

Surface Analysis of Nanomaterials

(나노소재표면분석)

Surface and Thin Film Analysis (표면 및 박막 분석)

장소: E6, Room 116

시간: 월7A-8A, 수7A-8A

2. Electron Spectroscopy for Chemical Analysis

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

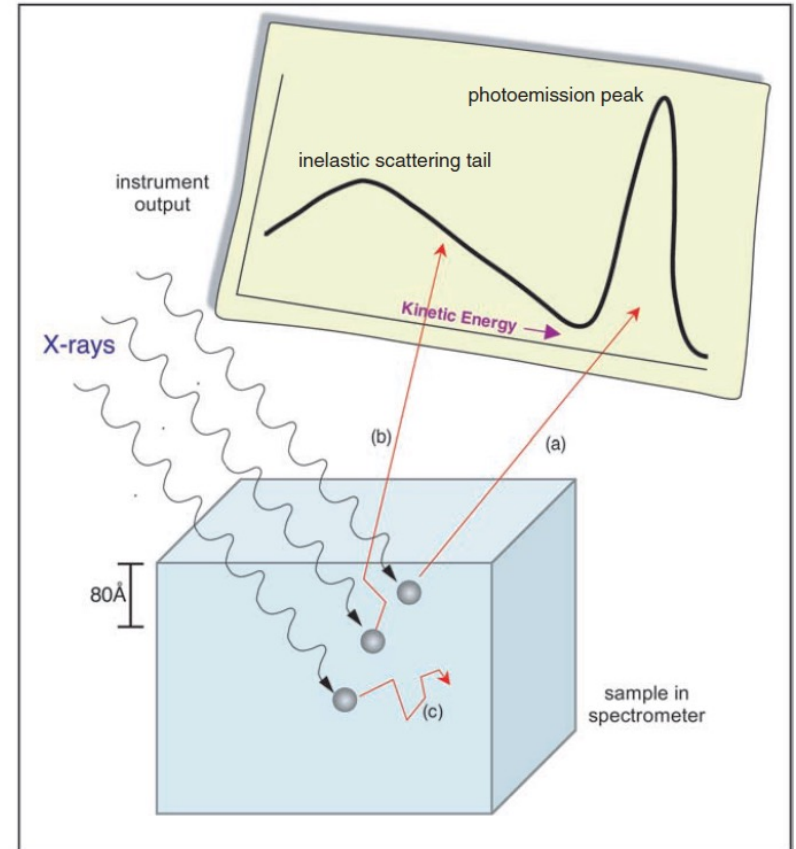


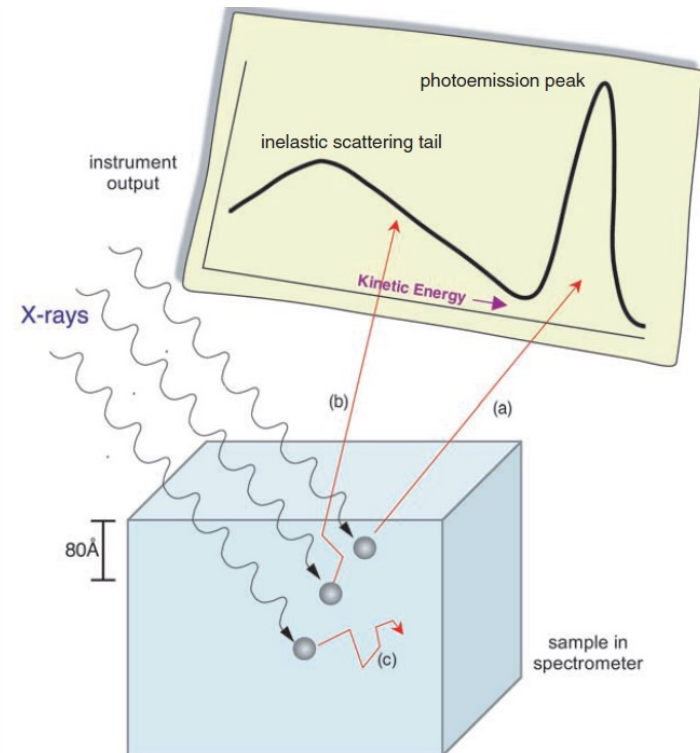
Figure 3.7 X-rays will penetrate deeply into a sample, and stimulate electron emission throughout the specimen. Only those electrons emitted from the surface zone that have suffered no energy loss will contribute to the photoemission peak (a). Electrons emitted from the surface zone that have lost some 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.



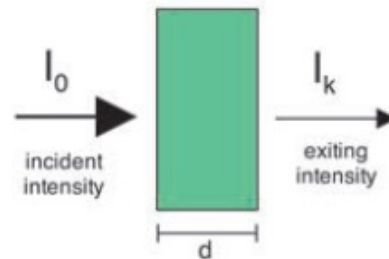
Electron Spectroscopy for Chemical Analysis

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



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

λ = 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, λ , 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^a

IMFP (λ) – 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 Δx of a substance in the limit as Δx approaches zero (Δx 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 = 3λ (ID where percentage of detected electrons is 95 %).

^aDefinitions adapted from ISO 18115:2001 and Powell [47].

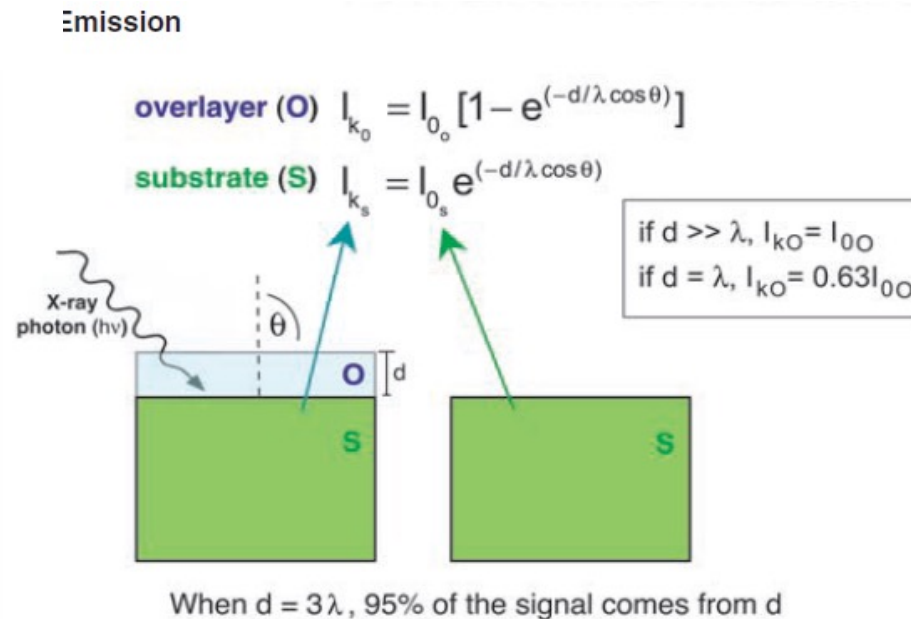
Table presents a series of definitions of other terms commonly used in ESCA to describe this decrease in elastic electron intensity associated with transport through matter.

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:

λ is in units of monolayers

a = monolayer thickness (nm)

λ_d (in 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

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

Where,

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

K is an instrumental constant, T

(KE) is the transmission function of the analyzer,

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

σ_{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,

θ 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 γ 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

σ_{ij} photoionization cross-section

- the probability that the incident X-ray will create a photoelectron from the j th orbital of element i .
- λ 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

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

- 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

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

Electron Spectroscopy for Chemical Analysis

Quantification

Examples – Standard sample

polytetrafluoroethylene (PTFE)

- PTFE is composed exclusively of chains of 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 C_{1s} peaks other than the CF_2 peak at 292 eV indicate the presence of a surface contaminant. The most common contaminant is adsorbed hydrocarbon, which has a C_{1s} peak at 285 eV

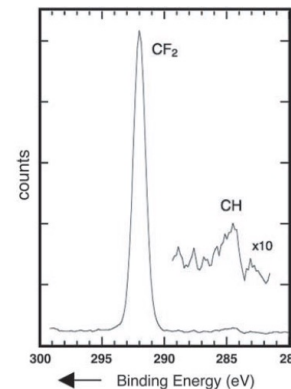


Figure 3.9 The ESCA C_{1s} spectrum of polytetrafluoroethylene. The peak at 292 eV corresponds to the CF_2 groups present in this sample. The weak peak at 285 eV corresponds to a small amount (~ 0.3 atomic percentage) of a hydrocarbon contaminant present on the surface of the sample

Table 3.6 Quantitation results for polytetrafluoroethylene^a

Atomic percentage F = 67.1 ± 0.4
Atomic percentage C = 32.9 ± 0.5
F/C atomic ratio = 2.04 ± 0.04

^aNumber of samples = 22.

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 $\rightarrow L_{ij}(\gamma)$ can be considered a constant.

Table 3.8 Quantitation results for a polyurethane sample

Element	Orbital	KE (eV)	σ	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: $T(\text{KE})$ is constant over the range of detected photoelectron kinetic energies, $\lambda(\text{KE})$ varies as $\text{KE}_{0.7}$, $h\nu = 1486.6 \text{ eV}$, and $\theta = 55^\circ$.

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

Table 3.9 Quantitation results for a polyurethane sample^a

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

^aNumber of samples = 8.

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