

# Surface Analysis of Nanomaterials

(나노소재표면분석)

:Surface and Thin Film Analysis

(표면 및 박막분석)

장소: 공과대학 6호관 510호

시간: 목 (6-A, 6-B, 7-A, 7-B, 8-A, 8-B)

## 2. Electron Spectroscopy for Chemical Analysis

# Electron Spectroscopy for Chemical Analysis

## Summary

### Electronic configuration of Atoms

The electrons of an atom are typically divided into two categories: **valence** and **core electrons**.

- Valence electrons occupy the outermost shell or highest energy level of an atom
- Core electrons are those occupying the innermost shell or lowest energy levels.

The electron configuration of a oxygen atom is

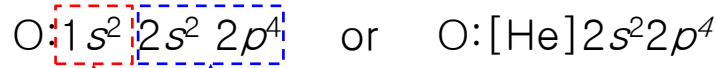


# Electron Spectroscopy for Chemical Analysis

## Summary

### Electronic configuration of Atoms

The electron configuration of a oxygen atom

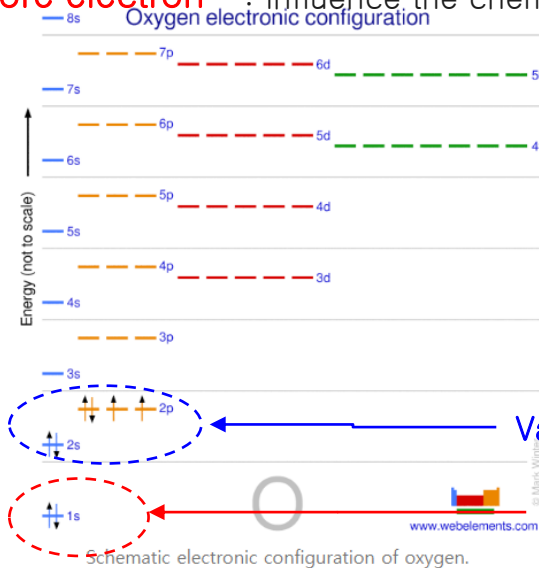


**Valance electron**

: valence electrons can participate in the formation of chemical bonding

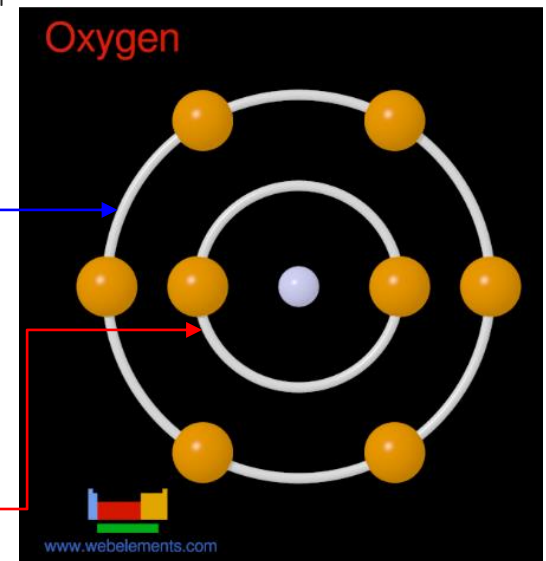
**Core electron**

: influence the chemical reactivity of an atom



**Valance electron**

**Core electron**



# Electron Spectroscopy for Chemical Analysis

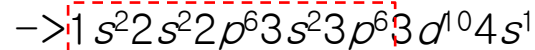
## Summary

### Electronic configuration of Atoms

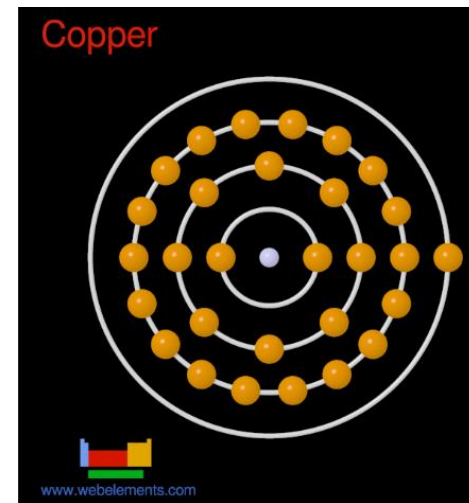
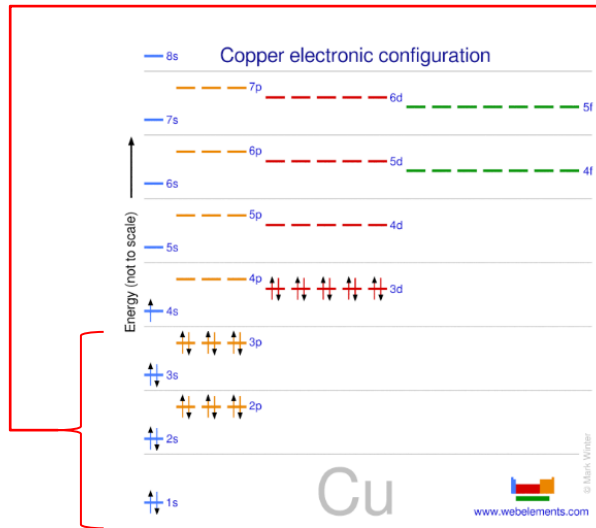
#### Example. Copper (Cu)

What are the core and valence electrons in copper?

– the electron configuration of copper with 29 electrons:



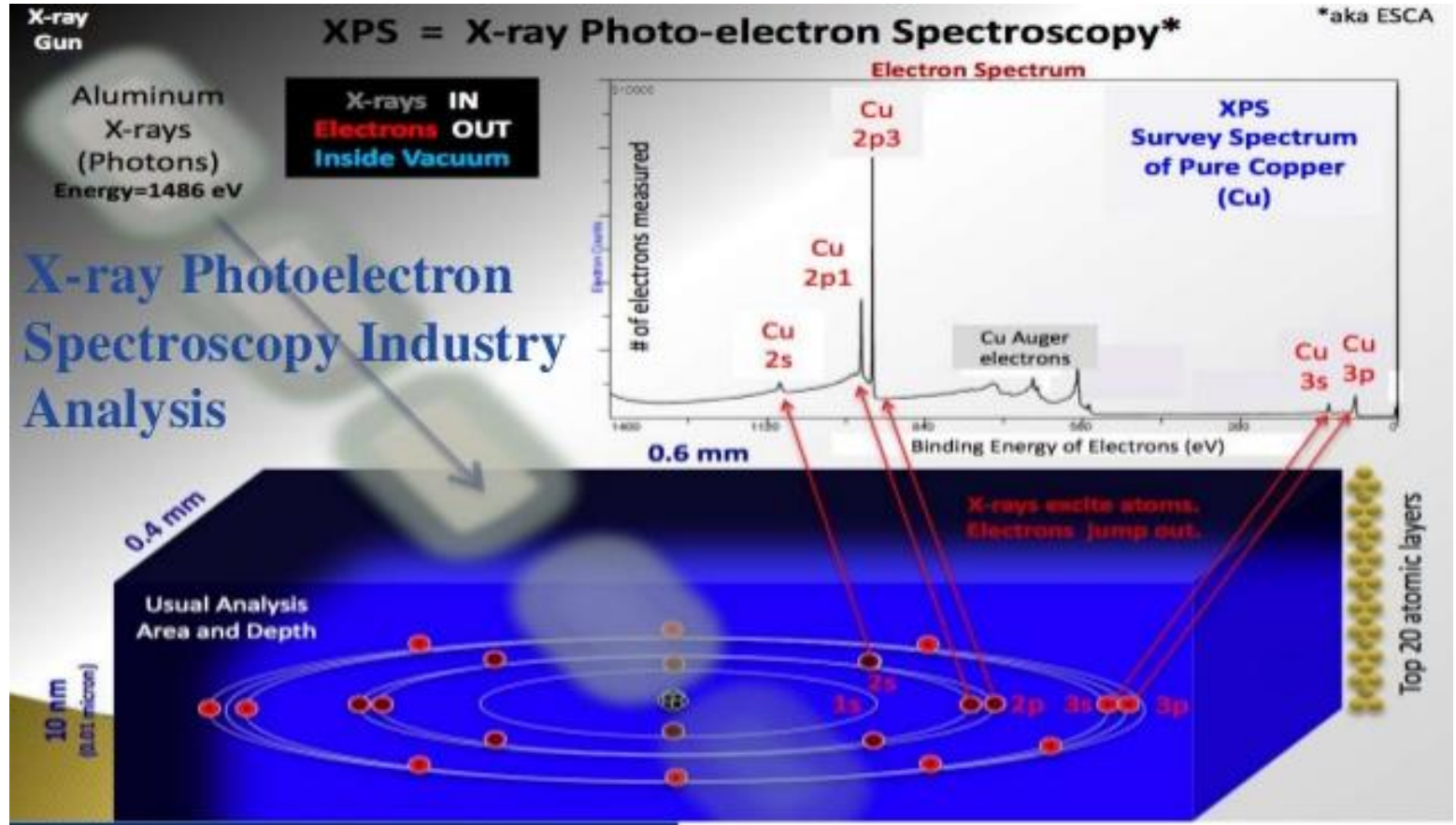
Core electron



# Electron Spectroscopy for Chemical Analysis

## Summary

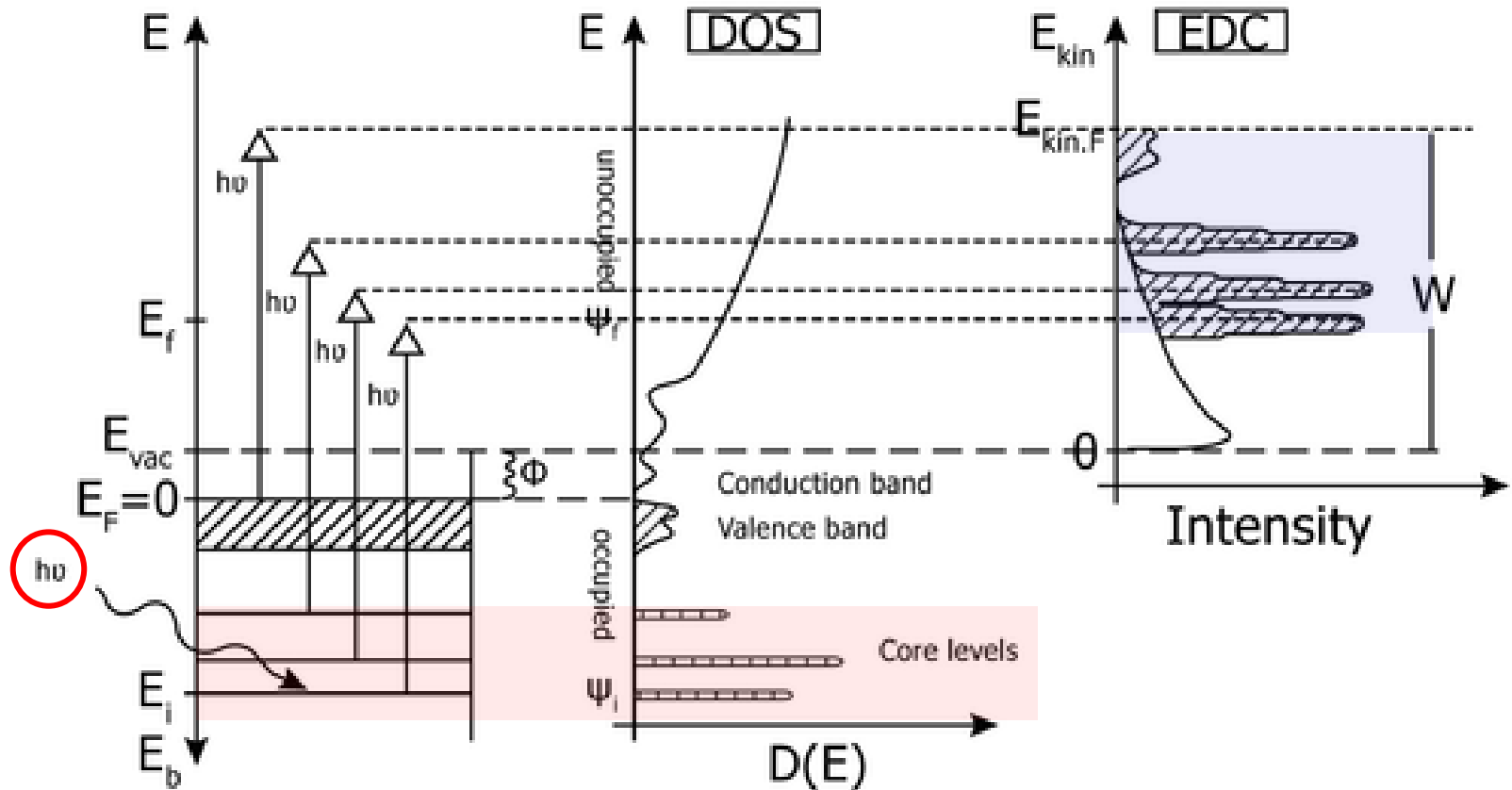
### Electronic configuration of copper and its XPS spectrum



# Electron Spectroscopy for Chemical Analysis

## Summary

Relationship between **band structure**, **Density of State** and **KE**



# Electron Spectroscopy for Chemical Analysis

## Peak Widths

The observed width of a given photoelectron peak

determined by the **lifetime of the core hole**, **instrumental resolution**, and **satellite features**

### 1) lifetime of the core hole

$$\Gamma = h/\tau$$

where  $\Gamma$  is the intrinsic peak width in eV,  $h$  is the Planck constant in eV-seconds, and  $\tau$  is the core hole lifetime in seconds

- For the  $C_{1s}$  orbital,  $\Gamma$  is  $\sim 0.1$  eV. For a given element, the value of  $\Gamma$  is typically larger for inner shell orbitals versus outer shell orbitals.
- This is because an inner shell core hole can be filled by electrons from the outer shells.
- the deeper the orbital, the shorter the core hole lifetime and the larger the intrinsic peak width

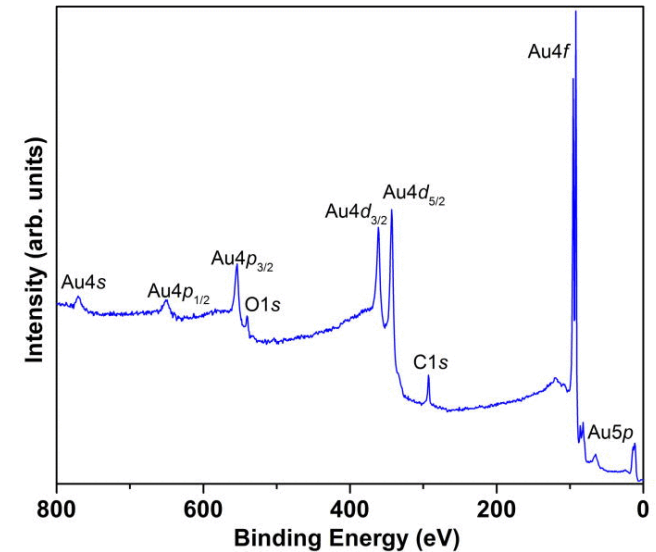


# Electron Spectroscopy for Chemical Analysis

## Peak Widths

### 1) lifetime of the core hole

For example  
the intrinsic peak widths of Au increase  
in the order  $4f < 4d < 4p < 4s$ , the order  
of increasing  $E_B$ .



- Similarly, the value of  $\tau$  for a given orbital (e.g. 1s) increases as the atomic number of the element increases, since the valence electron density,
- Therefore the probability of filling the core hole, increases with increasing atomic number.

# Electron Spectroscopy for Chemical Analysis

## Peak Widths

### 2) Instrumental effects

a photoemission peak width can be broaden

- the energy spread of the incident X-rays
- the resolution of the analyzer

For insulating materials

additional peak broadening can occur from the energy spread of the flooding electrons and the resulting energy spread in the surface potential

The contributions that the intrinsic and instrumental effects make to the peakwidth are given, to a first approximation, by:

$$\text{FWHM}_{\text{tot}} = (\text{FWHM}_n^2 + \text{FWHM}_x^2 + \text{FWHM}_a^2 + \text{FWHM}_{\text{ch}}^2 + \dots)^{1/2}$$

where FWHM is the full-width at half-maximum of the observed peak (tot), core hole lifetime ( $n$ ), X-ray source ( $x$ ), analyzer ( $a$ ), and charging contribution ( $ch$ ).

# Electron Spectroscopy for Chemical Analysis

## Peak Widths

### 3) satellite features

- These can arise from several sources such as vibrational broadening, multiplet splitting, and shake-up satellites.
- These features typically have asymmetric lineshapes and, depending on their  $E_B$ , may or may not be resolvable from the main photoemission peak.

For example (metallic sample)

- Upon leaving the sample, a photoelectron can transfer a portion of its KE to excite a valence band electron into the conduction band.
- Because of the continuous ranges of energies available to this process, an asymmetric tail on the high  $E_B$  (low KE) side of the photoemission peak is observed for metallic samples
- The degree of peak asymmetry depends on the density of states near  $E_F$

# Electron Spectroscopy for Chemical Analysis

## Peak Widths

### 3) satellite features

For example (Vanadium)

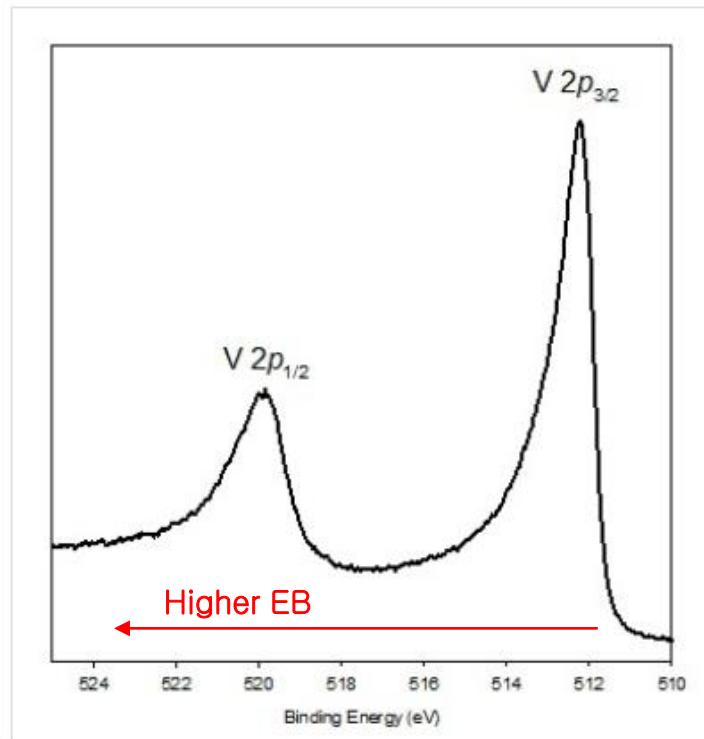


Figure 1. Asymmetric peak shapes in the V 2p spectrum of an argon ion sputter cleaned surface of vanadium metal [2].

– For conductive samples, such as metals and graphite, there is a distribution of unfilled one-electron levels (conduction electrons) that are available for shake-up like events following core electron photoemission.

–When this occurs, instead of a discrete structure like that seen for shake-up satellites, a tail on the higher binding energy side of the main peak – an asymmetric peak shape is evident

Ref) M.C. Biesinger, L.W.M. Lau, A.R. Gerson, R.St.C. Smart, 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) 887–898.

# Electron Spectroscopy for Chemical Analysis

## PEAK FITTING

– To maximize the information extracted from ESCA spectra, the area and  $E_B$  of each subpeak for a given orbital (e.g.  $C_{1s}$ ) must be determined

: Typically, the spacing between subpeaks is similar to observed peak widths ( $\sim 1$  eV)

### Peak-fitting procedure

Parameters used in such procedures include

- background
- peak shape (Gaussian, Lorentzian, asymmetric, or mixtures thereof)
- peak position
- peak height
- peak width

The most common method used to model the background (inelastic scattering) was developed by Shirley [D.A. Shirley, Phys. Rev. B 5, 4709–4714 (1972)]

We will discuss this later

# Electron Spectroscopy for Chemical Analysis

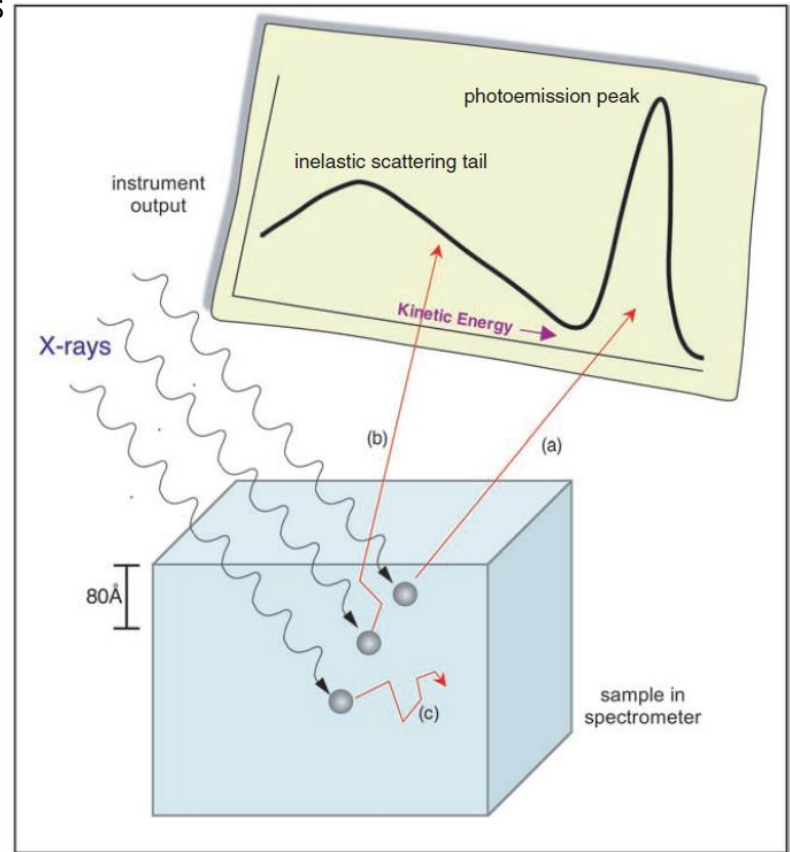
## Inelastic Mean Free Path and Sampling Depth

X-rays can readily travel through solids

- the X-rays will penetrate 1000nm or more into matter while electrons of this energy will only penetrate approximately 10 nm

- ESCA, in which only emitted electrons are measured, is **surface sensitive**

- Electrons emitted from X-ray excitation below the uppermost surface zone cannot penetrate far enough to escape from the sample and reach the detector



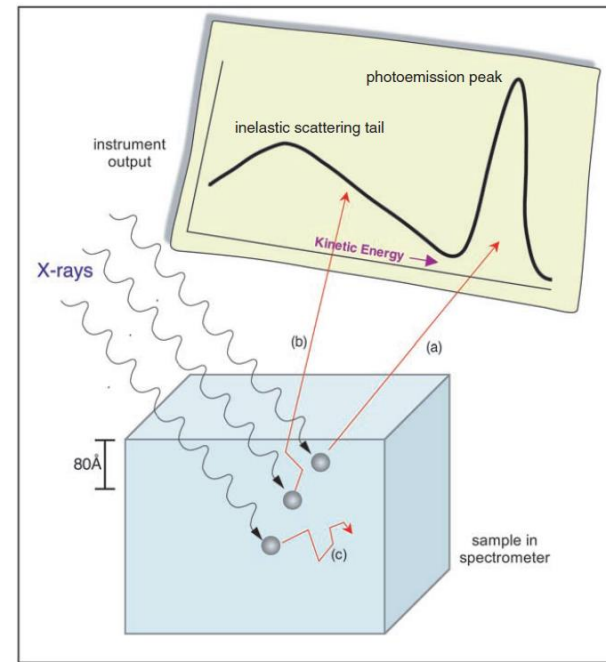
**Figure 3.7** X-rays will penetrate deeply into a sample, and stimulate electron emission throughout the specimen. Only those electrons emitted from the surface zone that have suffered no energy loss will contribute to the photoemission peak (a). Electrons emitted from the surface zone that have lost some energy due to inelastic interactions will contribute to the scattering background (b). Electrons emitted deep within a sample will lose all their kinetic energy to inelastic collisions and will not be emitted (c)

# Electron Spectroscopy for Chemical Analysis

## Inelastic Mean Free Path and Sampling Depth

What happens during the ESCA experiment?

- Concerned with only the **intensity** of the emitted photoelectrons (i.e., the **total number emitted**) that have not lost any energy.
- If an electron suffers energy loss, but still has sufficient energy to escape from the surface, it will contribute to the background signal, but not to the photoemission peak **(b)**
- the ESCA sampling depth refers to a characteristic, average length in a solid that the electron can travel with no loss of energy.



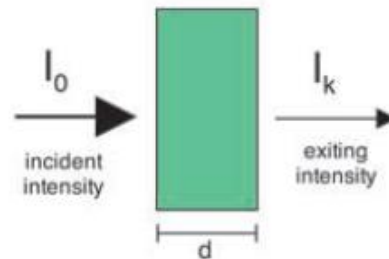
# Electron Spectroscopy for Chemical Analysis

## Inelastic Mean Free Path and Sampling Depth

What happens during the ESCA experiment?

- The decrease in the number of photoemitted electrons that have suffered no energy loss travelling through matter, where each unit thickness of matter the electrons travel through will absorb the same fraction of the energy, is described by Beer's law (Below).

### Transmission



$$I_k = I_0 e^{(-d/\lambda \cos \theta)}$$

$\lambda$  = inelastic mean free path  
(an absorption coefficient)

For electrons transmitted through a sample, Beer's law of molecular absorption explains the total intensity loss for electrons that lose no energy in traversing the sample.

- The inelastic mean free path (IMFP) term,  $\lambda$ , in this equation is that thickness of matter through which 63% of the traversing electrons will lose energy.



# Electron Spectroscopy for Chemical Analysis

## Inelastic Mean Free Path and Sampling Depth

**Table 3.4** Definitions for electron transport in materials<sup>a</sup>

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**IMFP ( $\lambda$ )** – Inelastic Mean Free Path. The average distance that an electron with a given energy travels between successive inelastic collisions.

**ED** – Mean Escape Depth. The average depth normal to the surface from which the photoelectrons escape.

**AT** – Attenuation Length. The quantity  $l$  in the expression  $\Delta x/l$  for the fraction of a parallel beam of X-rays or electrons that are removed by passing through a thin layer  $\Delta x$  of a substance in the limit as  $\Delta x$  approaches zero ( $\Delta x$  is in the direction of the beam).

**ID** – Information Depth. The maximum depth, normal to the surface, from which useful information is obtained.

**Sampling Depth** =  $3\lambda$  (ID where percentage of detected electrons is 95 %).

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<sup>a</sup>Definitions adapted from ISO 18115:2001 and Powell [47].

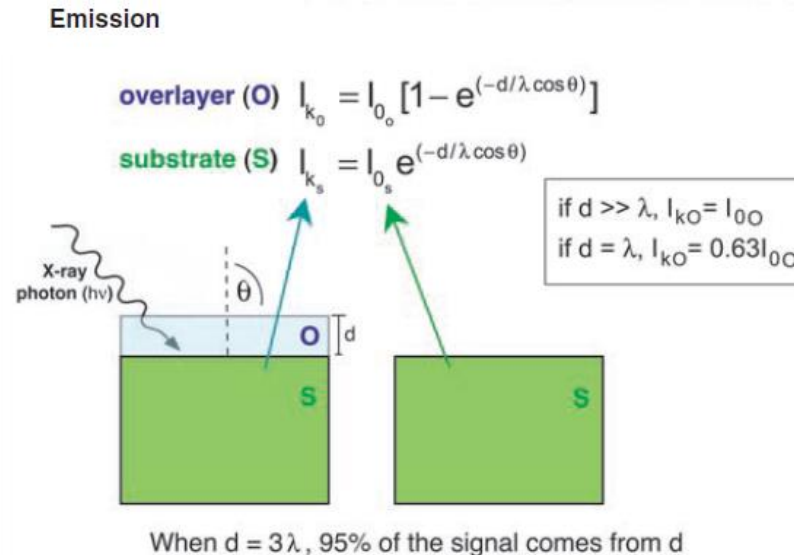
Table presents a series of definitions of other terms commonly used in ESCA to describe this decrease in elastic electron intensity associated with transport through matter.

# Electron Spectroscopy for Chemical Analysis

## Inelastic Mean Free Path and Sampling Depth

What happens during the ESCA experiment?

How will the electron flux from this source (the sample) be attenuated, if we cap this electron source with a thin overlayer?



For electron emission from a thick sample, modifications of Beer's law can explain the photoemission intensity from an overlayer or from the substrate covered by an overlayer

# Electron Spectroscopy for Chemical Analysis

## Inelastic Mean Free Path and Sampling Depth

What happens during the ESCA experiment?

- The actual values for the IMFP of electrons in matter are a function of the energy of the electrons and nature of the sample through which they travel.
- Over the range of electron kinetic energies of most interest in ESCA, the IMFP increases with electron KE.
- Equations that relate IMFP to electron energy and the type of material through which the electron is traversing have been developed by Seah and Dench

$$\text{IMFP} = \lambda = 538\text{KE}^{-2} + 0.41(a\text{KE})^{0.5} \quad (\text{for elements})$$

$$\text{IMFP} = \lambda = 2170\text{KE}^{-2} + 0.72(a\text{KE})^{0.5} \quad (\text{for inorganic compounds})$$

$$\text{IMFP} = \lambda_d = 49\text{KE}^{-2} + 0.11\text{KE}^{0.5} \quad (\text{for organic compounds})$$

where:

$\lambda$  is in units of monolayers

$a$  = monolayer thickness (nm)

$\lambda_d$  (in  $\text{mg m}^{-2}$ )

KE = electron kinetic energy (in eV)

# Electron Spectroscopy for Chemical Analysis

## Quantification

by measuring the **peak areas** and **correcting** them for the appropriate instrumental factors, the **percentage of each element detected can be determined**

The equation for quantification

$$I_{ij} = KT(\text{KE})L_{ij}(\gamma)\sigma_{ij} \int_0^r n_i(z)e^{-z/\lambda(\text{KE})\cos \theta} dz$$

Where,

$I_{ij}$  is the area of peak  $j$  from element  $i$ ,

$K$  is an instrumental constant,  $T$

$(\text{KE})$  is the transmission function of the analyzer,

$L_{ij}(\gamma)$  is the angular asymmetry factor for orbital  $j$  of element  $i$ ,

$\sigma_{ij}$  is the photoionization cross-section of peak  $j$  from element  $i$ ,

$n_i(z)$  is the concentration of element  $i$  at a distance  $z$  below the surface,

$\lambda(\text{KE})$  is the inelastic mean free path length,

$\theta$  is the take-off angle of the photoelectrons measured with respect to the surface normal.

– It is only necessary to determine the relative relationship, not the absolute values, of the quantities in Equation

# Electron Spectroscopy for Chemical Analysis

## Quantification

### Parameters

$K$  instrumental constant

– quantities such as the X-ray flux, area of the sample irradiated, and the solid angle of photoelectrons accepted by the analyzer

$L_{ij}(\gamma)$  The angular asymmetry factor

– the type of orbital the photoelectron is emitted from and the angle  $\gamma$  between the incident X-rays and the emitted photoelectrons.

– If only s orbitals are used for quantitation,  $L_{ij}(\gamma)$  will be the same for all peaks and therefore will cancel.

– This situation is frequently encountered with polymeric samples since the 1s orbitals of many elements present in organic polymers (C, N, O, and F) are detectable by ESCA.

– Even for samples where different types of orbitals are used for quantification, the variation of  $L_{ij}(\gamma)$  is typically small and is usually neglected for solids.

# Electron Spectroscopy for Chemical Analysis

## Quantification

### Parameters

$KE$  Transmission function

- the efficiency of the collection lens, the energy analyzer, and detector
- Most manufactures provide information about the transmission function of their instruments

$\sigma_{ij}$  photoionization cross-section

- the probability that the incident X-ray will create a photoelectron from the  $j$ th orbital of element  $i$ .
- $\lambda$  depends both on the sample type (elemental, inorganic species, or organic species) and the KE of the photoelectron. Both quantities must be properly accounted for to obtain good quantitative results.
- The  $\cos \theta$  term accounts for the decrease in sampling depth as the surface normal of the sample is rotated away from the axis of the acceptance lens.

# Electron Spectroscopy for Chemical Analysis

## Quantification

### QUANTIFICATION METHODS

- The concentration of element  $i$ ,  $n_i$ , is the unknown quantity in Equation

$$I_{ij} = KT(\text{KE})L_{ij}(\gamma)\sigma_{ij} \int n_i(z)e^{-z/\lambda(\text{KE})\cos \theta} dz$$

- Once  $n_i$  is known for each element present in the ESCA spectrum, the atomic percentages can be calculated as:

$$\%n_i = 100 \left( n_i / \sum n_i \right)$$

Where,  $\%n_i$  is the atomic percent of element  $i$ . Atomic ratios ( $n_i/n_k$ ) can also be calculated

- Usually assumed that the **elemental concentrations are homogeneous** within the ESCA sampling depth

$$I_{ij} = KT(\text{KE})L_{ij}(\gamma)\sigma_{ij}n_i\lambda(\text{KE})\cos \theta$$

# Electron Spectroscopy for Chemical Analysis

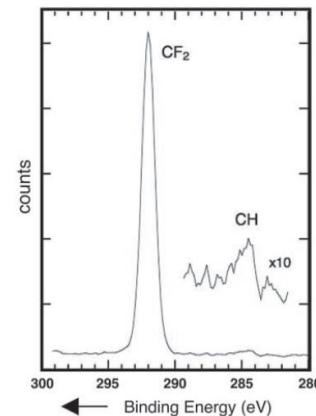
## Quantification

### Examples – Standard sample

#### polytetrafluoroethylene (PTFE)

- PTFE is composed exclusively of chains of  $\text{CF}_2$  units giving an F/C atomic ratio of 2.0.
- This polymer is known to be unreactive, and have low surface energy, so it is relatively easy to prepare a clean PTFE surface.
- The presence of oxidation or contamination can be readily determined by examination of the ESCA spectra.
- Since only F and C are present in PTFE, the detection of O by ESCA indicates the presence of surface oxidation or a surface contaminant.

–Likewise, any  $\text{C}_{1s}$  peaks other than the  $\text{CF}_2$  peak at 292 eV indicate the presence of a surface contaminant. The most common contaminant is adsorbed hydrocarbon, which has a  $\text{C}_{1s}$  peak at 285 eV



**Table 3.6** Quantitation results for polytetrafluoroethylene<sup>a</sup>

Atomic percentage F =  $67.1 \pm 0.4$   
Atomic percentage C =  $32.9 \pm 0.5$   
F/C atomic ratio =  $2.04 \pm 0.04$

<sup>a</sup>Number of samples = 22.

**Figure 3.9** The ESCA  $\text{C}_{1s}$  spectrum of polytetrafluoroethylene. The peak at 292 eV corresponds to the  $\text{CF}_2$  groups present in this sample. The weak peak at 285 eV corresponds to a small amount ( $\sim 0.3$  atomic percentage) of a hydrocarbon contaminant present on the surface of the sample



# Electron Spectroscopy for Chemical Analysis

## Quantification

### Examples – Standard sample

#### a polyurethane

In the quantification experiments only C,N, and O were detected, and the 1s peak areas were used for quantification  $\rightarrow L_j(\gamma)$  can be considered a constant.

**Table 3.8** Quantitation results for a polyurethane sample

Element	Orbital	KE (eV)	$\sigma$	Peak area (counts $\times$ eV)	Atomic percentage
Carbon	1s	1200	1.00	26 557	76.9
Nitrogen	1s	1085	1.80	4478	7.7
Oxygen	1s	955	2.93	13 222	15.4

The spectra were acquired on a Surface Science Instruments

X–probe spectrometer with the following characteristics:  $\pi(KE)$  is constant over the range of detected photoelectron kinetic energies,  $\lambda(KE)$  varies as  $KE^{0.7}$ ,  $h\nu = 1487$  eV, and  $\theta = 55^\circ$ .

$$\%n_i = (I_{ij}/\sigma_{ij}KE^{0.7}) / \sum (I_{ij}/\sigma_{ij}KE^{0.7})$$

**Table 3.9** Quantitation results for a polyurethane sample<sup>a</sup>

Element	Atomic percentage	
	ESCA	Stoichiometry
Carbon	76.6 $\pm$ 1.0	76.0
Nitrogen	7.9 $\pm$ 0.5	8.0
Oxygen	15.5 $\pm$ 0.8	16.0

<sup>a</sup>Number of samples = 8.

# Next

Spectral Features

Instrumentation

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