Surface Analysis of Nanomaterials

(나노소재표면분석)

:Surface and Thin Film Analysis

(표면 및 박막분석)

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시간: 목 (1-A, 1-B, 2-A, 2-B, 3-A, 3-B)

2. Electron Spectroscopy for Chemical Analysis

Electron Spectroscopy for Chemical Analysis

ESCA is called X-ray photoelectron spectroscopy (XPS)

– Of all the contemporary surface characterization methods, electron spectroscopy for chemical analysis (ESCA)

ESCA falls in the category of analytical methods referred to as electron spectroscopies

Auger electron spectroscopy (AES)

high-resolution electron energy loss spectroscopy (HREELS)

Electron Spectroscopy for Chemical Analysis

BASIC ESCA Experiment

For ESCA, the photon source is in the X-ray energy range

The irradiated atoms emit electrons (photoelectrons) after direct transfer of energy from the photon to core-level electrons.

Photoelectrons emitted from atoms near the surface can escape into the vacuum chamber and be separated according to energy and counted.

The energy of the photoelectrons is related to the atomic and molecular environment from which they originated.
-> binding energy and their information

The number of electrons emitted is related to the concentration of the emitting atom in the sample.
-> quantitative and qualitative analysis

Electron Spectroscopy for Chemical Analysis

BASIC ESCA Experiment

Again

Deep core electrons have binding energies corresponding to the energies of photons that lie in the X-ray region.

When a solid absorbs a photon with an energy in excess of the binding energy of an electron, a photoelectron is emitted and the kinetic energy of the photoelectron is related to the energy of the photon.

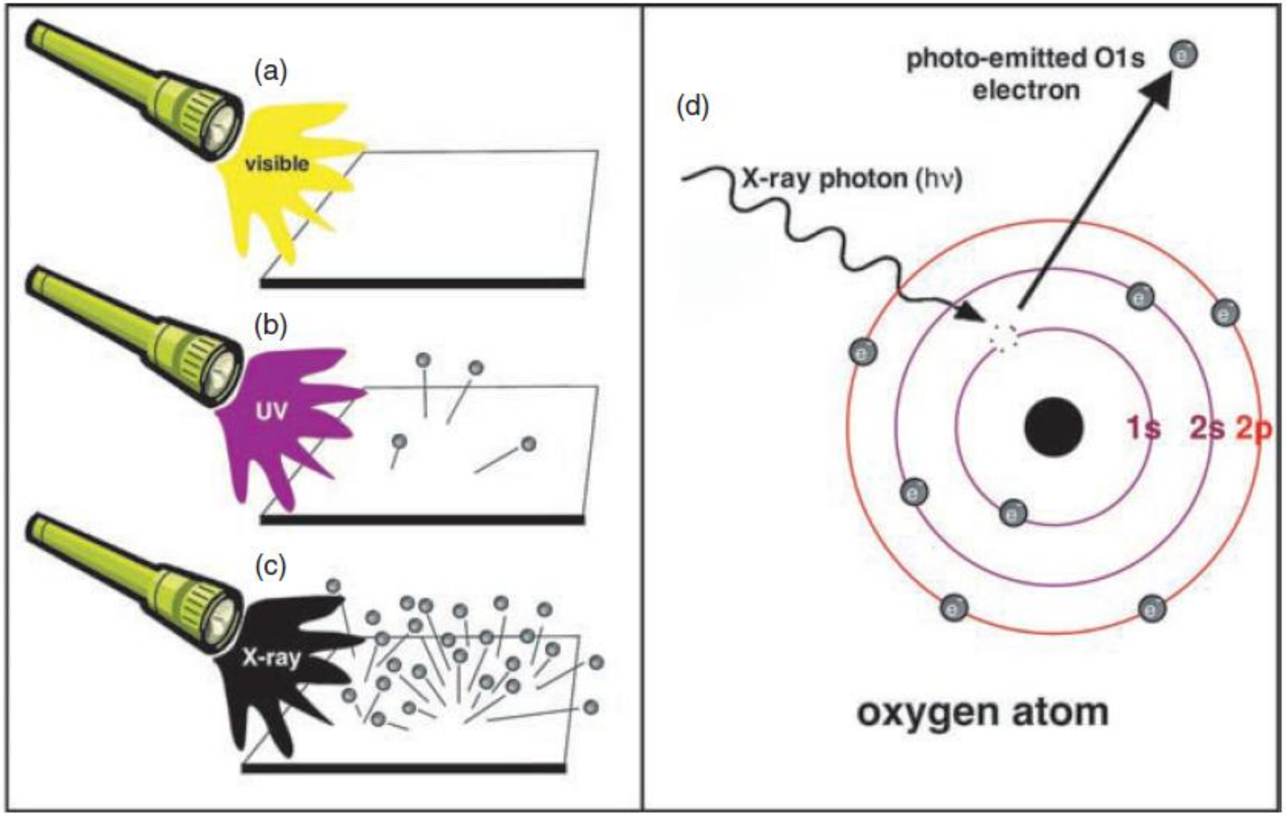
Deep core electrons do not participate in bonding and their energies are characteristic of the atom from which they originate.

The energy of core electrons does not depend on the environment of the atom. Therefore, XPS is particularly useful for elemental analysis of a sample. Not only can XPS identify the composition of a sample but it can also be used to determine quantitatively the composition.

Electron Spectroscopy for Chemical Analysis

BASIC ESCA Experiment

The surface to be analyzed is placed in a vacuum environment and then irradiated with photons.



The X-ray photon transfers its energy to a core-level electron imparting enough energy for the electron to leave the atom

Electron Spectroscopy for Chemical Analysis

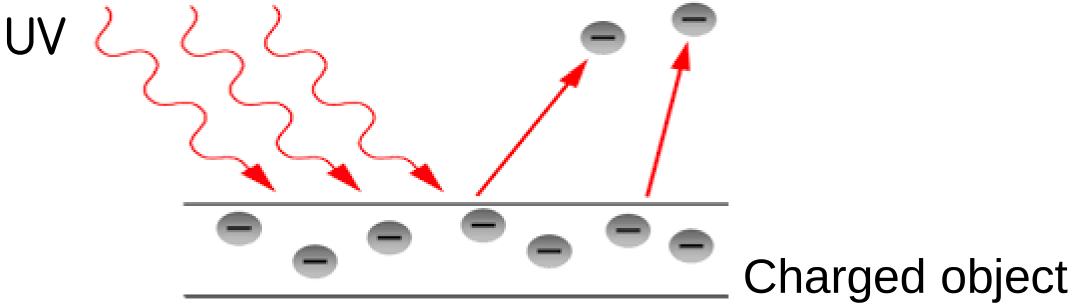
A History of the Photoelectron Effect and ESCA

Fundamental to the development of ESCA

1880s Heinrich Rudolf Hertz

noticed that metal contacts in electrical systems, when exposed to light, exhibit an enhanced ability to spark

-> a charged object loses its charge more readily when illuminated by ultraviolet radiation (UV)



Electron Spectroscopy for Chemical Analysis

1888 Wilhelm Hallwachs

observed that a negatively charged zinc plate lost its charge when exposed to ultraviolet (UV) light, but that positively charged zinc plates were not affected

1899 J.J. Thompson

subatomic particles (electrons) were emitted from the zinc plate exposed to light

1909 Albert Einstein

photons of light directly transferred their energy to electrons within an atom, resulting in the emission of the electrons without energy loss using Planck's 1900 quantization of energy concept

-> these ideas form the foundation for the theoretical understanding of ESCA.

Electron Spectroscopy for Chemical Analysis

Straightforward history of ESCA as an analytical method

1914 Robinson and Rawlinson

studied photoemission from X-ray irradiated gold and, using photographic detection, observed the energy distribution of electrons produced
- publish a recognizable gold photoemission spectrum

1951 Steinhardt and Serfass

first applied photoemission as an analytical tool

1950s and 1960s

Kai Siegbahn

developed the instrumentation and theory of ESCA to give us the method we use today. Siegbahn also coined the term ‘electron spectroscopy for chemical analysis’, later modified by his group to ‘electron spectroscopy for chemical applications.’

Electron Spectroscopy for Chemical Analysis

INFORMATION PROVIDED BY ESCA

The most basic ESCA analysis of a surface will provide qualitative and quantitative information on all the elements present (except H and He)

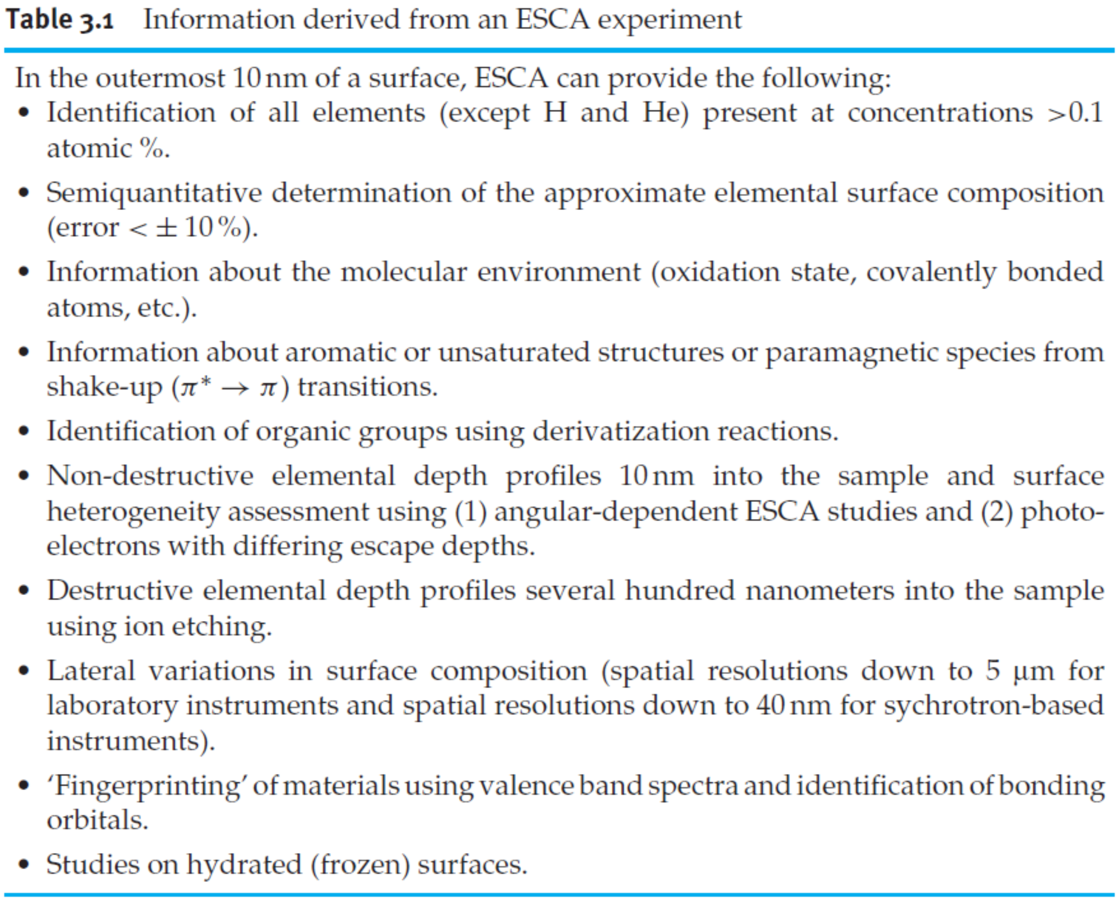


Table 3.1 Information derived from an ESCA experiment

In the outermost 10 nm of a surface, ESCA can provide the following:

- Identification of all elements (except H and He) present at concentrations >0.1 atomic %.
- Semiquantitative determination of the approximate elemental surface composition (error < ± 10 %).
- Information about the molecular environment (oxidation state, covalently bonded atoms, etc.).
- Information about aromatic or unsaturated structures or paramagnetic species from shake-up ($\pi^* \rightarrow \pi$) transitions.
- Identification of organic groups using derivatization reactions.
- Non-destructive elemental depth profiles 10 nm into the sample and surface heterogeneity assessment using (1) angular-dependent ESCA studies and (2) photoelectrons with differing escape depths.
- Destructive elemental depth profiles several hundred nanometers into the sample using ion etching.
- Lateral variations in surface composition (spatial resolutions down to 5 μm for laboratory instruments and spatial resolutions down to 40 nm for sychrotron-based instruments).
- 'Fingerprinting' of materials using valence band spectra and identification of bonding orbitals.
- Studies on hydrated (frozen) surfaces.

information about the chemistry, electronic structure, organization, and morphology of a surface.

Electron Spectroscopy for Chemical Analysis

X-ray Interaction with Matter, the Photoelectron Effect and Photoemission from Solids

An understanding of the photoelectric effect and photoemission is essential to appreciate the surface analytical method, ESCA

What happen when a photon impinges upon an atom?

(1) the photon can pass through with no interaction

(2) the photon can be scattered by an atomic orbital electron leading to partial energy loss

(3) the photon may interact with an atomic orbital electron with total transfer of the photon energy to the electron, leading to electron emission from the atom

One of three events may occur

Electron Spectroscopy for Chemical Analysis

X-ray Interaction with Matter, the Photoelectron Effect and Photoemission from Solids

(1) the photon can pass through with no interaction

-> no interaction occurs

(2) the photon can be scattered by an atomic orbital electron leading to partial energy loss

-> 'Compton scattering' and can be important in high-energy processes https://www.youtube.com/watch?v=QsCmslcSIEs

(3) the photon may interact with an atomic orbital electron with total transfer of the photon energy to the electron, leading to electron emission from the atom

-> accurately describes the photoemission process that is the basis of ESCA. Total transfer of the photon energy to the electron is the essential element of photoemission

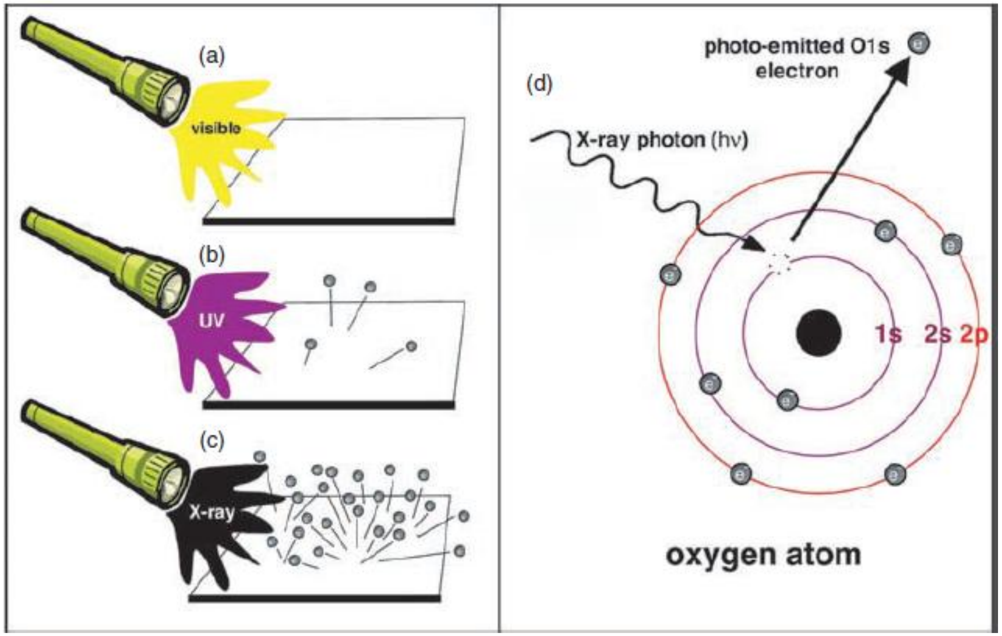
Electron Spectroscopy for Chemical Analysis

Four observations associated with this photoelectric effect

https://www.youtube.com/watch?v=0b0axfyJ4oo&t=17s

First, no electrons will be ejected from an atom regardless of the illumination intensity unless the frequency of excitation is greater than or equal to a threshold level characteristic for each element.
Thus, if the frequency (energy) of the excitation photon is too low, no photoemission will be observed.
As the energy of this photon is gradually increased, at some value, we will begin to observe the photoemission of electrons from the atom

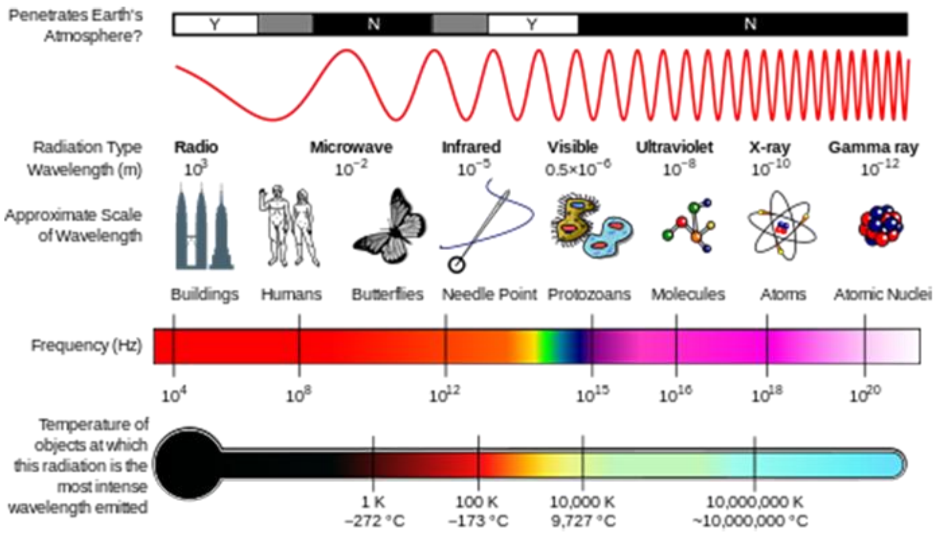
More photoelectron emitted



Electron Spectroscopy for Chemical Analysis

Four observations associated with this photoelectric effect

Second, once the threshold frequency is exceeded, the number of electrons emitted will be proportional to the intensity of the illumination (i.e., once we've irradiated the sample with photons of sufficient energy to stimulate electron emission, the more photons we irradiate the sample with, the more photoelectrons will be produced)



Electron Spectroscopy for Chemical Analysis

Four observations associated with this photoelectric effect

How is energy related to the wavelength of radiation?

radiation either as waves or as individual particles called photons

The energy associated with a single photon is given by $E = h\nu$,
where E is the energy (SI units of J),
h is Planck's constant ($h = 6.626 \times 10^{-34}$ J s), and
ν is the frequency of the radiation (SI units of s^{-1} or Hertz, Hz)

Frequency is related to wavelength by $\lambda=c/\nu$,
where c, the speed of light, is 2.998×10^{8} m s^{-1}.
wavenumber, $\sigma=1/\lambda$, which is commonly reported in units of cm^{-1}.

The energy of a single photon that has the wavelength λ is given by:

$$E = \frac{hc}{\lambda} = \frac{1.986 \times 10^{-16}\ \mathrm{J\ nm\ photon}^{-1}}{\lambda}$$

Electron Spectroscopy for Chemical Analysis

Four observations associated with this photoelectric effect

Third, the kinetic energy (KE) of the emitted electrons is linearly proportional to the frequency of the exciting photons – if we use photons of higher energy than our threshold value, the excess photon energy above the threshold value will be transferred to the emitted electrons.

Finally, the photoemission process from excitation to emission is extremely rapid (10^{-16} s). The basic physics of this process can be described by the Einstein equation, simply stated as:

$$E_B = h\nu - \text{KE}$$

Where, E_B is the binding energy of the electron in the atom (a function of the type of atom and its environment),
$h\nu$ is the energy of the X-ray source (a known value),
KE is the kinetic energy of the emitted electron that is measured in the ESCA spectrometer

Electron Spectroscopy for Chemical Analysis

About Binding energy in ESCA

E_B, the quantity that provides us with valuable information about the photoemitting atom, is easily obtained from $h\nu$ (known) and KE (measured).

Binding energies are frequently expressed in electron volts (eV; 1 eV = 1.6 × 10_{-19} joules).

$$E_B = h\nu - \mathrm{KE}$$

Electron Spectroscopy for Chemical Analysis

The binding energy of an electron in an atom

A negatively charged electron will be bound to the atom by the positively charged nucleus

The closer the electron is to the nucleus, the more tightly we can expect it to be bound

Binding energy will vary with the type of atom (i.e., a change in nuclear charge) and the addition of other atoms bound to that atom (bound atoms will alter the electron distribution on the atom of interest).

Different isotopes of a given element have different numbers of neutrons in the nucleus, but the same nuclear charge. Changing the isotope will not appreciably affect the binding energy

Electron Spectroscopy for Chemical Analysis

The binding energy of an electron in an atom

Weak interactions between atoms such as those associated with crystallization or hydrogen bonding will not alter the electron distribution sufficiently to change the measured binding energy

the variations we see in the binding energy that provide us with the chemical information content of ESCA are associated with covalent or ionic bonds between atoms

- > These changes in binding energy are called **binding energy shifts or chemical shifts**

For gases, the binding energy of an electron in a given orbital is identical to the ionization energy or first ionization potential of that electron.

But, In solids, the influence of the surface is felt, and additional energy must be accounted for to remove an electron from the surface.

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