

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

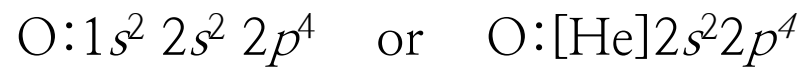
Electron Spectroscopy for Chemical Analysis

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



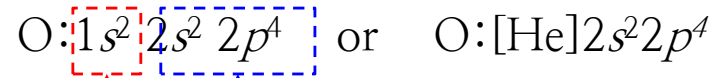
What else?

Carbon (C), Nitrogen (N), Boron (B)

Electron Spectroscopy for Chemical Analysis

Electronic configuration of Atoms

The electron configuration of a oxygen atom

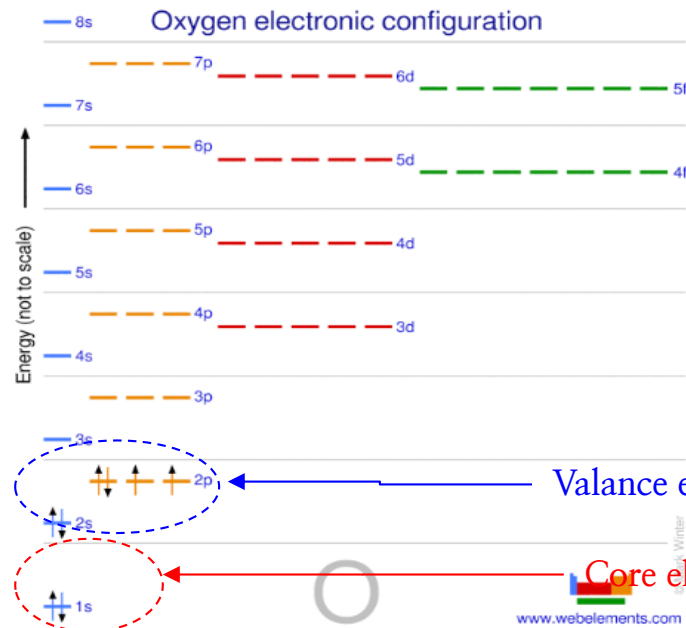


Valance electron

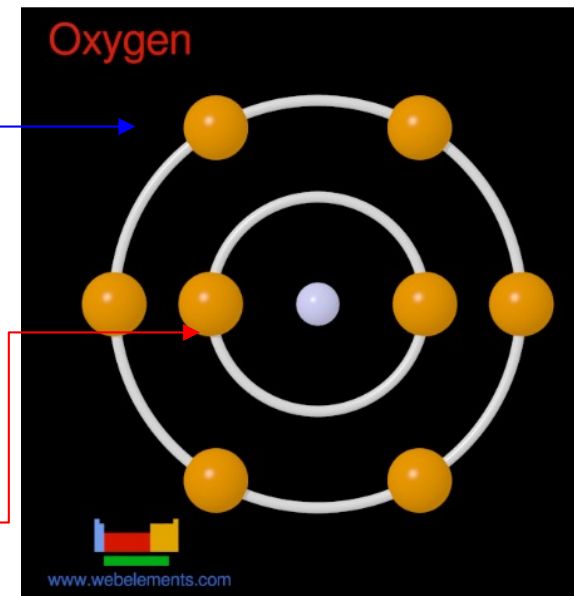
: valence electrons can participate in the formation of chemical bonding

Core electron

: influence the chemical reactivity of an atom



Schematic electronic configuration of oxygen.



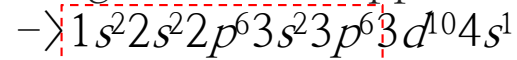
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Electronic configuration of Atoms

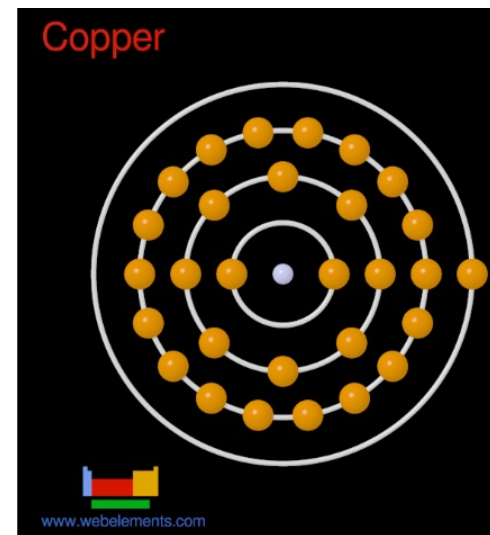
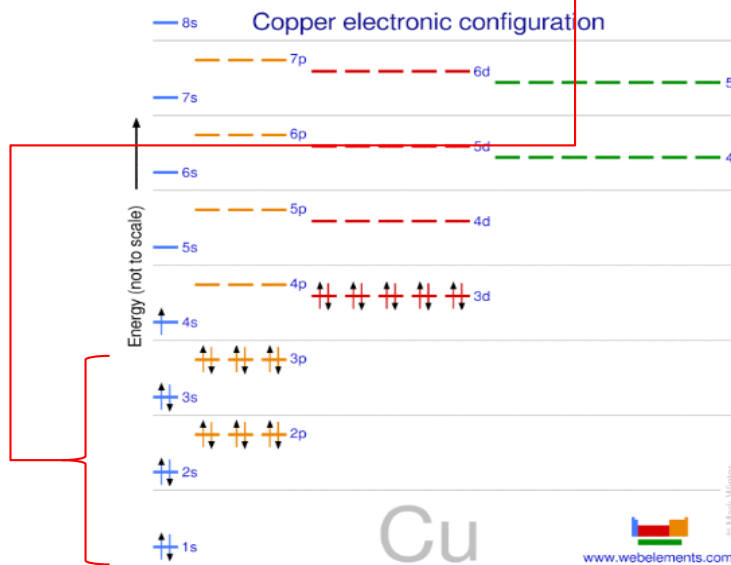
Example. Copper (Cu)

What are the core and valence electrons in copper?

– the electron configuration of copper with 29 electrons:



Core electron



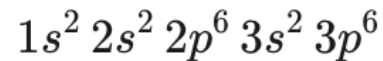
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Electronic configuration of Atoms

Example. Copper (Cu)

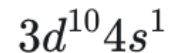
Separation of the electrons into two groups

Core electrons



- Strongly bound to the nucleus
- Occupy inner atomic shells
- Have relatively large binding energies
- Their binding energies are sensitive to the chemical environment

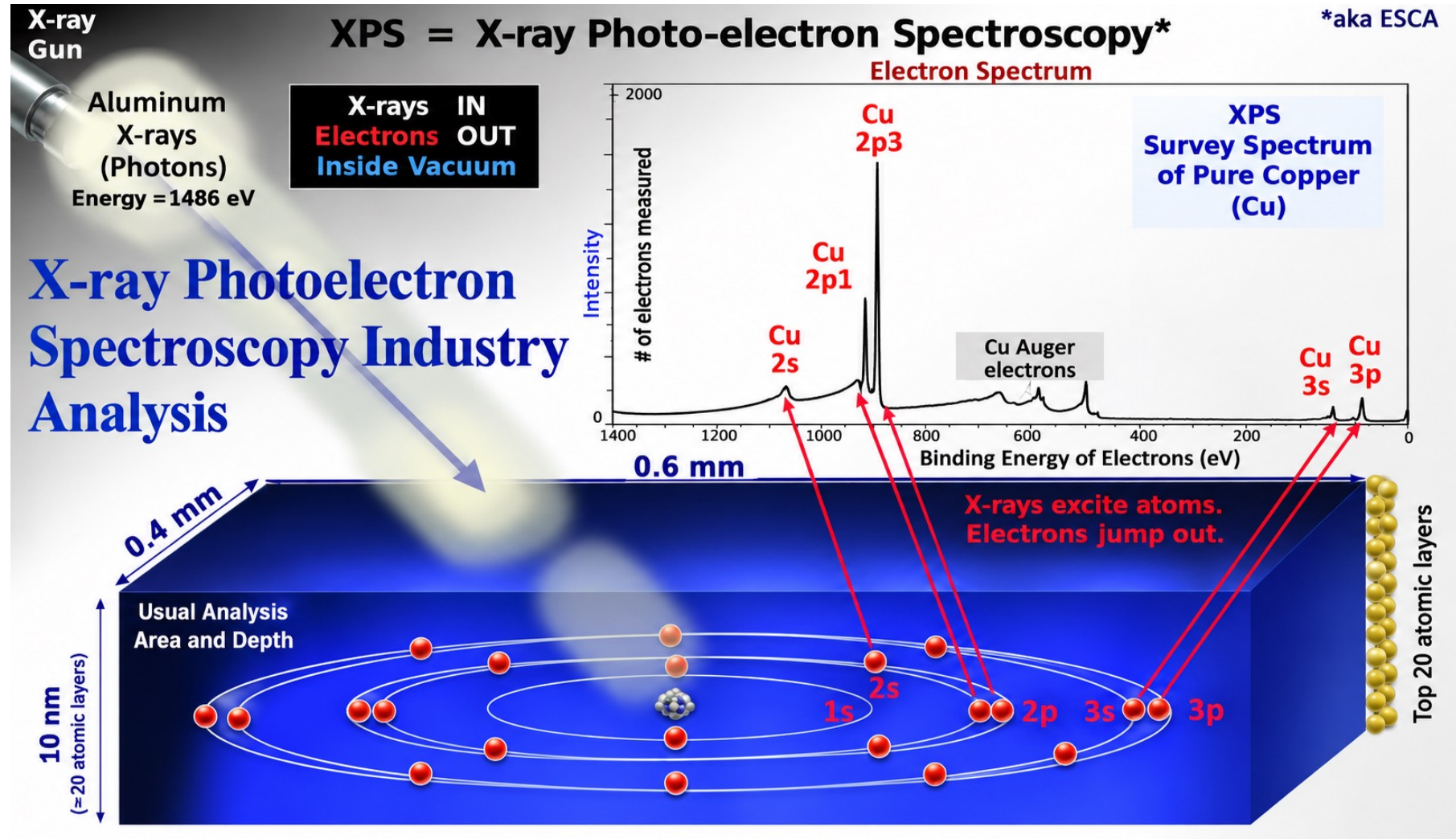
Valence electrons



- Located in the outermost occupied states
- Participate in bonding and electrical conduction
- Form the valence electronic structure of metallic Cu

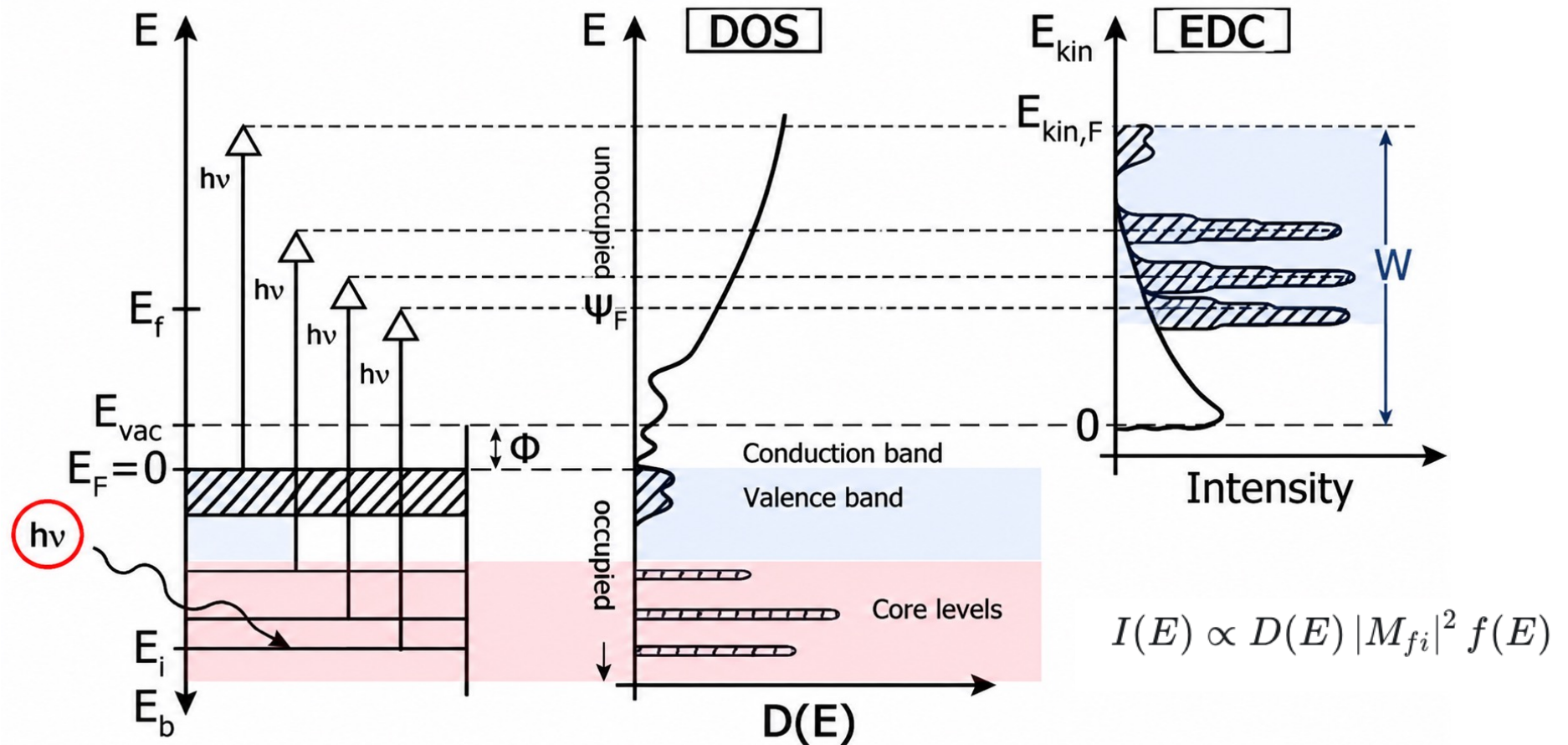
Electron Spectroscopy for Chemical Analysis

Electronic configuration of copper and its XPS spectrum



Electron Spectroscopy for Chemical Analysis

Relationship between **Electronic structure**, **Density of States (DOS)** and **Measured Photoelectron Spectrum (EDC)**



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

$$\Gamma = \frac{\hbar}{\tau}$$

- Γ (Gamma): natural linewidth, or lifetime broadening
 - τ (tau): lifetime of the core-hole state
 - $\hbar$: reduced Planck constant
-
- For the C1s orbital, is ~ 0.1 eV. For a given element, the value of Γ 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

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Peak Widths

A shorter core-hole lifetime produces a broader XPS peak.

$$\Gamma = \frac{\hbar}{\tau}$$
$$\begin{array}{lcl} \tau \downarrow & \Rightarrow & \Gamma \uparrow \\ \tau \uparrow & \Rightarrow & \Gamma \downarrow \end{array}$$

Lifetime Broadening of Core Levels

- Photoemission creates a core hole with a finite lifetime, τ .
- A finite lifetime causes an intrinsic uncertainty in energy.
- Therefore, each core-level peak has a natural linewidth, Γ .

Short lifetime $\rightarrow$ broad peak
Long lifetime $\rightarrow$ narrow peak

Observed linewidth = natural linewidth + instrumental broadening + X-ray linewidth + ...

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Peak Widths

XPS Survey Spectrum of Gold

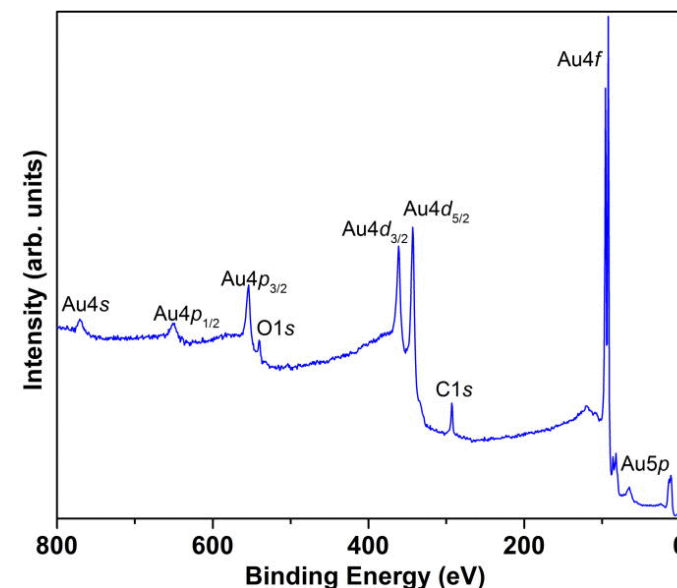
The intrinsic linewidth increases with increasing binding energy(E_B):

$$\text{Au } 4f < 4d < 4p < 4s$$

- Deeper core holes generally have **shorter** lifetimes.
- According to lifetime broadening,

$$\Gamma = \frac{\hbar}{\tau}$$

Shorter lifetime $\rightarrow$ broader XPS peak



- Similarly, the value of Γ 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

Why Do Deeper Core Holes Have Shorter Lifetimes?

- A core hole is an **unstable excited state** created after photoelectron emission.
- The hole can be filled by electrons from higher-energy levels.
- The released energy is dissipated through:
 - Auger electron emission
 - Coster – Kronig transitions
 - X-ray fluorescence

$$\frac{1}{\tau} = \sum_i W_i$$

W_i : transition rate for each relaxation pathway

τ : lifetime of the core-hole state

Deeper Core Level → More Decay Channels

- A deeper core hole generally provides **more energetically allowed relaxation pathways**.
- More decay channels increase the total decay rate.
- Therefore, the core-hole lifetime becomes shorter.

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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

Total Peak Width in XPS

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

- FWHM_n : natural linewidth
 - determined by the core-hole lifetime
 - $\Gamma \approx \hbar/\tau$
- FWHM_x : X-ray source broadening
 - finite linewidth of the incident X-ray
- FWHM_a : Analyzer broadening
 - limited energy resolution of the electron analyzer
- FWHM_{ch} : Chemical/environmental broadening
 - multiple chemical states, inhomogeneous bonding environments, charging, etc.

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

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

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Peak Widths

Why Can Metal XPS Peaks Become Asymmetric?

Asymmetric XPS Peaks in Conductive Materials

- In metals, many empty electronic states exist just above the Fermi level.
- After a core electron is emitted, some conduction electrons can be excited to these empty states.
- This additional excitation consumes part of the available energy.
- As a result, the emitted photoelectron has slightly **lower kinetic energy**.

$$E_{\text{kin}} \downarrow \Rightarrow E_B \uparrow$$

- Therefore, extra intensity appears on the higher binding-energy side of the main peak.

Key message

Energy loss to conduction-electron excitation produces a high-binding-energy tail.

$$\text{Core photoemission} \rightarrow \text{electron-hole excitation} \rightarrow E_{\text{kin}} \downarrow \rightarrow E_B \uparrow$$

Electron Spectroscopy for Chemical Analysis

Peak Widths

From Shake-up Excitation to an Asymmetric Peak

Why Is the Tail Continuous Rather Than a Separate Satellite?

- In an atom or molecule, excitation may occur between discrete energy levels.
- This can produce a distinct shake-up satellite peak.
- In a metal, however, conduction-electron states form an almost continuous distribution near E_F .
- Many different low-energy excitations are therefore possible.
- These overlapping energy-loss processes form a continuous tail, rather than a separate peak.

Many low-energy excitations → continuous energy loss → asymmetric peak

Electron Spectroscopy for Chemical Analysis

Peak Widths

3) satellite features

For example (Vanadium)

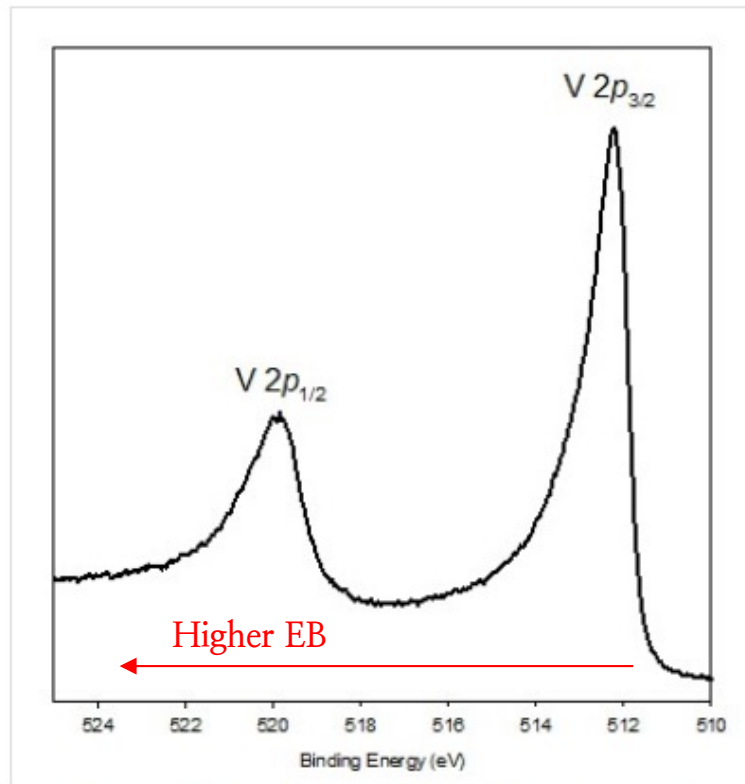


Figure 1. Asymmetric peak shapes in the V 2p spectrum of an argon ion sputter cleaned surface of vanadium metal [2].

- The main V 2p peak is sharp on the lower- E_B side.
- A long tail develops toward the **higher- E_B side**.
- This asymmetric line shape is characteristic of metallic electronic screening and electron-hole excitations.

Discrete excitation → satellite peak

Continuous excitation in a metal → asymmetric tail

Electron Spectroscopy for Chemical Analysis

Peak Fitting

- To maximize the information extracted from ESCA spectra, the area and EB 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 (~ 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

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