelectron spectra.

In XPS terminology, this type of change is referred to as a *chemical shift*.

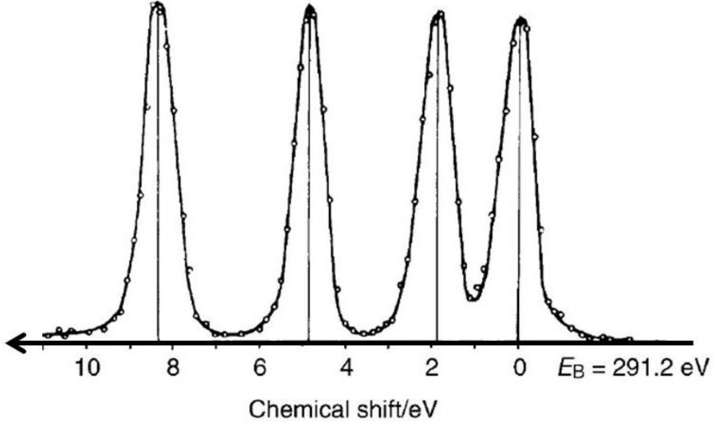
F. Typical XPS spectra

Peak positions: initial-state and final-state effects

Example initial state effects

ethyl trifluoroacetate

$CF_3COOCH_2CH_3$



XP spectrum of an organic molecule

The C 1s spectrum of ethyl trifluoroacetate ($CF_3COOCH_2CH_3$) is plotted as function of chemical shift.

Based on initial state effect arguments comment on the spectrum.

Four peaks are observed

→ four different chemical environments of carbon in the molecule.

-The carbon atom of the CF_3 group, which is adjacent to three strongly electronegative fluorine atoms, results in the largest chemical shift. The fluorine atoms lead to a depletion of the electron density on the carbon atom and consequently, it holds on to the 1s electron more strongly.

- The acetate carbon atom has two neighbouring, fairly electronegative, oxygen atoms which have a similar but smaller effect, giving the second largest chemical shift.

- The carbon atom of the CH2 group has one neighbouring oxygen atom and the third largest chemical shift.

- Finally the CH3 group leads to the smallest chemical shift (lowest ionization energy).

J. Electron Spectr. Relat. Phen. 2 (1974) 405-434

F. Typical XPS spectra

Peak positions: initial-state and final-state effects

Final State effects

Final-state effects arise from disturbances in the electronic structure of the atom after photoelectron emission.

The emission of photoelectrons creates a positively charged core hole within the atom. Electrons near this positive charge will rearrange to partially screen the hole (vacancy screening). In other words, the electrons readjust in order to lower the total energy.

The outcome of these final-state effects is the appearance of secondary spectral features, such as shake-up and shake-off satellite peaks.

F. Typical XPS spectra

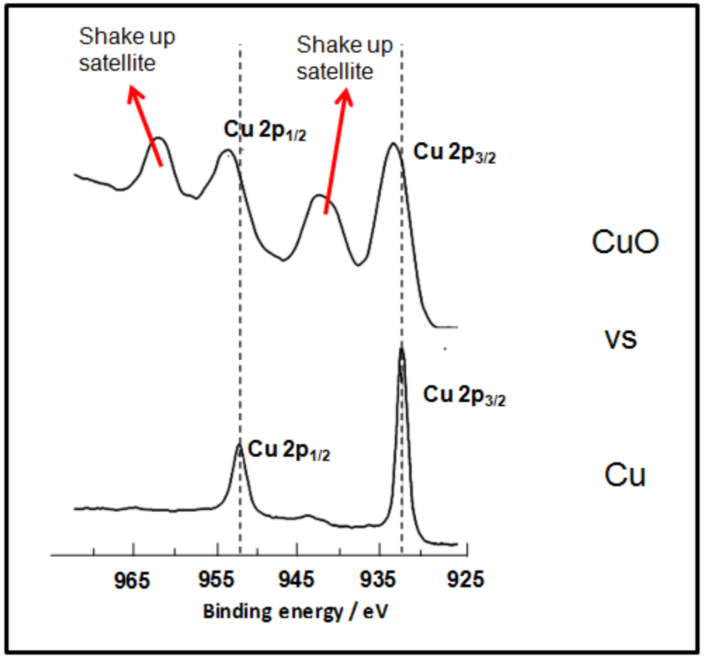
Peak positions: initial-state and final-state effects

Example, final state effect

The shake-up process occurs when a valence electron is excited to a higher energy level.

The energy required for this transition is taken from the primary emitted electron, and consequently a satellite peak appears at a higher binding energy relative to the main peak.

Shake-up processes are final-state effects.



G. Exercise

The following spectrum corresponds to an Au/TiO_2 catalyst and was recorded using Al Kα X-ray radiation (1486.6 eV). The spectrum is presented as a function of kinetic energy. Peak A (1399.0 eV) and peak B (1395.3 eV) correspond to the Au 4f doublet.

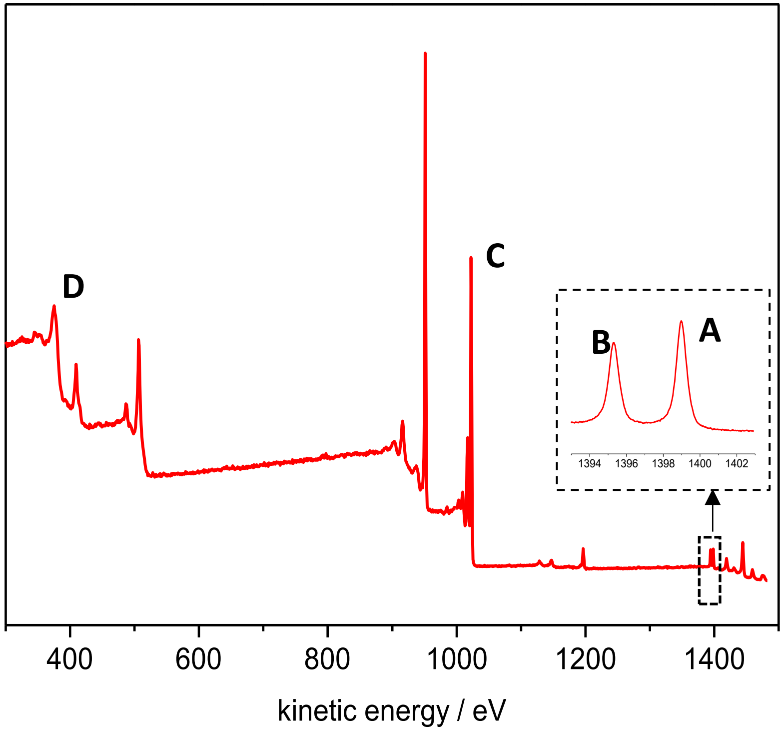
(i) Calculate the binding energy of peak A and peak B.

(ii) Identify peaks A and B.

(iii) Calculate theoretically the intensity ratio between peak A and peak B.

(iv) Repeating the experiment using Mg Kα radiation causes peak C to shift to lower kinetic energy, while peak D remains at the same kinetic energy. Explain this observation and assign peaks C and D to the Ti LMM Auger transition and the Ti $2p_{3/2}$peak.

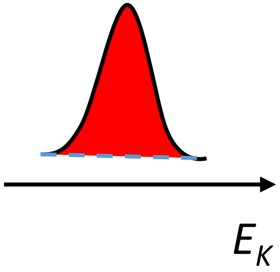
Note: The work function of the sample is *$\Phi s = 3.8$ eV*



H. Quantitative analysis

The intensity of XPS peaks is proportional to the number of atoms detected within the analyzed surface region.

The intensity is the integrated signal under a given peak, although it is often approximated by the peak height (after background subtraction / baseline subtraction).

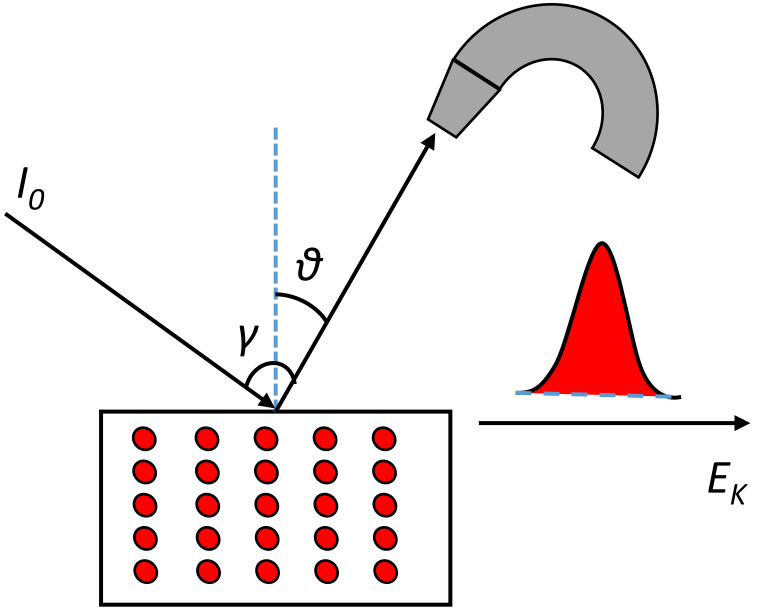


H. Quantitative analysis

Consider a photopeak with kinetic energy E_A originating from atoms of an element A, uniformly distributed with concentration N_A within a solid M with a clean surface.

The sample is illuminated with a uniform X-ray intensity I_0 of photon energy $h\nu$ at an incidence angle γ with respect to the analysis direction. The analyzer collects electrons at an angle θ relative to the surface normal, and the entrance slit is small. The intensity of the photopeak is given by the general expression:

$$I_A = \sigma_A(h\nu)\, L(\gamma)\, I_0\, N_A\, \lambda_M(E_A)\, \cos\theta\, G(E_A)\, D(E_A)$$



- The term $\sigma_A(h\nu)$ is the photoionization cross section for the specific electronic level.

  The term $L(\gamma)$,the angular asymmetry of the emitted photoelectron signal, and the cross section are fundamental physical properties of the atom–radiation interaction, and tabulated values for them are available in the literature.
- The quantity $\lambda_M(E_A)$ is the inelastic mean free path of the photoelectrons in the solid.
- The factor $G(E_A)$ (etendue) expresses the efficiency of the analyzer in collecting and focusing onto the detector the photoelectrons with the appropriate pass energy. For hemispherical analyzers, it is generally:
- $G(E_A) = (E_A)^{-\nu}$
- where ν typically ranges between 0.5 and 1, depending on the construction characteristics of the analyzer.
- Finally, the factor $D(E_A)$ represents the detection efficiency after the electrons exit the analyzer and depends on the type of detector used.

H. Quantitative analysis

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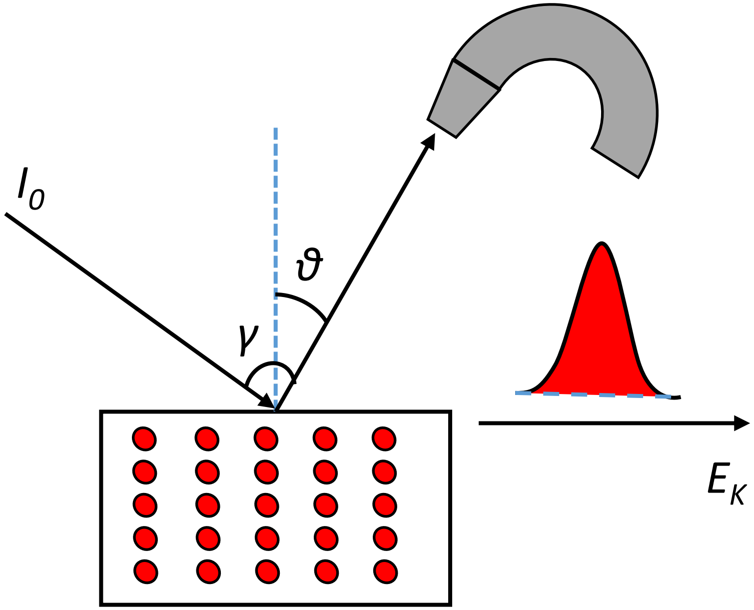


Since several of the factors on the right-hand side of the equation are often unknown, a simple way to eliminate them is to express I_A relative to the corresponding intensity $I_A(\infty)$ of the same photopeak of element A measured in a reference sample under identical instrumental and experimental conditions.

The reference sample is usually the pure element A, and in that case $I_A(\infty)$ can be regarded as the **atomic sensitivity factor (ASF)** for the specific electronic level of element A.

H. Quantitative analysis

Quantitative analysis in homogeneous samples

Let us consider a solid M composed of elements A and B with atomic concentrations N_A and N_B ,respectively. If the atomic sensitivity factors $I_A(\infty)$ and $I_B(\infty)$ are known, then according to the relation it follows that:

$$I_A / I_A(\infty) = \{N_A / N_A(\infty)\} * \{\lambda_M(E_A) / \lambda_A(E_A)\}$$

$$I_B / I_B(\infty) = \{N_B / N_B(\infty)\}_* \{\lambda_M(E_B) / \lambda_B(E_B)\}$$

where the $I(\infty)$ values have been measured on the same instrument and under the same conditions as the corresponding I values.

$$I_A / I_B = (N_A / N_B) * \{IA(\infty) / I_B(\infty)\} * \{N_B(\infty) / N_A(\infty)\} * \{\lambda_M(E_A).\lambda_B(E_B) / \lambda_M(E_B).\lambda_A(E_A)\}$$

$N_I(\infty)$ are the atomic concentrations in the pure reference samples, and $\lambda_I(E_J)$ are the IMFP values of photoelectrons with energy E_J within the solid.

A simpler form of the above equation is based on **relative sensitivity factors (RSF),** S_i ,for various electronic levels of different elements, which are available in tabulated form.

$$I_A / I_B = (N_A / N_B)(S_A / S_B)$$

H. Quantitative analysis

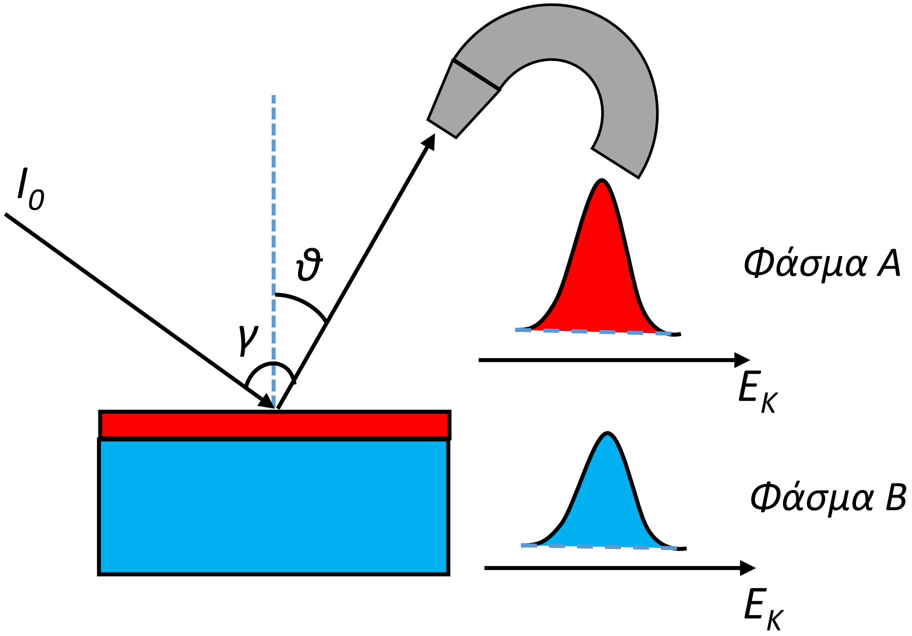
Quantitative analysis in heterogeneous samples

If elements A and B are randomly distributed within the analyzed region of the sample, quantitative analysis is not always possible.

A particularly simple case arises when a thin, uniform layer of pure elemental solid A with thickness d_A lies on top of a pure elemental substrate B.

In this case, the determination of d_A is the objective of the quantitative analysis.

$$I_B = I_B(0)\exp\{-d_A/\lambda_A(E_B)\cos\vartheta\}$$
$$I_A = I_A(\infty)[1-\exp\{-d_A/\lambda_A(E_A)\cos\vartheta\}$$



$I_B(0)$ is the intensity for the pure solid B. $I_A(\infty)$ is the intensity measured under the same conditions when d_A approaches infinity (practically, when $d_A > 5\lambda_A(E_A)\cos\theta$

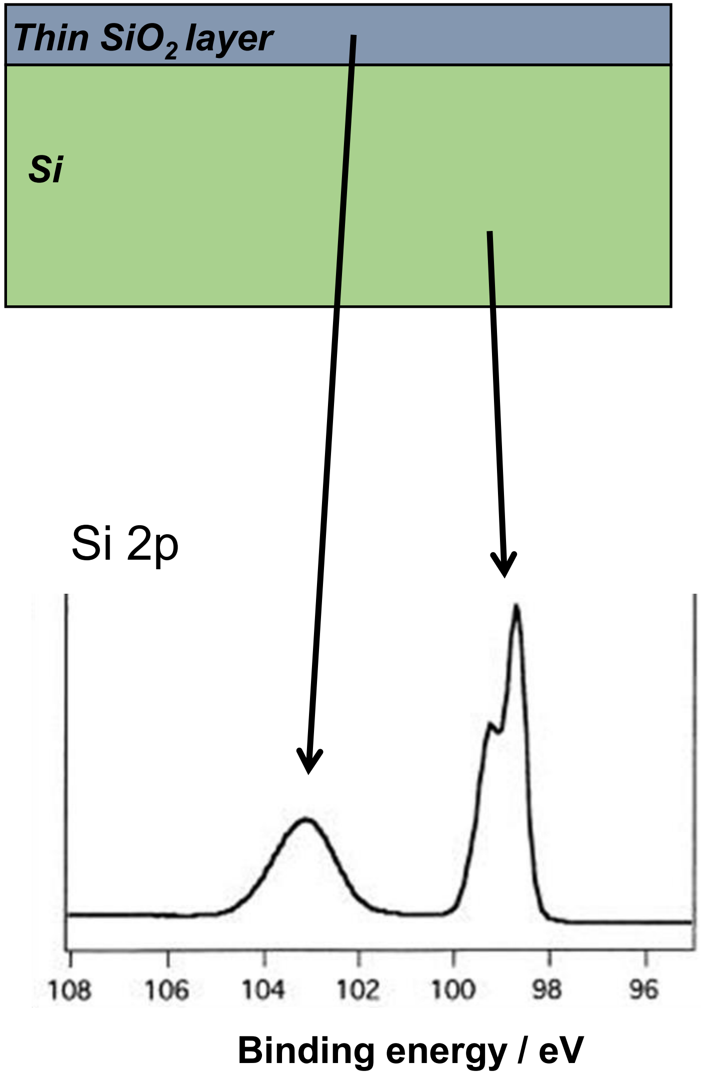
Examples

1. **Thin films**
2. **Clusters on surfaces**
3. **Metal nanoparticles**

Example 1

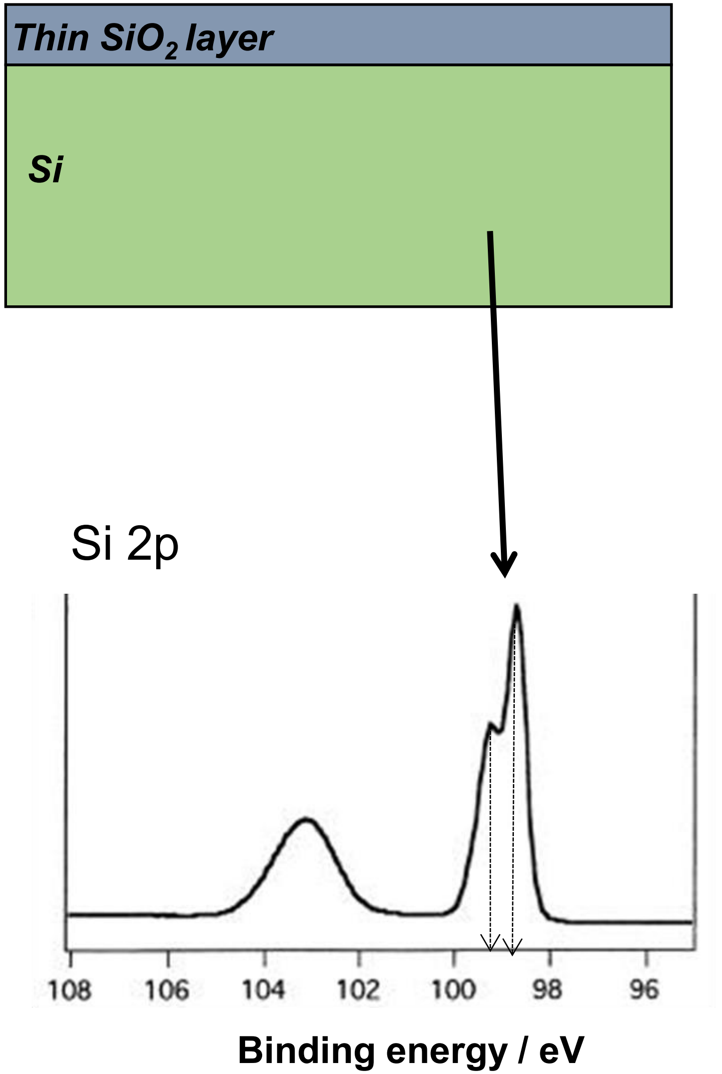
Oxide thin films

OXIDE SURFACE



Si 2p appears as a doublet

1. Why?
2. What are the two components of the doublet?
3. What is the expected ratio of the two components?



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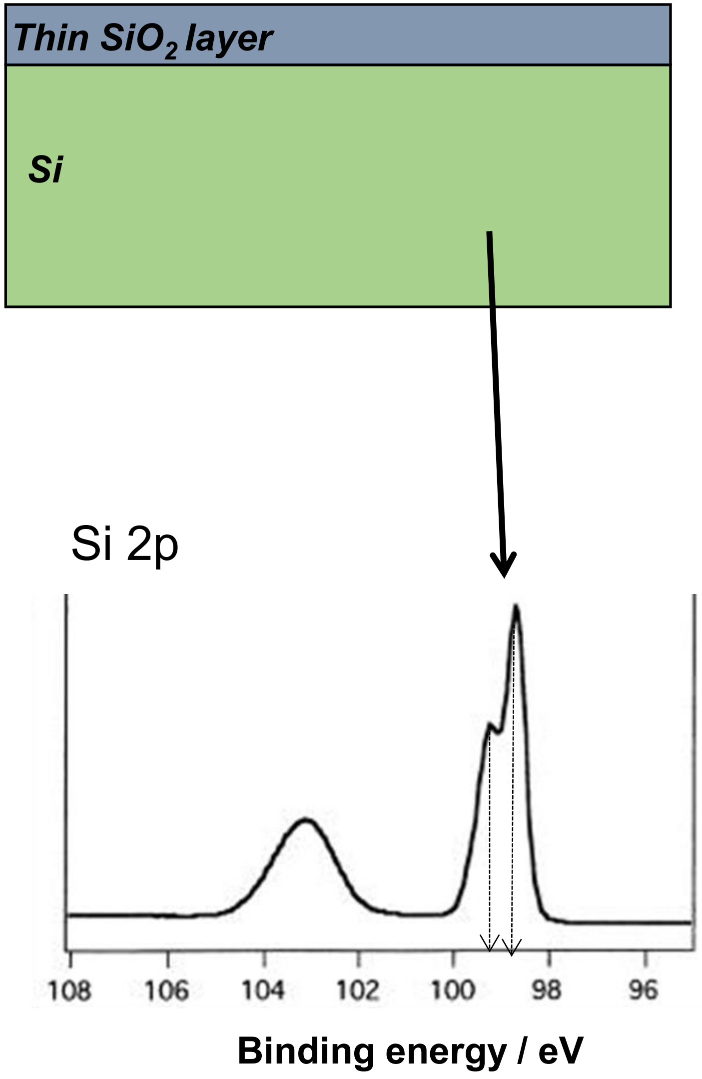

1. **When photoemission occurs from a level with a non zero orbital angular momentum (i.e. *$l = 1, 2, 3...$*)**, then the unpaired spin can be paired with or against the orbital angular momentum giving rise two states (doublet).

   Each state can be described by an overall angular momentum
   $j = |l + s|$

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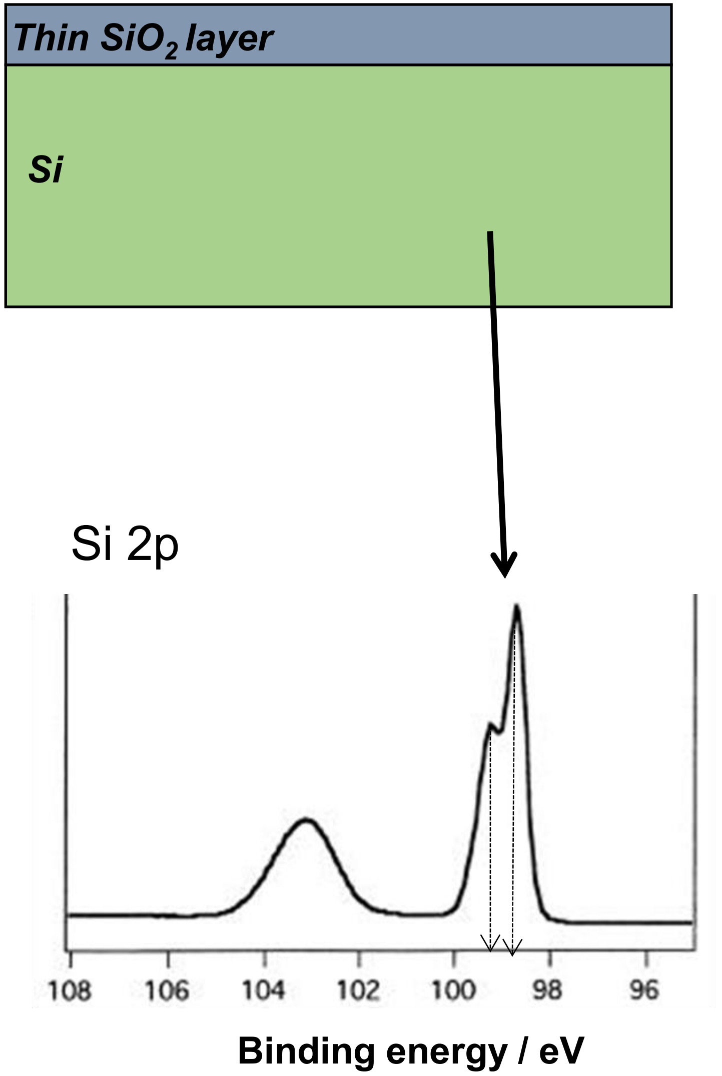

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j = |l + s|

2. **The two components of the doublet are:**

j_2 = l + s = 1 + ½ = 3/2 → Therefore the first peak is Si $2p_{3/2}$

j_1 = l + s = 1 - ½ = 1/2 → Therefore the first peak is Si $2p_{1/2}$

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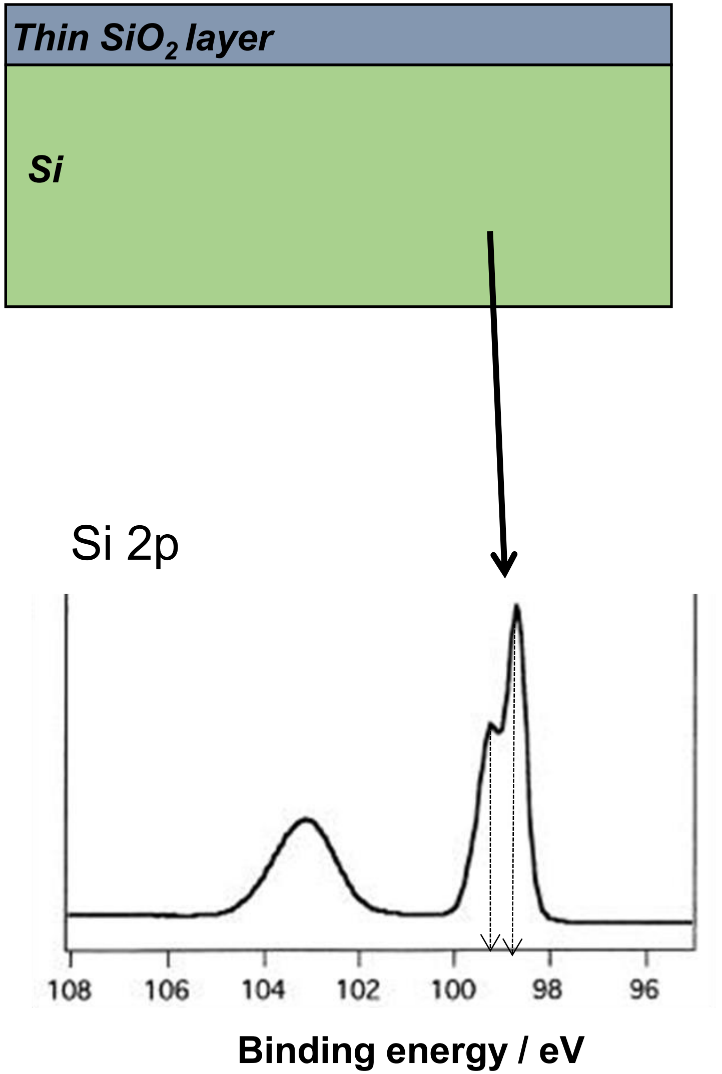

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$g_j = 2j+1$

$(2j_2+1) : (2j_1+1) = 2 : 1$

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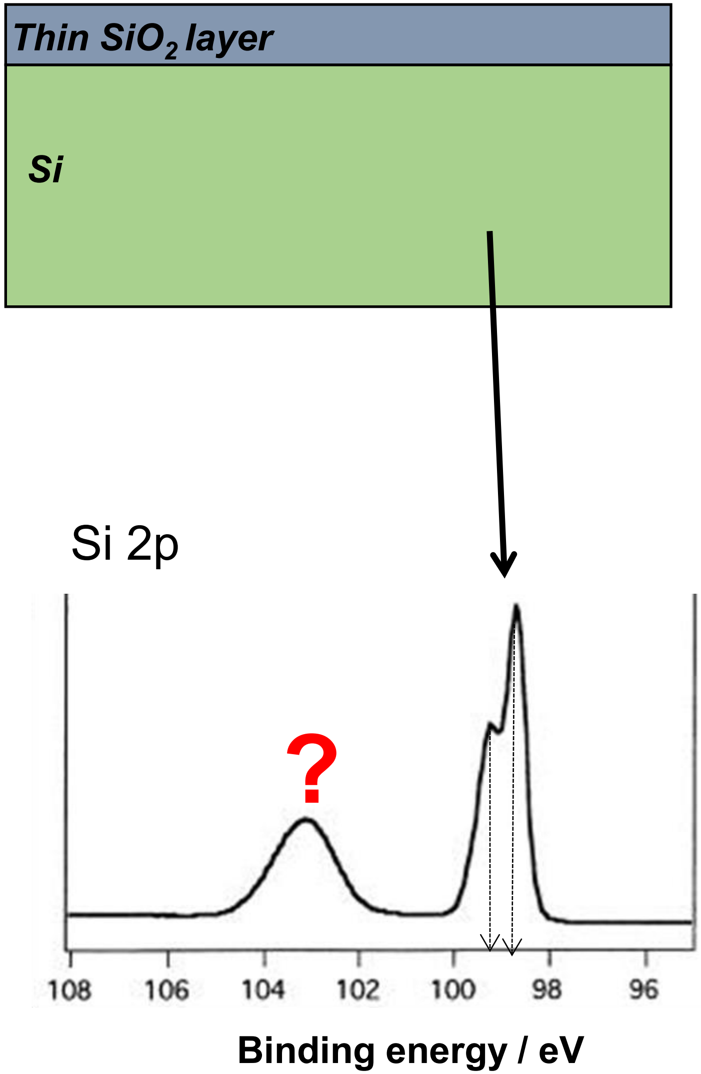
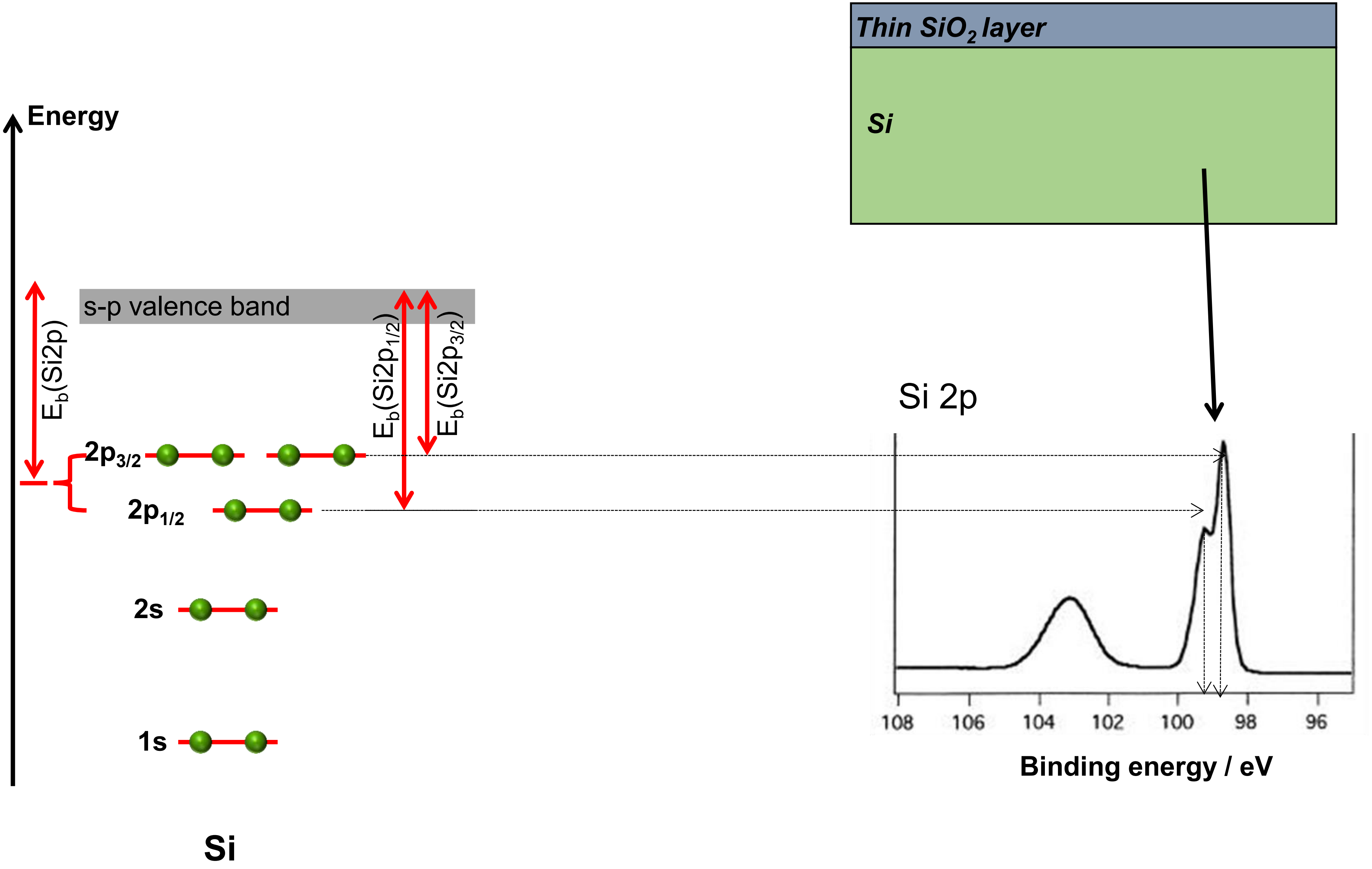
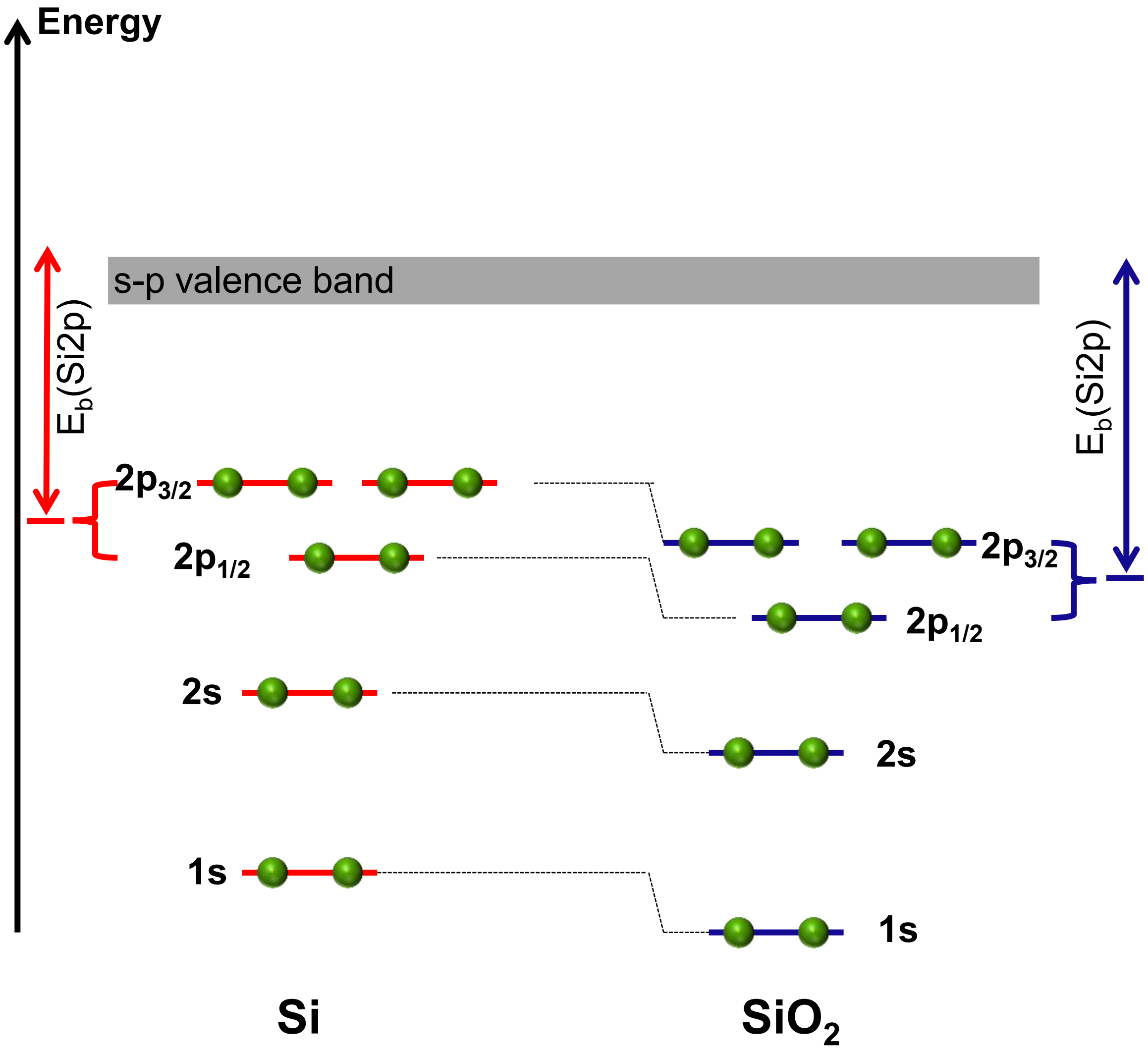
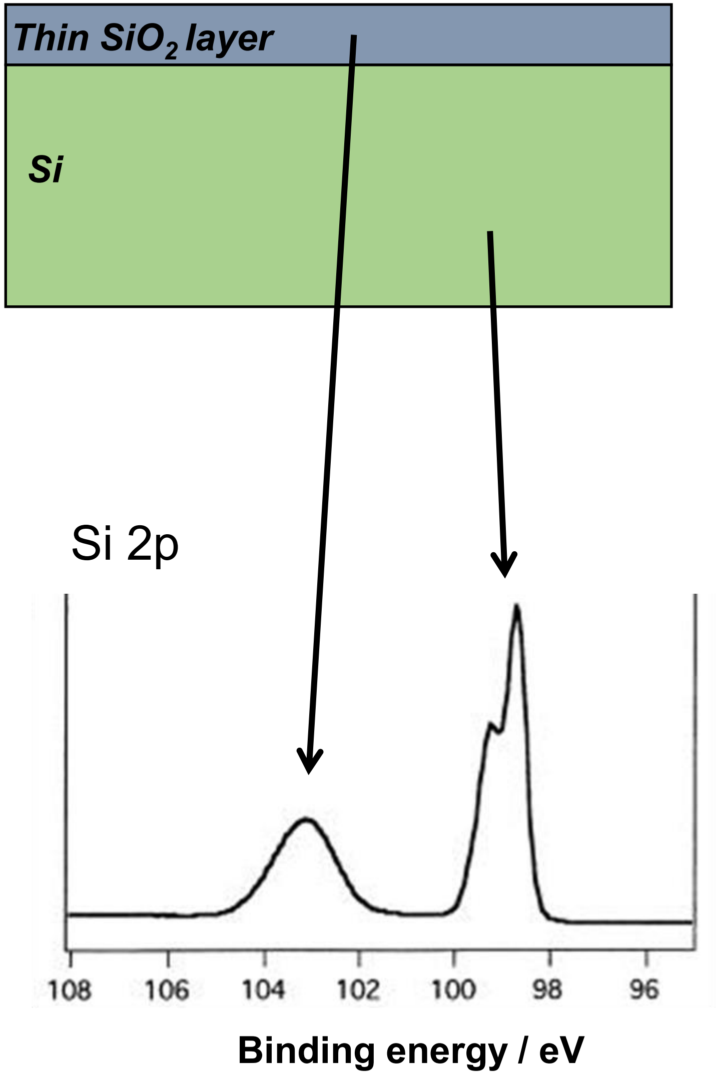
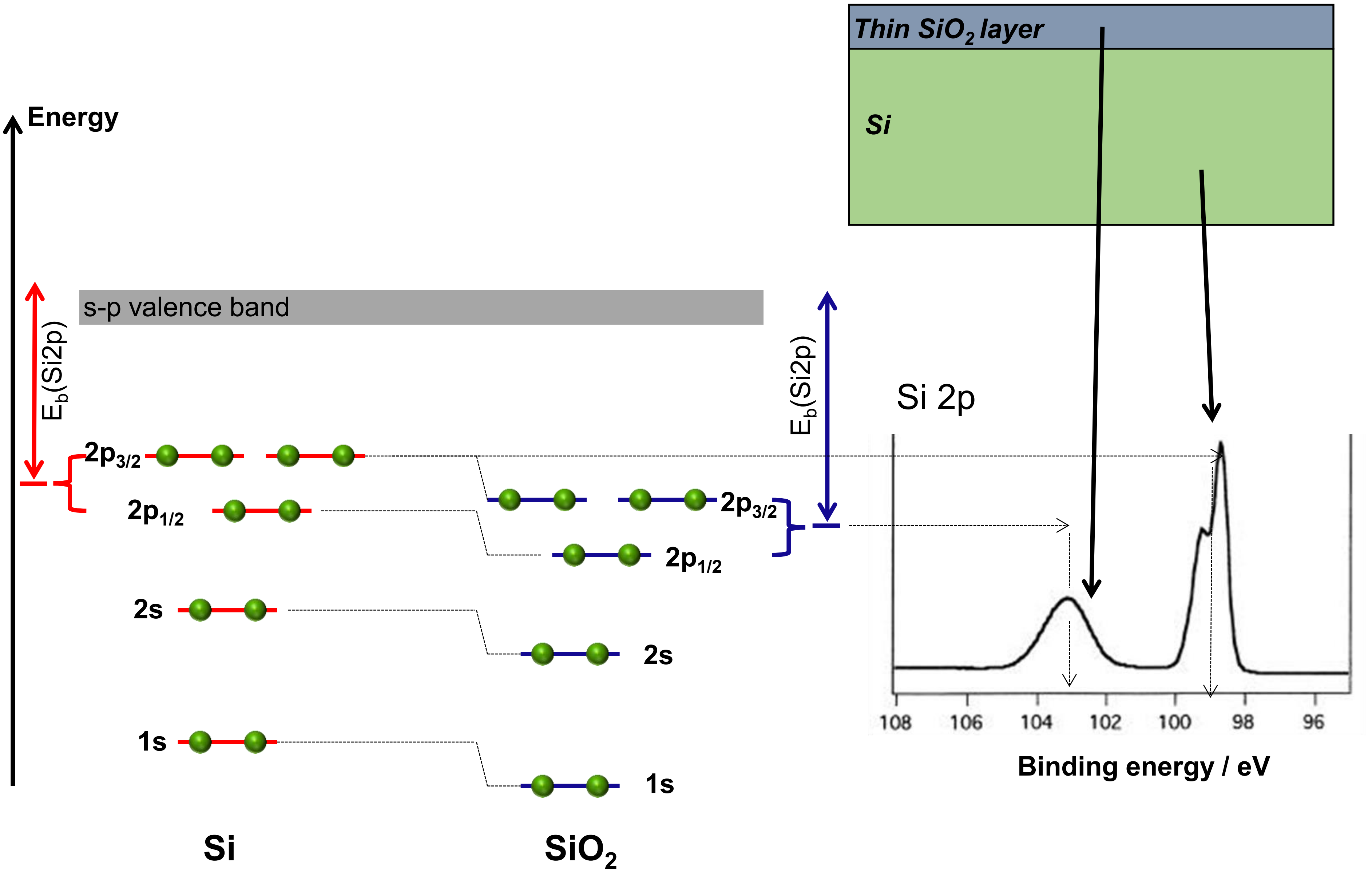



Thin SiO_2 layer
Si
Energy
s-p valence band
$E_b(Si2p)$
$E_b(Si2p_{1/2})$
$E_b(Si2p_{3/2})$
$2p_{3/2}$
$2p_{1/2}$
2s
1s
Si
Si 2p
108
106
104
102
100
98
96
Binding energy / eV

The increased oxidation state of Si in SiO_2 results to a decrease of the orbital energy and therefore an in the binding energy






Thin SiO_2 layer
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$2p_{3/2}$
$2p_{1/2}$
2s
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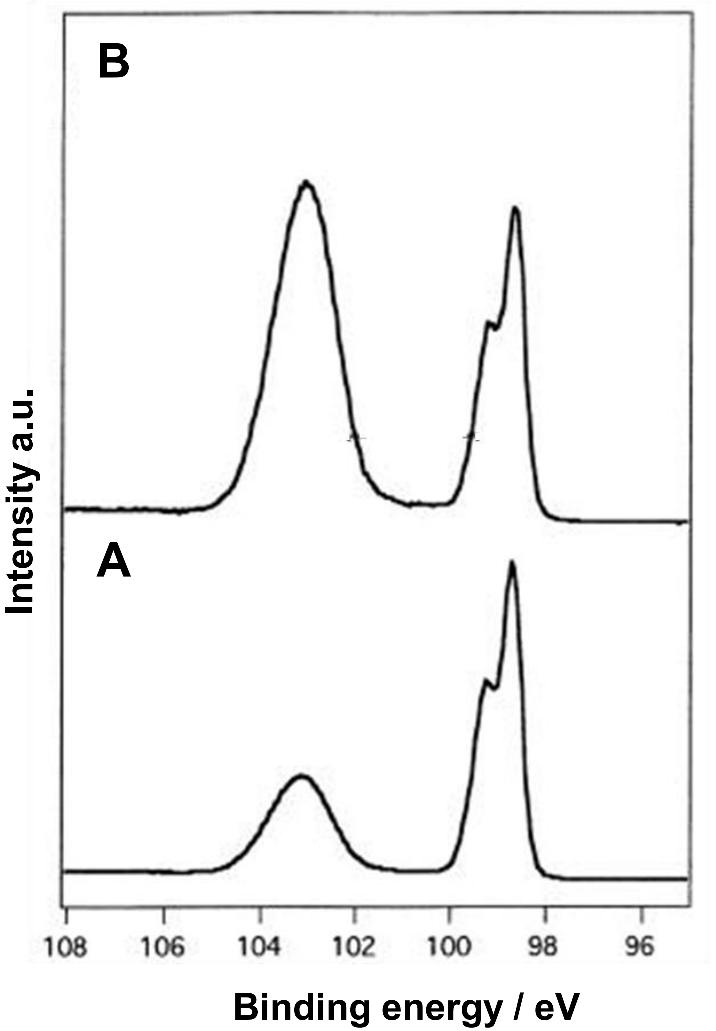
$2p_{3/2}$
$2p_{1/2}$
2s
1s
Si 2p
108
106
104
102
100
98
96
Binding energy / eV
Si
SiO_2

Exercise:

XP spectra A and B correspond to a Si wafer after oxidizing its surface with O_2.
Spectrum A was obtained at **normal emission** geometry while spectrum B was obtained at **grazing emission** geometry.

Account for the differences between spectra A and B.



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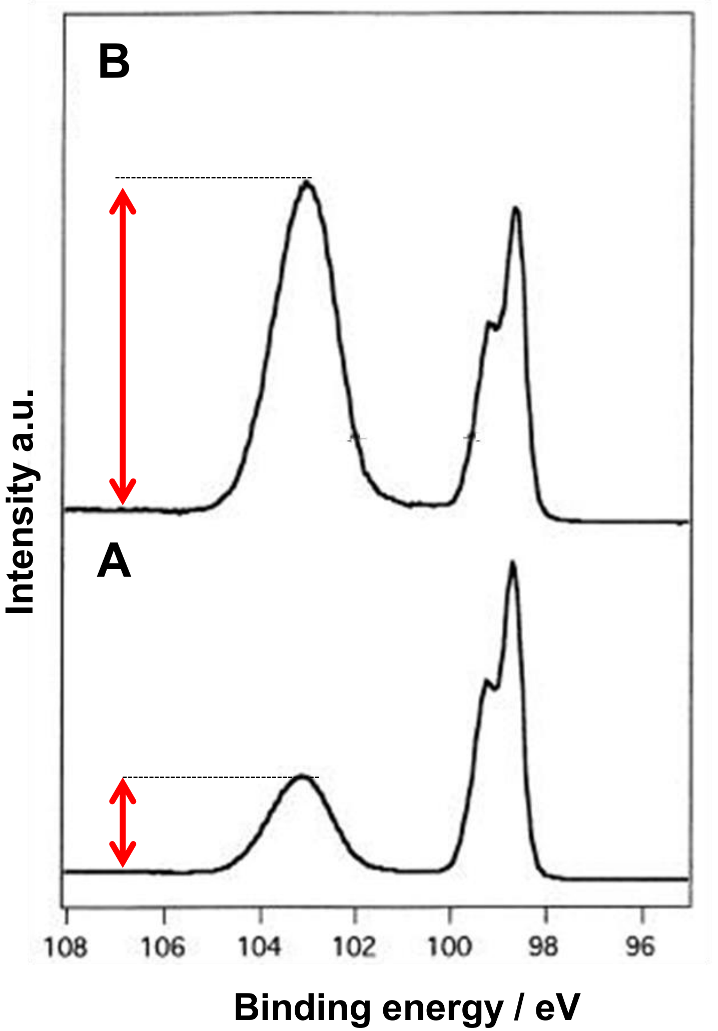

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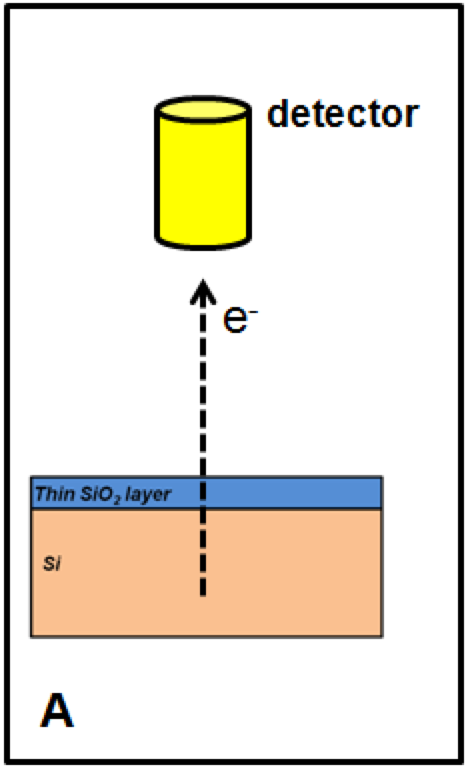
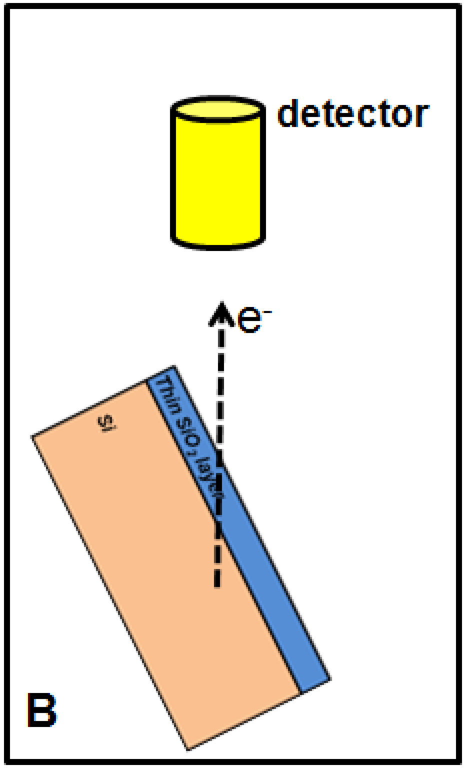
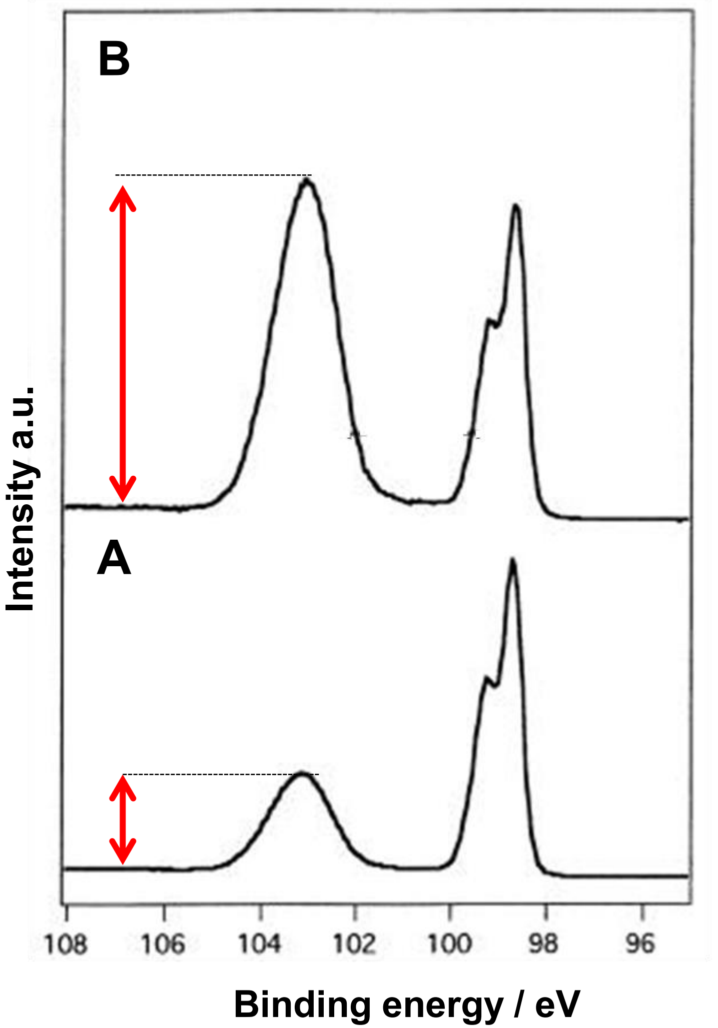
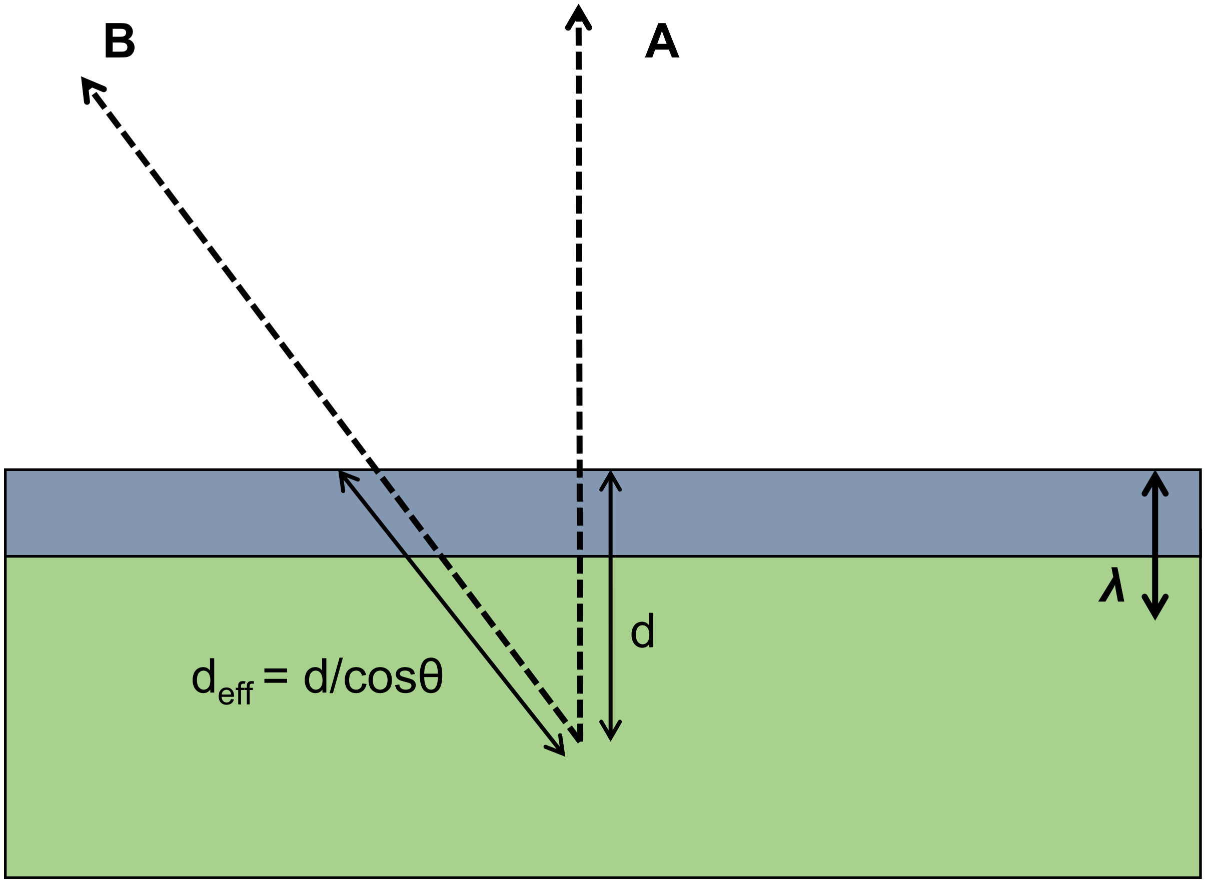


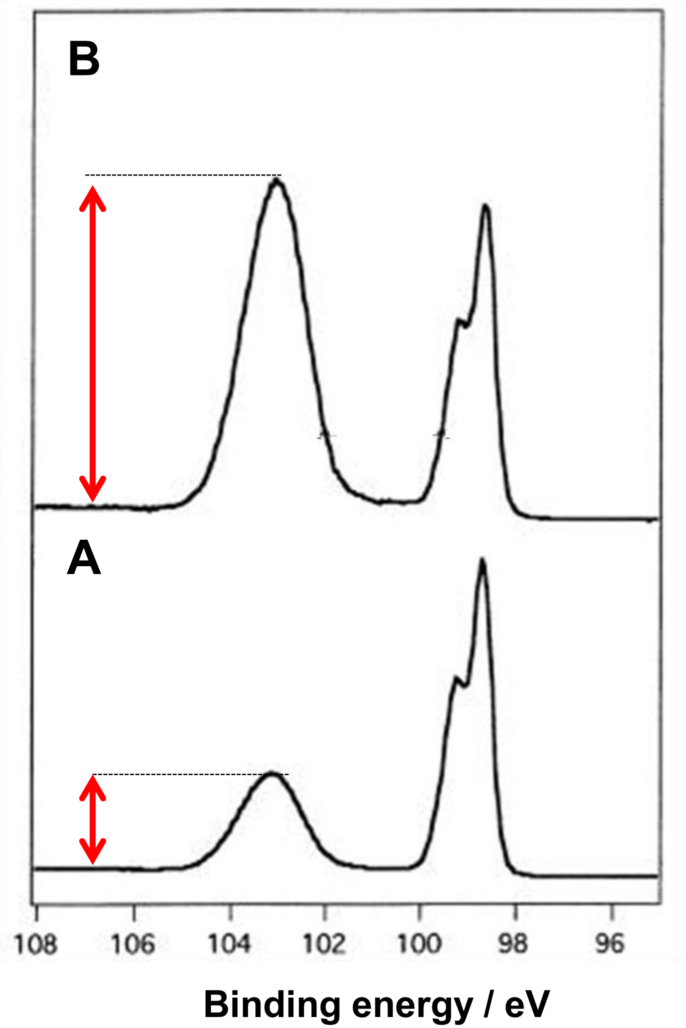




$$I=I_o exp(-d/\lambda cos\theta)$$

OXIDE SURFACE

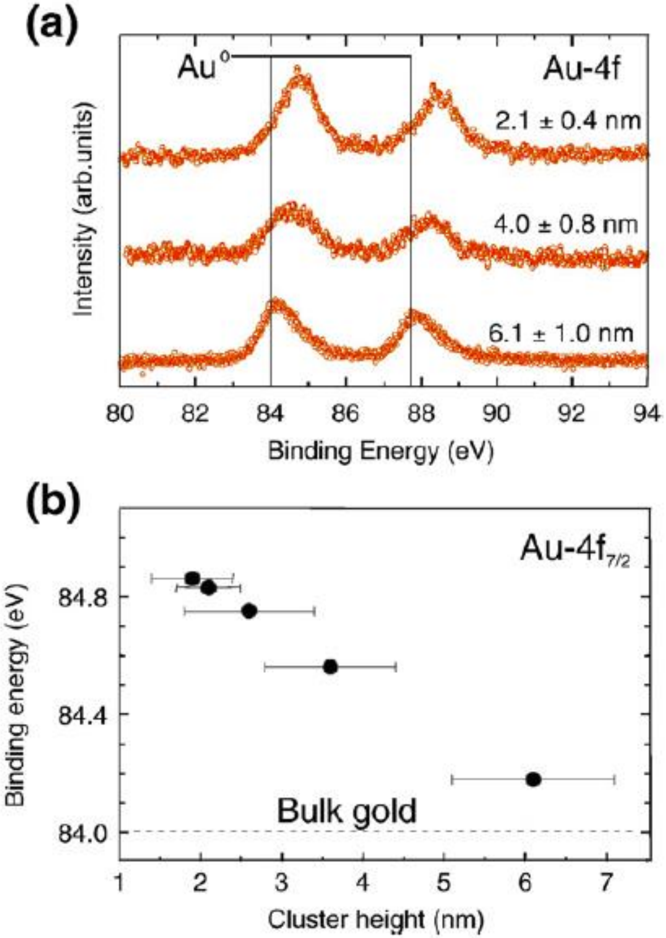




Example 2

Metal nanoparticles

Au NPs supported on polycrystalline TiC



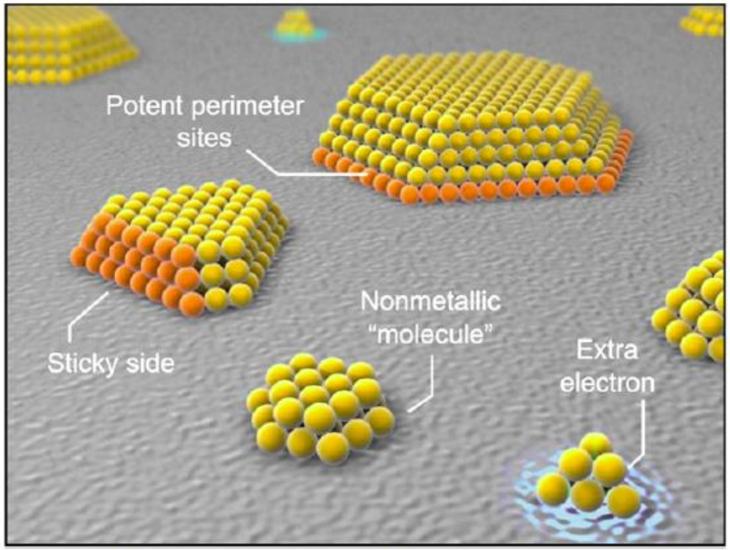


Fig. 4. Possible mechanisms responsible for the enhanced reactivity of nanoscale gold. From A. Cho, Science 299 (2003) 1684. Reprinted with permission from AAAS.

Increasingly positive binding energy shifts with decreasing particle size

The origin of such shifts is debated. Shift can be assigned

- Either to changes in the electronic structure of the clusters (initial state effects)
- Or to positive charge left on the cluster surface during the photoemission process (final state effects).

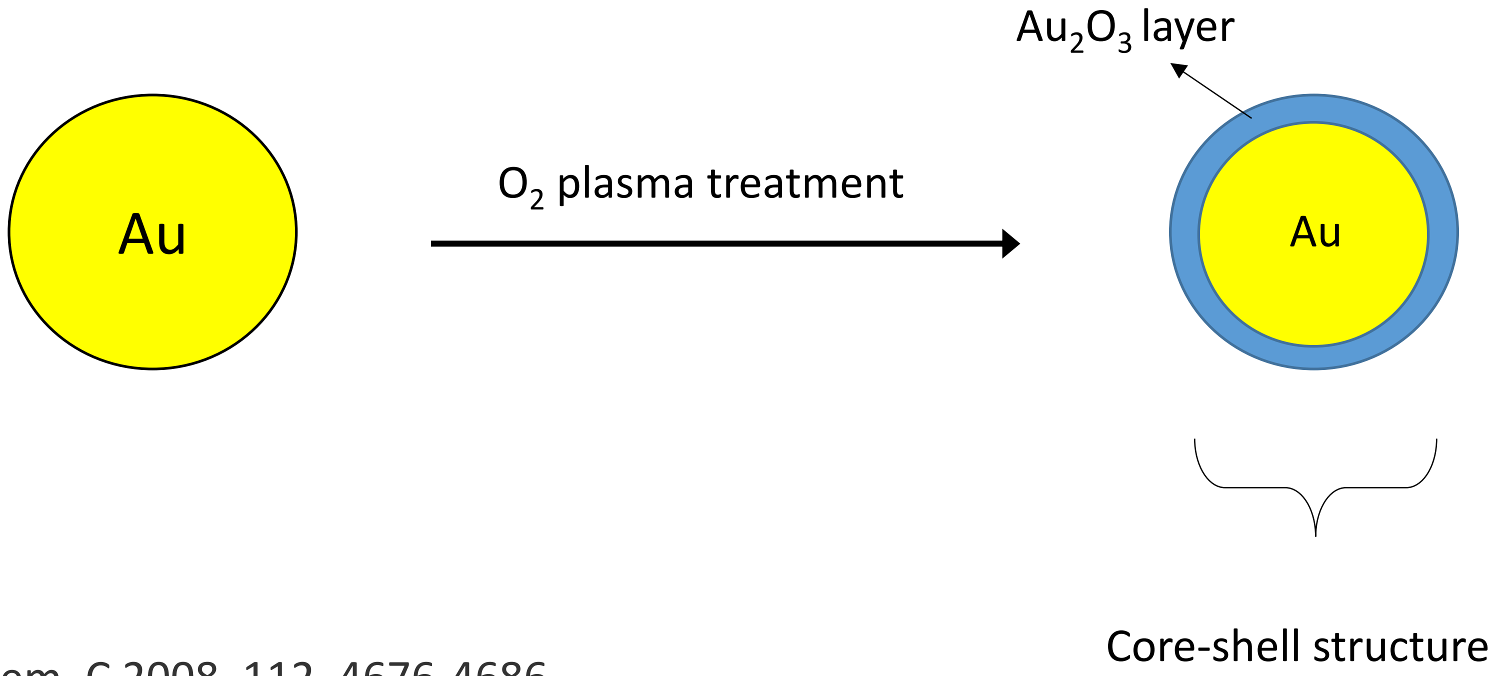
Thin Solid Films Volume 2010, 518, 3127-3150

Example 3

Metal nanoparticle core-shell structure

Gold nanoparticles with two different size distributions of 1.5 and 5 nm (synthesized by inverse micelle encapsulation and deposited on reducible (TiO_2) and nonreducible (SiO_2) supports).

The particles were oxidized by O_2 plasma treatment (90 W, 5.5 10^{-5} mbar, 100 min) at 150 K.



Au_2O_3 layer

Au

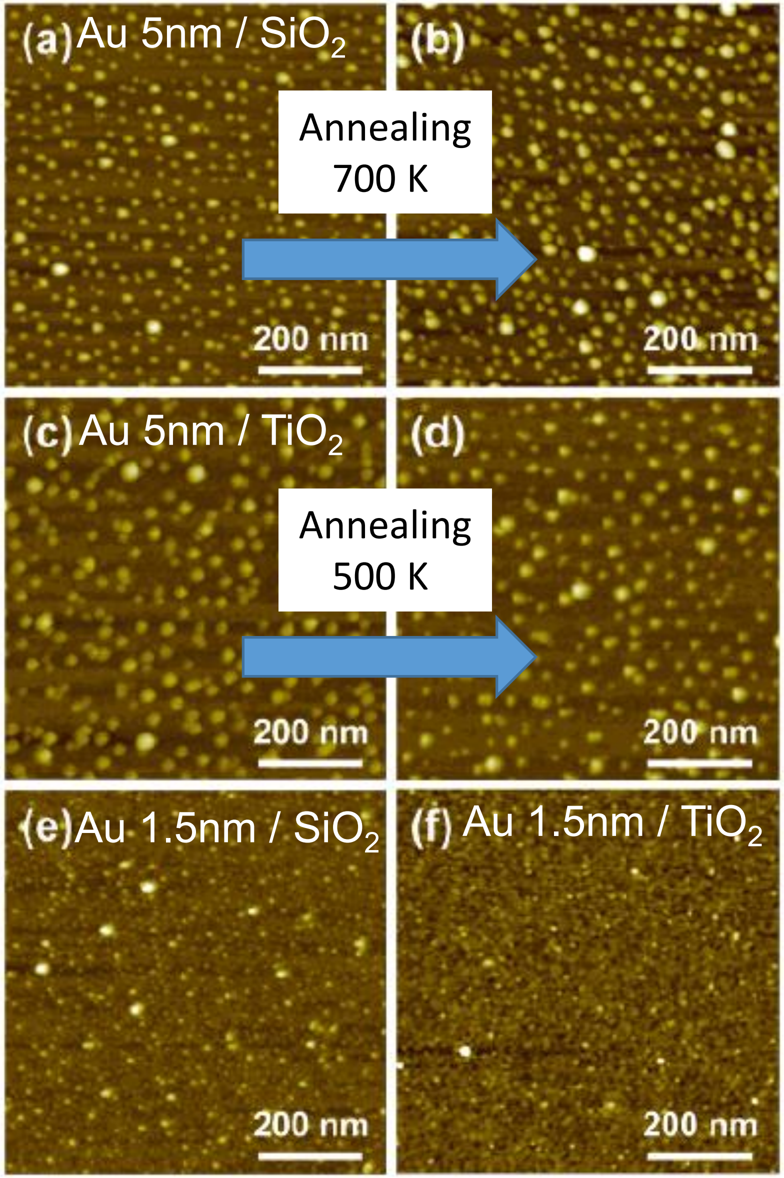
O_2 plasma treatment

Au

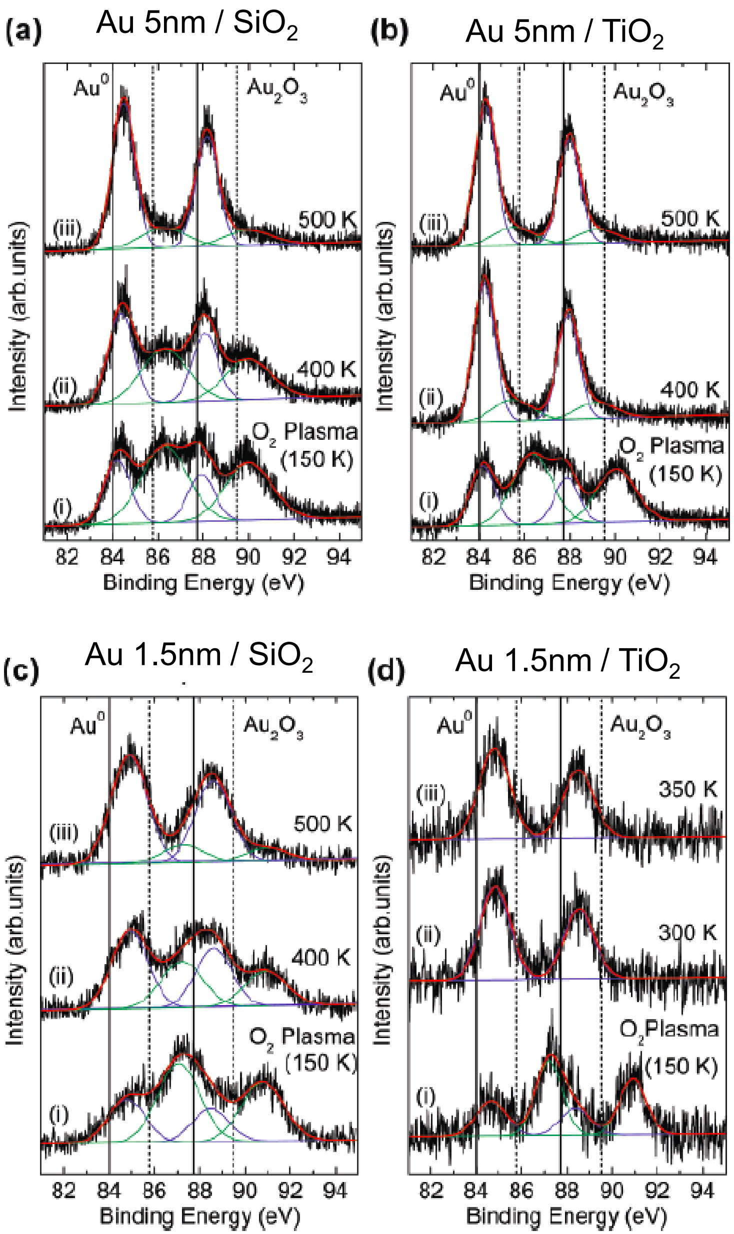
Core-shell structure

J. Phys. Chem. C 2008, 112, 4676-4686

Tapping-mode AFM images of the oxidised core-shell particles



Annealing did not change the particle size



In all cases, after plasma treatment of the particles, two doublets are observed with maxima at (~84.6 and ~88.4) and (~86.9 and ~90.6) which are assigned to the $4f_{7/2}$ and $4f_{5/2}$ core levels of Au^0 and Au^{3+} in Au_2O_3.

(Also shown in the figure the binding energies of bulk metallic gold (84.0 and 87.7 eV, solid lines) and Au^{3+} (85.8 and 89.5 eV, dashed lines).

The binding energy (BE) for both 5 nm and 1.5 nm particles are shifted to higher binding energies as compared to the bulk Au^o and Au^{3+} materials.

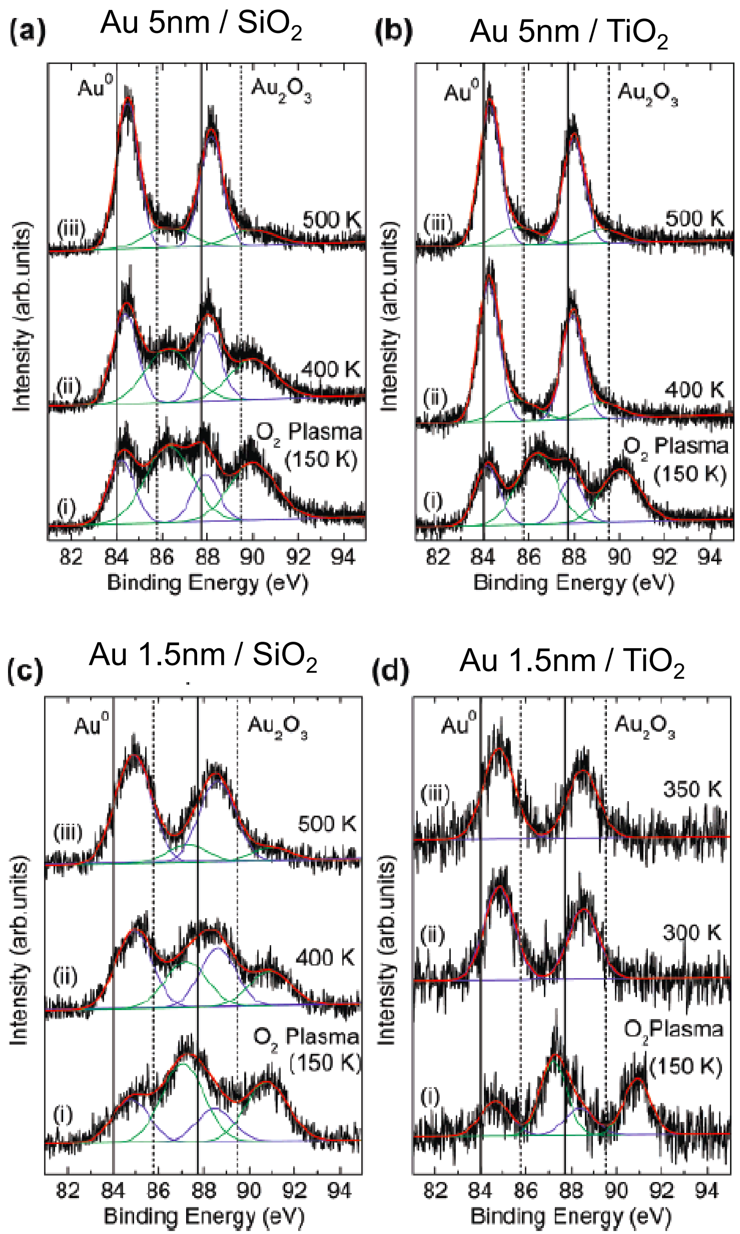
Positive BE shifts are observed for the smaller (1.5 nm) particles as compared to the 5 nm particles.

Reduction of the Au oxide layer is observed as the samples are annealed:

- Clear differences in the stability and decomposition of Au_2O_3 are observed as a function of the average particle size.

- Au surface oxide (and subsurface oxide) is present on larger particles at higher temperatures.

J. Phys. Chem. C 2008, 112, 4676-4686



Effect of the substrate

The XPS suggests: reduced stability of gold oxide on Au NPs supported on TiO_2.

Au-TiO_2 is a system where strong metal-support interactions are present.

Fast reduction of Au^{3+} in Au/TiO_2, and enhanced gold oxide stability in Au/SiO_2.

J. Phys. Chem. C 2008, 112, 4676-4686

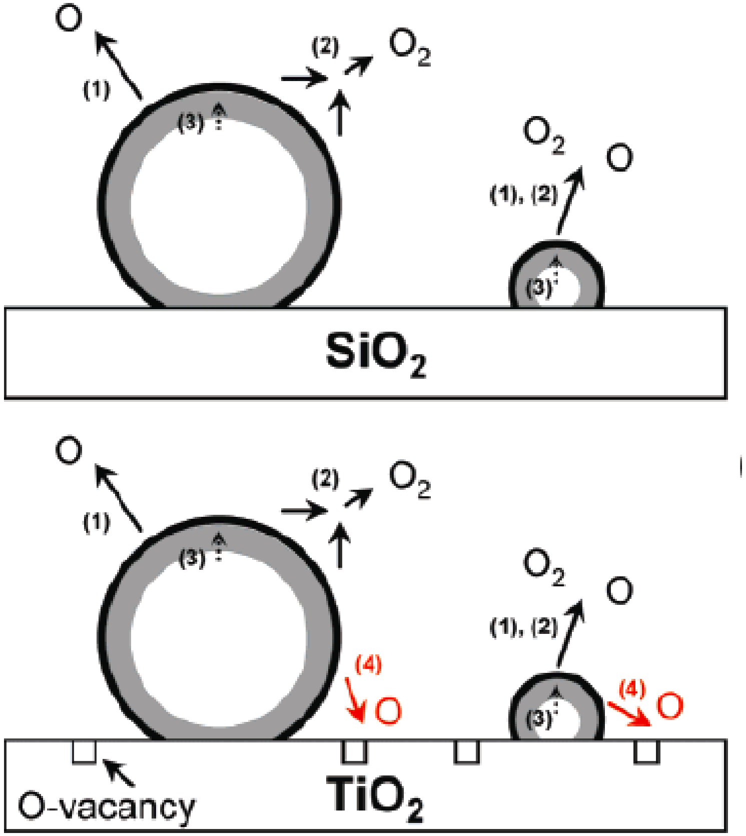


Figure 4. Schematic model illustrating different mechanisms for Au_2O_3 decomposition on large and small NPs supported on SiO_2 and TiO_2. Four processes are depicted: (1) direct desorption of atomic oxygen, (2) recombination of atomic oxygen and desorption as molecular oxygen, (3) segregation of subsurface oxygen to the NP's surface, and (4) atomic oxygen from the NP shell spills over to the TiO_2 substrate and replenishes oxygen vacancies created on TiO_2 upon sample annealing.

J. Phys. Chem. C 2008, 112, 4676-4686

Effect of the substrate

Reduced stability of gold oxide on Au NPs supported on TiO_2.

Au-TiO_2 is a system where strong metal-support interactions are present.

In both cases, however, the main decomposition pathways of the Au oxide are steps (1)-(3) shown in the figure.

In the case of Au-TiO_2 an alternative reduction pathway is available upon annealing the nanoparticles:

Oxygen spillover from the cluster's oxidized surface shell to O vacancies formed in the reducible TiO_2 substrate upon annealing is an alternative decomposition pathway.

Questions

1. How is (i) the kinetic energy of emitted photoelectrons and (ii) the kinetic energy of emitted Auger electrons affected by the photon energy of the X-rays?

2. In which region of the XPS spectrum do the valence electrons appear, and why?

3. Describe the XPS experimental setup.

4. Electron detection at low emission angles and at angles normal to the surface are both commonly used in XPS measurements of solid samples. Which of the two provides greater surface sensitivity, and why?

5. Using a diagram, explain the principles of XPS spectroscopy. (Your answer should include the XPS equation.)

6. What do we mean by the terms *initial-state effects* and *final-state effects*, and how do they influence the electron binding energy in XPS spectroscopy?

7. What do we mean by the term “work function” of a metal?

8. Using an energy-level diagram, describe the KL_2L_3 Auger transition and write an equation that describes the energy of the emitted Auger electron.

9. Which of the following photopeaks will appear as doublets and which as single peaks? Calculate theoretically the intensity ratio of the two components of each doublet.
Fe 2p, Th 4d, N 1s, Au 4f

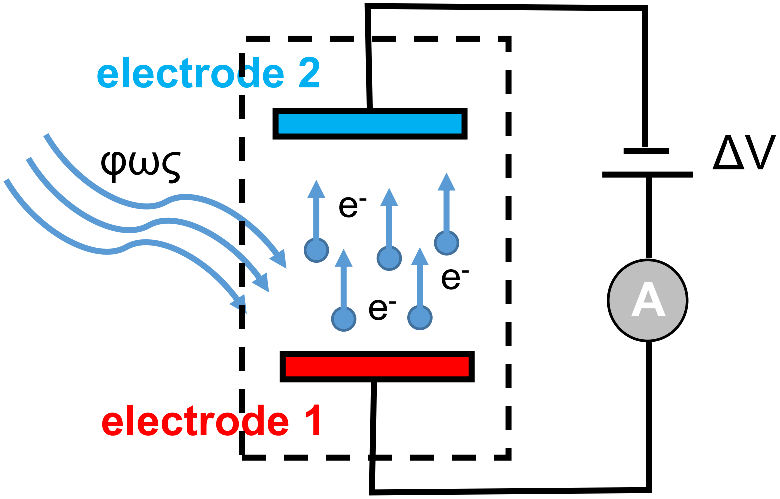
10. The following values correspond to the binding energies of the atomic orbitals of aluminum:

1s = 1560 eV
2s = 118 eV
$2p_3/_2$ = 73 eV

Calculate the kinetic energy of the emitted Auger electron for the KL_1L_3 transition of an aluminum sample (Al metal). You may assume that the work function of the sample is 3.5 eV.

11. The experimental setup in the figure was used to study the photoelectric effect. Electrode 1 is illuminated with ultraviolet light of wavelength 240 nm, and the electrons emitted cross the vacuum and strike electrode 2, causing a current to flow through the wire connecting them. By gradually increasing the voltage between the two electrodes using the potentiometric device, it is observed that the current in the microammeter becomes zero when the voltage reaches 1.40 V.

(a) What is the energy of the photons in eV?
(b) What is the maximum kinetic energy of the emitted electrons, in eV?
(c) What is the work function of electrode 1 in eV?
(d) What is the maximum wavelength that would cause the emission of electrons from electrode 1?
(e) In which region of the electromagnetic spectrum does the wavelength calculated in (d) belong?



12. The following spectrum corresponds to an Au/TiO_2 catalyst and was recorded using Al Kα X-ray radiation (1486.6 eV). The spectrum is presented as a function of kinetic energy. Peak A (1399.0 eV) and peak B (1395.3 eV) correspond to the Au 4f doublet.

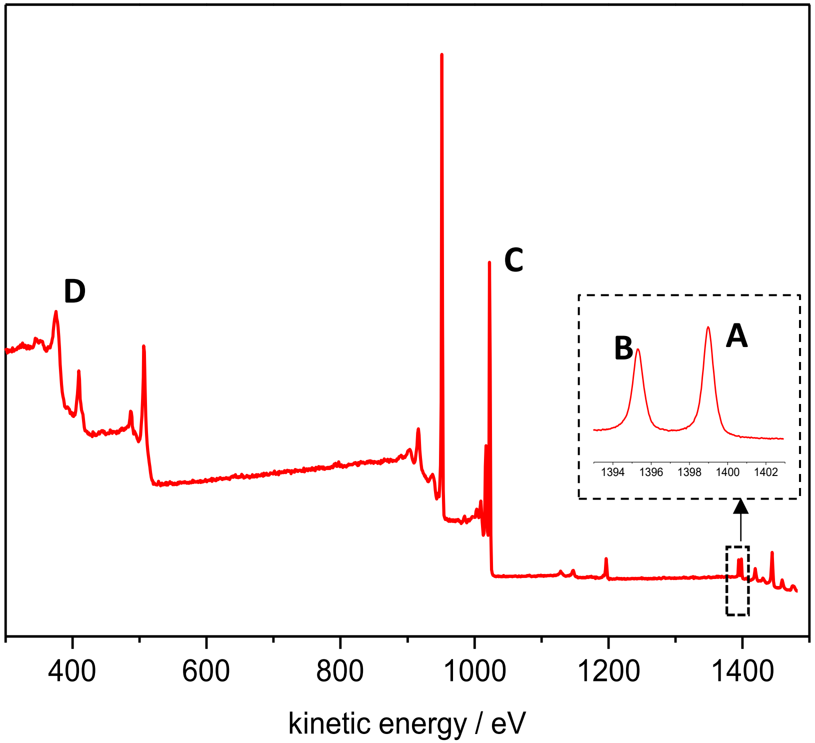
(i) Calculate the binding energy of peak A and peak B.

(ii) Identify peaks A and B.

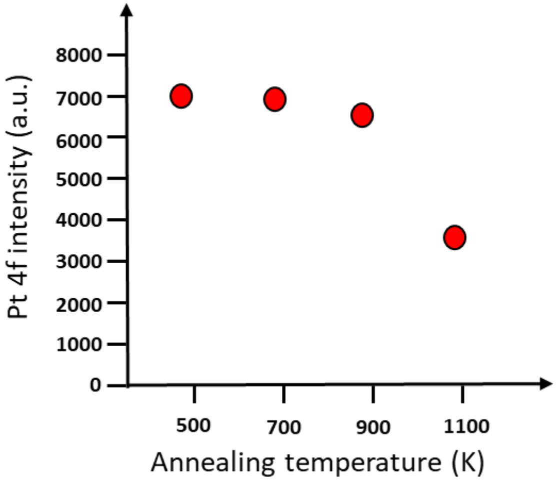
(iii) Calculate theoretically the intensity ratio between peak A and peak B.

(iv) Repeating the experiment using Mg Kα radiation causes peak C to shift to lower kinetic energy, while peak D remains at the same kinetic energy. Explain this observation and assign peaks C and D to the Ti LMM Auger transition and the Ti $2p_{3/2}$peak.

Note: The work function of the sample is $\Phi s = 3.8\ eV$



13. A catalyst consists of 5 nm Pt particles supported on an Al_2O_3 substrate. The catalyst was annealed at 500 K, 700 K, 900 K, and 1100 K and subsequently analyzed by XPS. The plot on the right shows the intensity of the Pt 4f peaks as a function of the annealing temperature. Provide a reasonable explanation for the observed changes.



14. The binding energies E_B for the four strongest XPS peaks of platinum are 71, 74, 314, and 331 eV. The strongest XPS peak of Al has a binding energy of 74 eV. The two strongest peaks of Mg are one XPS peak with a binding energy of 1305 eV and one Auger peak with a kinetic energy of 1183 eV.
Is it possible to easily detect small amounts of Al or Mg on platinum when the excitation source is X-rays with photon energy 1254 eV? How do things change if X-rays with photon energy 1487 eV are used instead?

15.

(a) In order to detect an amount of adsorbed atoms smaller than a single surface monolayer on some substrate, analysis with the highest possible surface sensitivity is required. Suppose you want to detect iodine atoms on platinum using XPS by measuring the most intense iodine peak, the $3d_{5/2}$ peak, which has a binding energy $E_B = 620\ eV$. Assuming that the photoionization cross section for a given level does not change significantly with the photon energy used, explain in which order of priority you would select the following three available photon energies: 650, 720, or 1950 eV.

(b) For each of the above photon energies, determine the iodine overlayer thickness required to reduce the intensity of the Pt $4f_{7/2}$peak (with $E_B = 71\ eV$) to 1% of its initial value for a clean surface.
Use the universal curve of the inelastic mean free path of electrons in solids, assuming that one monolayer always has a thickness of 0.3 nm.

(c) For each of the iodine thicknesses found in the previous question, calculate the intensity of the iodine $3d_{5/2}$ peak as a fraction of the intensity expected from an iodine layer of infinite thickness.