

Characterization of Surfaces & Interfaces Lesson 7

MSE 304

Nako Nakatsuka

Nako.Nakatsuka@epfl.ch

October 31st 2025

Plan of the Course: Fundamentals, Characterization, and Applications

1: Intro to Surfaces & Interfaces

2: Surfaces in the Real World - Adsorption

3: Surface Energetics & Interfacial Phenomena

4: Atomic Structure of Real Surfaces

5: Solid-Solid Interfaces

6: From Ideal Planes to Real Materials (Recap)

7: Characterization of Surfaces & Interfaces

8: Surface Chemistry

9: Characterization of Molecular Assembly

10: Biological Processes at Surfaces

11: Electronic Properties of Surfaces

12: Thin Film Technologies

13: Biosensor Fundamentals

14: Biosensing applications

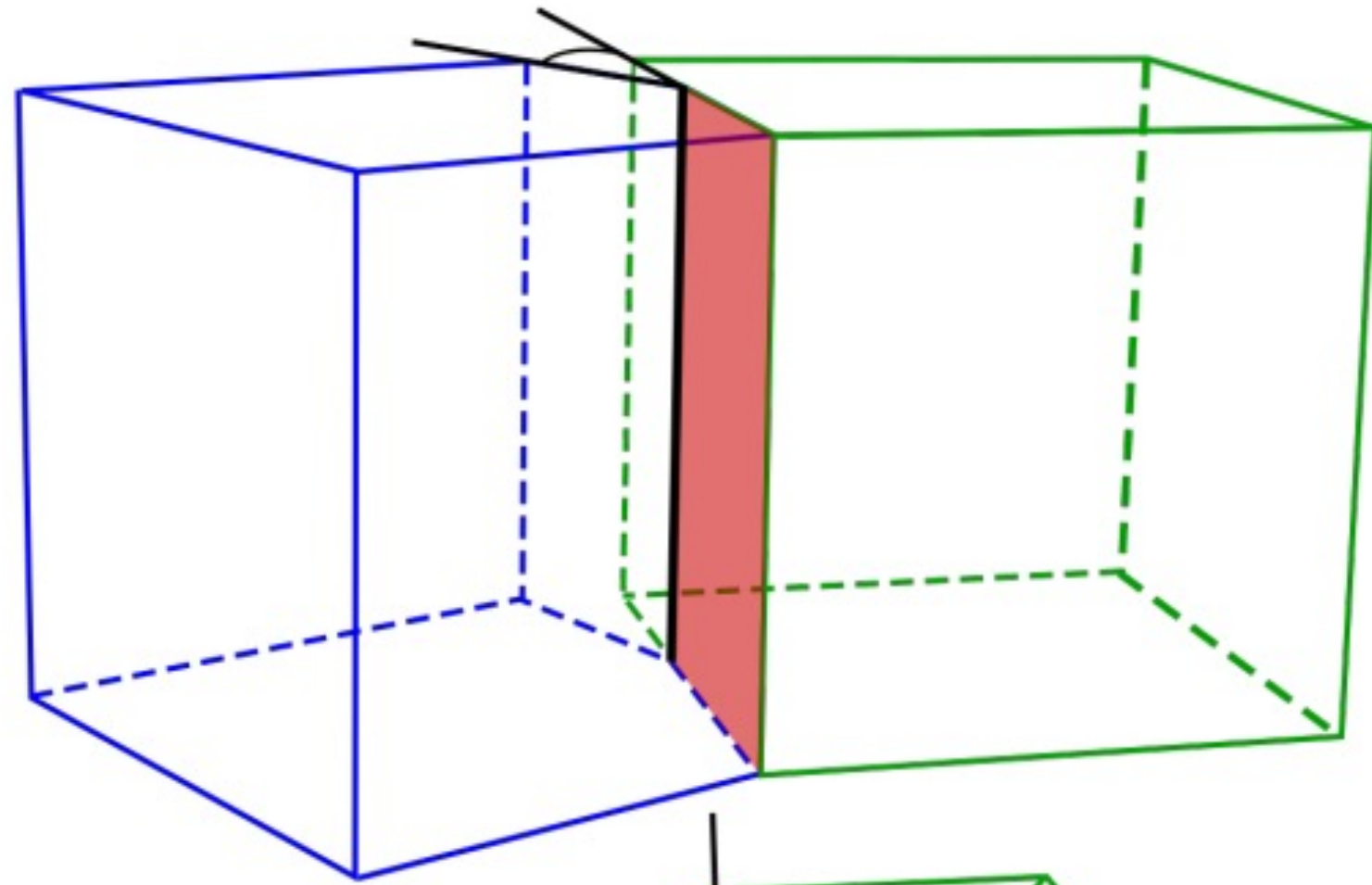


Recap from Lesson 5 – Solid-Solid Interfaces

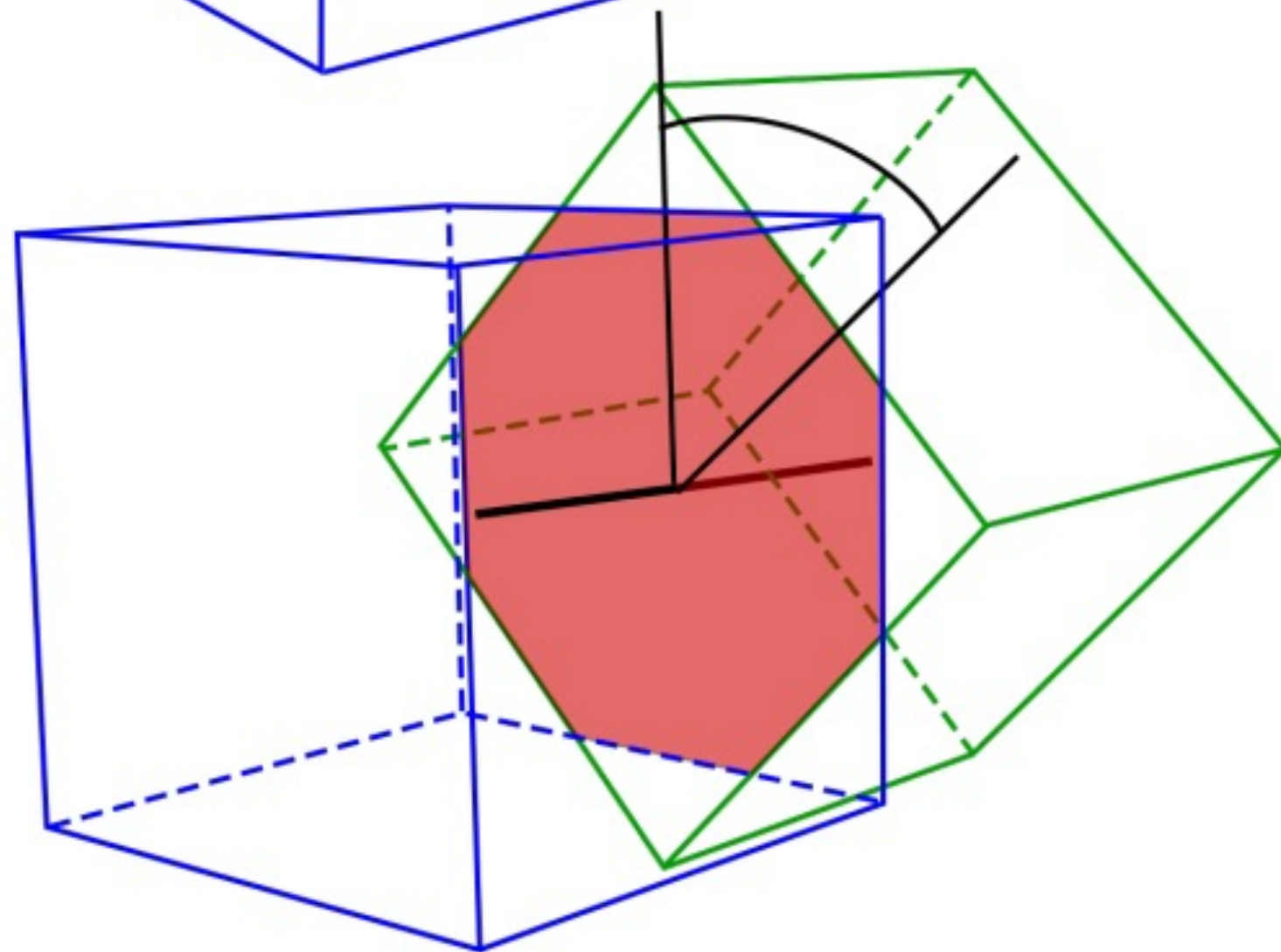
- Solid-solid interfaces can be homophase or heterophase
- Grain boundaries are 2-D defects that form microstructures
- Grain boundaries cost energy but can lower total system energy overall
- Different types of grain boundaries at surfaces
- Electron microscopy techniques (TEM) to visualize the nanoscale



Recap Based on Qs: Idealized Grain Boundary Construction



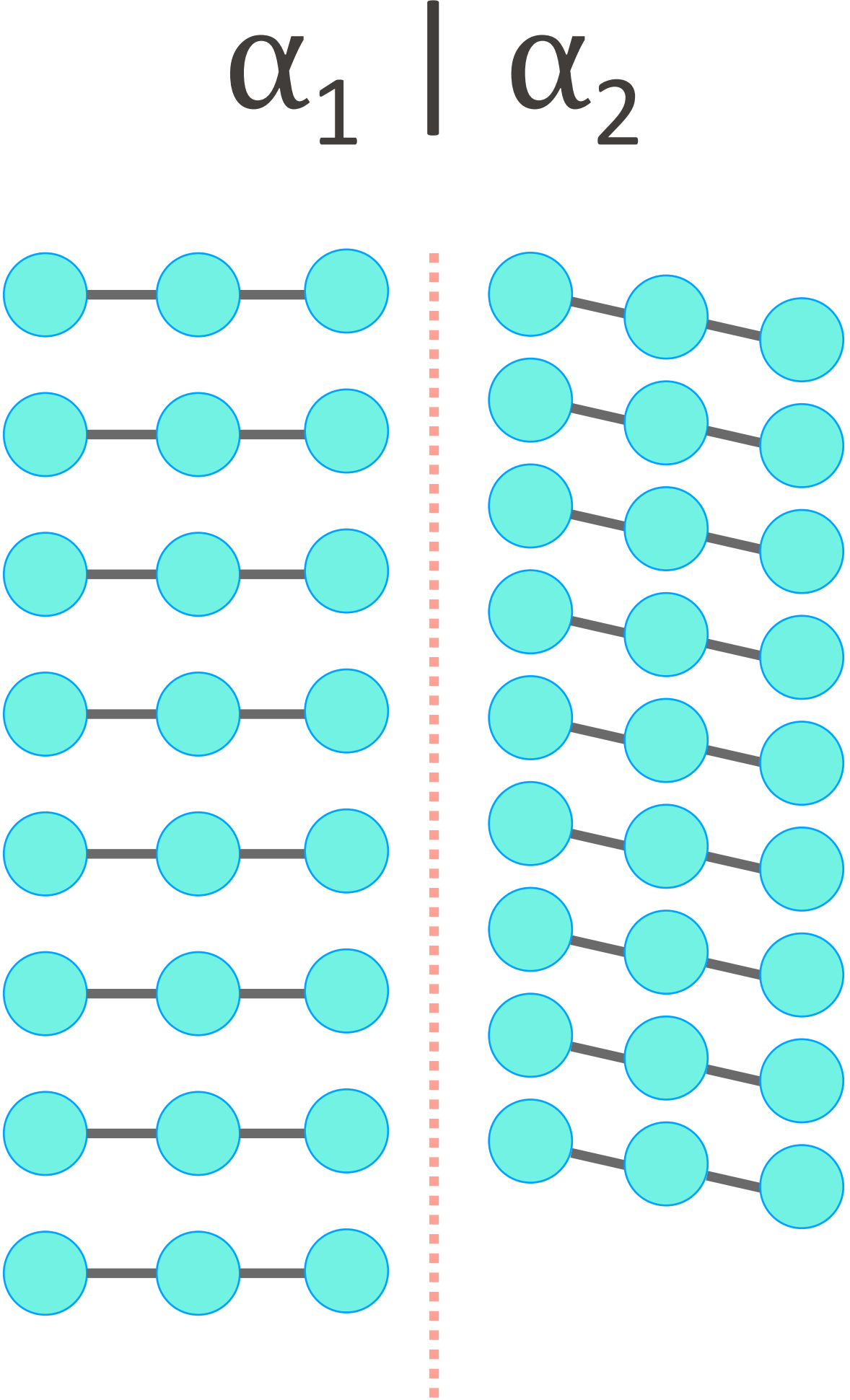
Tilt grain boundary



Twist grain boundary

Recap: Thermodynamics of Homophase Solid-Solid Interfaces

Interfacial energy between two solid phases



$$\gamma_{\alpha_1\alpha_2} = \gamma_{\alpha_1} + \gamma_{\alpha_2} - W_{\alpha_1\alpha_2}$$

$$W_{\alpha_1\alpha_1} \cong \gamma_{\alpha_1} + \gamma_{\alpha_2}$$

$$\gamma_{\alpha_1\alpha_2} = \sum_i b_i + E_l \quad \text{Elastic energy}$$

Energy per broken bond

Recap: Specific Cases of Solid-Solid Interfaces

Homogeneous grain boundary
with low angle

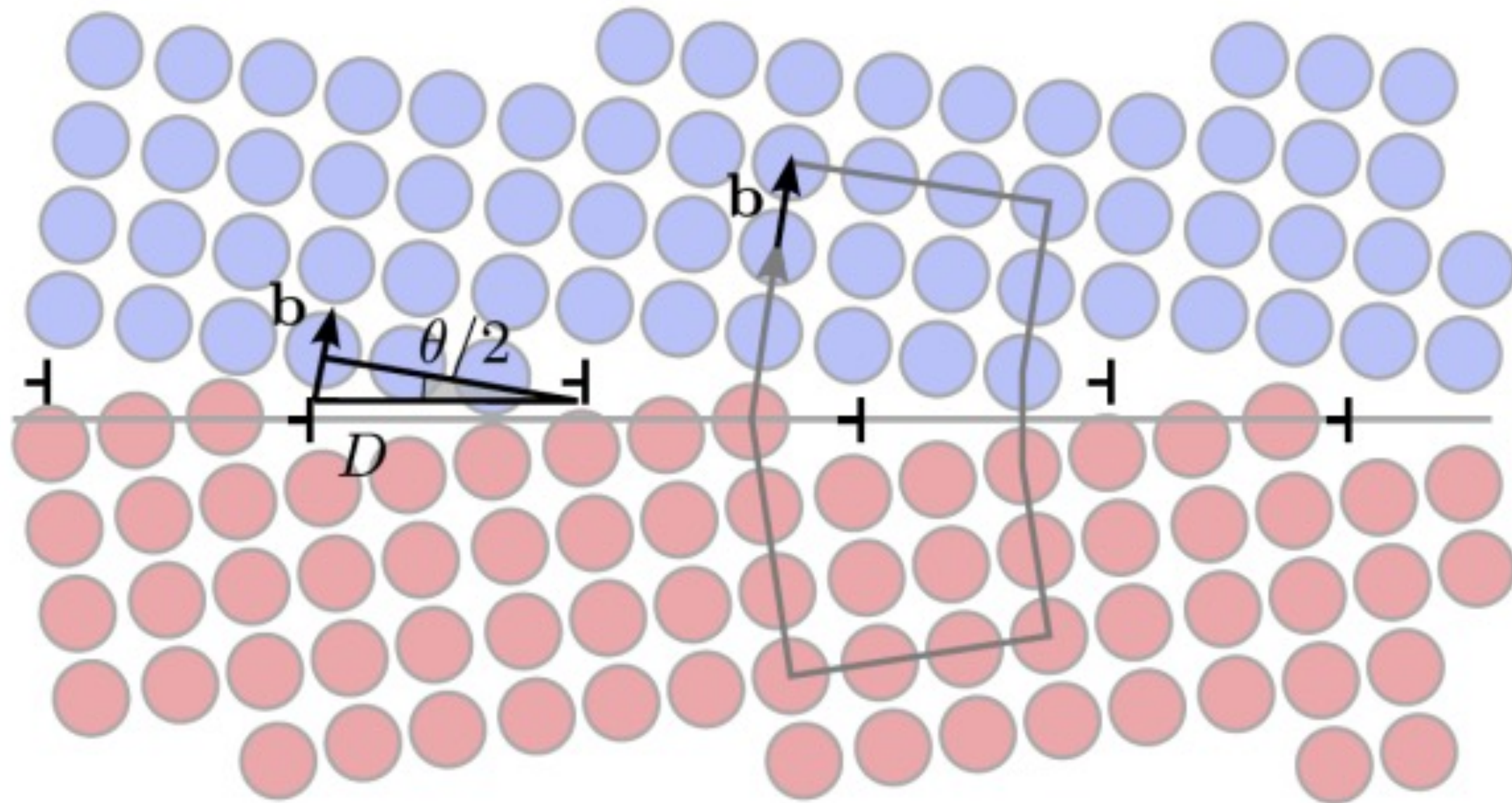
$\alpha_1 \mid \alpha_2$

Heterogeneous solid-solid
interface

$\alpha \mid \beta$

$$\gamma_{\alpha_1\alpha_2} = 2\gamma_{\alpha_1} - W_{\alpha_1\alpha_2} = E_l$$

Dislocations in Tilt Grain Boundaries



Low-angle tilt grain boundary with dislocations

D: distance between neighboring dislocations

b: Burgers vector (lattice distortion)

θ: misorientation angle between two grains

$$\gamma_{\alpha_1\alpha_2} = \gamma_{\alpha_1} + \gamma_{\alpha_2} - W_{\alpha_1\alpha_2}$$

Grain boundary interfacial energy

$$\gamma_{\alpha_1\alpha_2} = E_{\perp} \times (1/D)$$

Energy associated per dislocation

Density of dislocation

$$\frac{1}{D} \approx \frac{\theta}{b}$$

Larger $\theta \rightarrow$ more dislocations per unit length

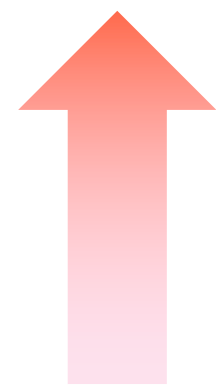
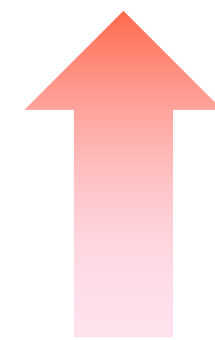
Smaller $\theta \rightarrow$ dislocations farther apart

Entropy vs. Enthalpy in Grain Boundaries

Grain boundaries increase the system's entropy → disorder and more microstates

BUT this entropy gain is small vs. enthalpy cost due to bond distortion and grain boundary energy

$$\Delta G = \Delta H - T\Delta S$$



More atomic disorder → more microstates
Dislocation density measures disorder

Broken bonds + elastic strain
 $\gamma_{GB} = \text{high}$

Different defects have different stabilizing factors:

- Point defects stabilized by **entropy** → always exist at equilibrium
- Grain boundaries dominated by **enthalpy** → system tries to remove them

Outline of Lesson 7

- Electron microscopy techniques – TEM vs. SEM
- Electron backscatter diffraction to visualize grain boundaries
- Energy-dispersive x-ray spectroscopy to obtain elemental composition
- X-ray photoelectron spectroscopy and secondary ion mass spectrometry
- Fundamentals: photoelectric effect, binding energy, work function



Electron Microscopy to Visualize Real Surfaces and Materials

Light Microscopy

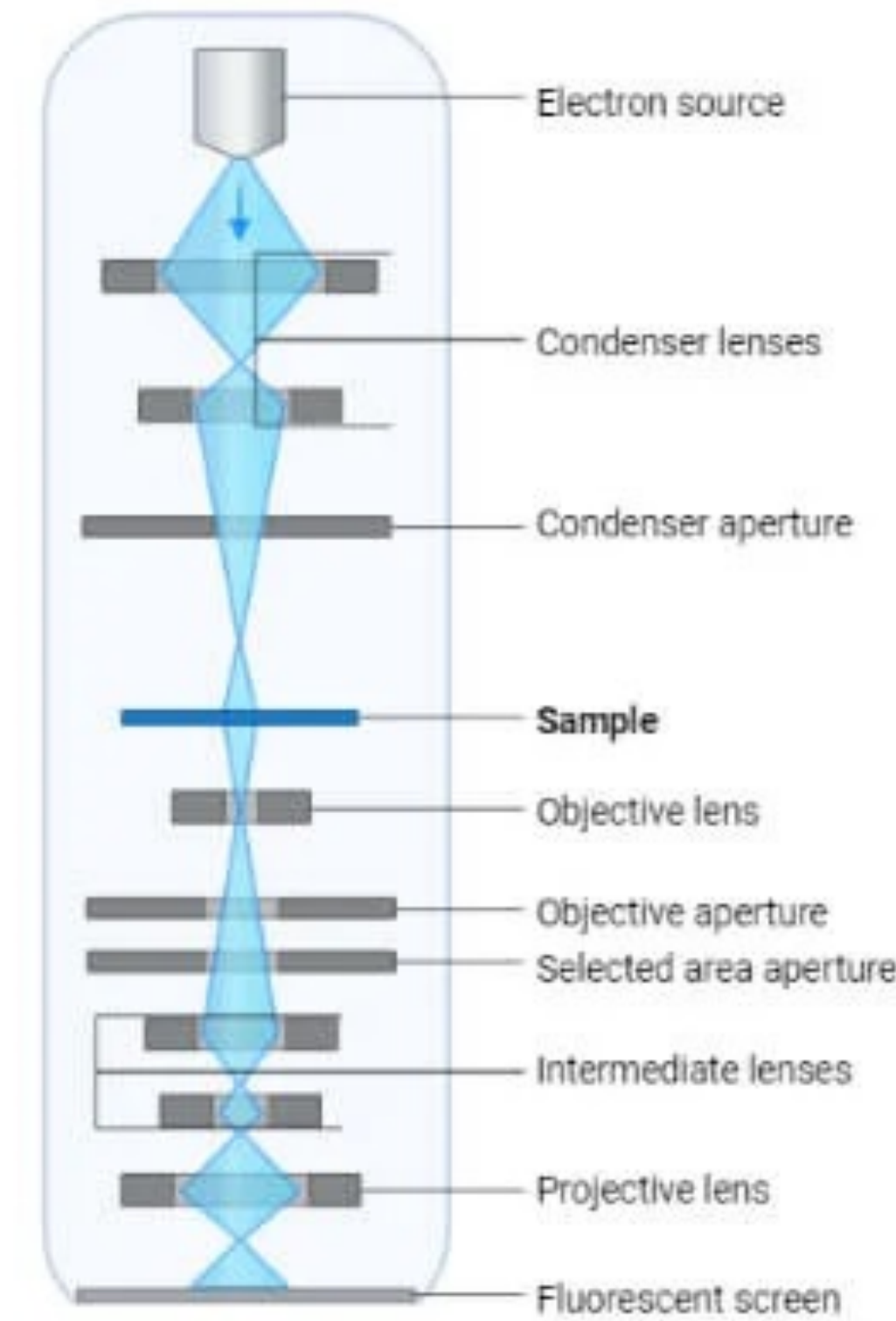
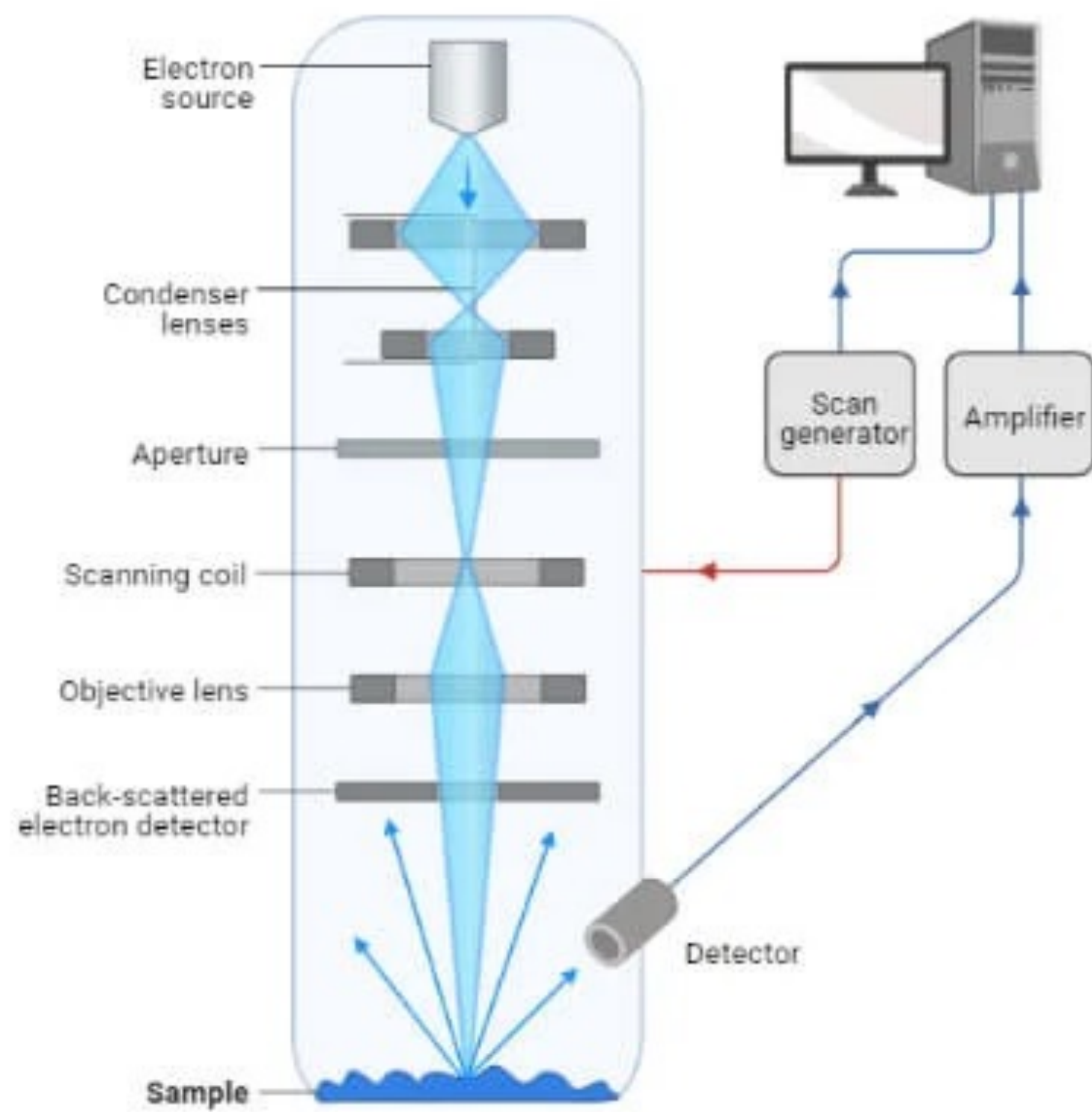
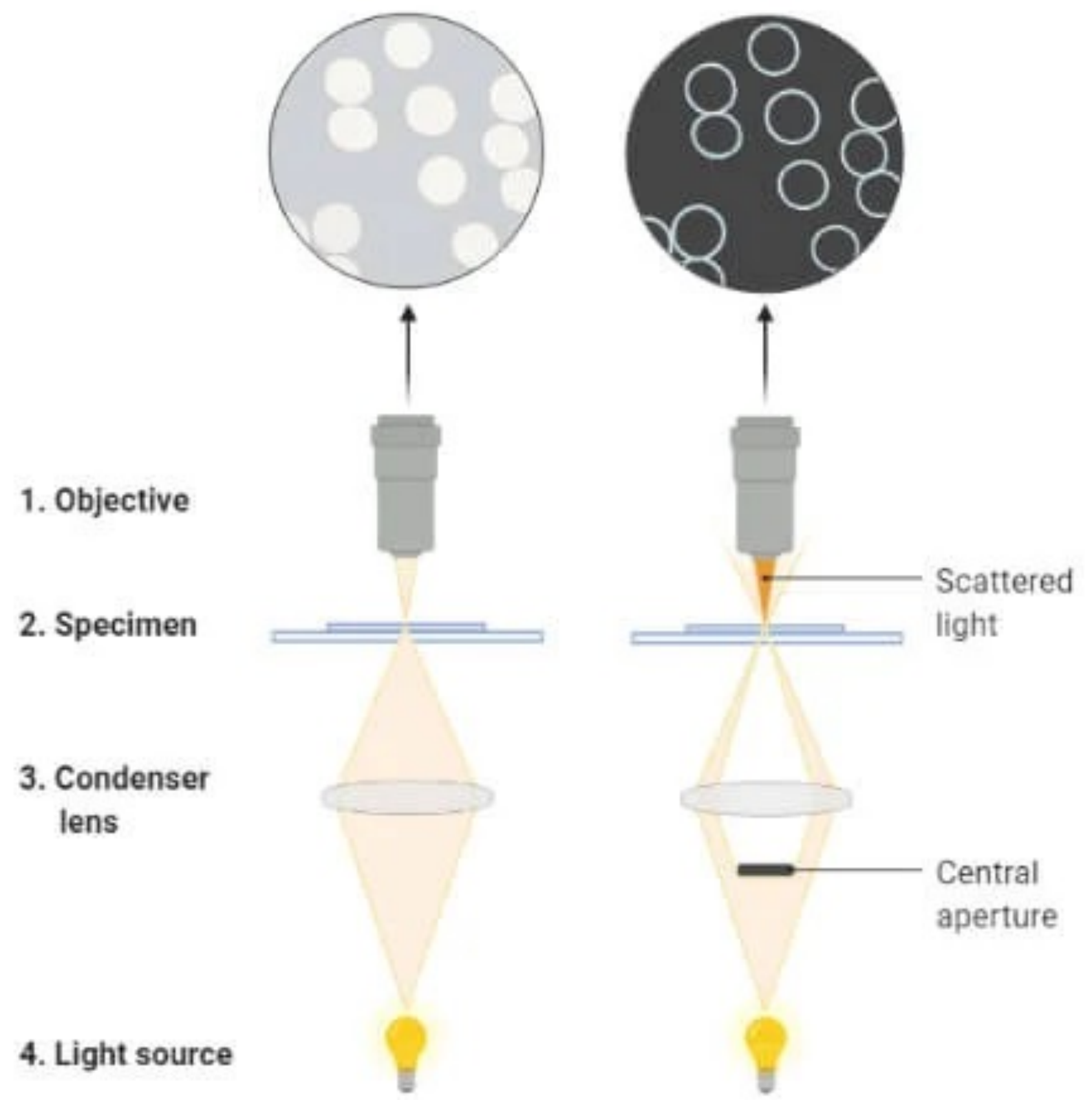
Electron Microscopy

Brightfield

Darkfield

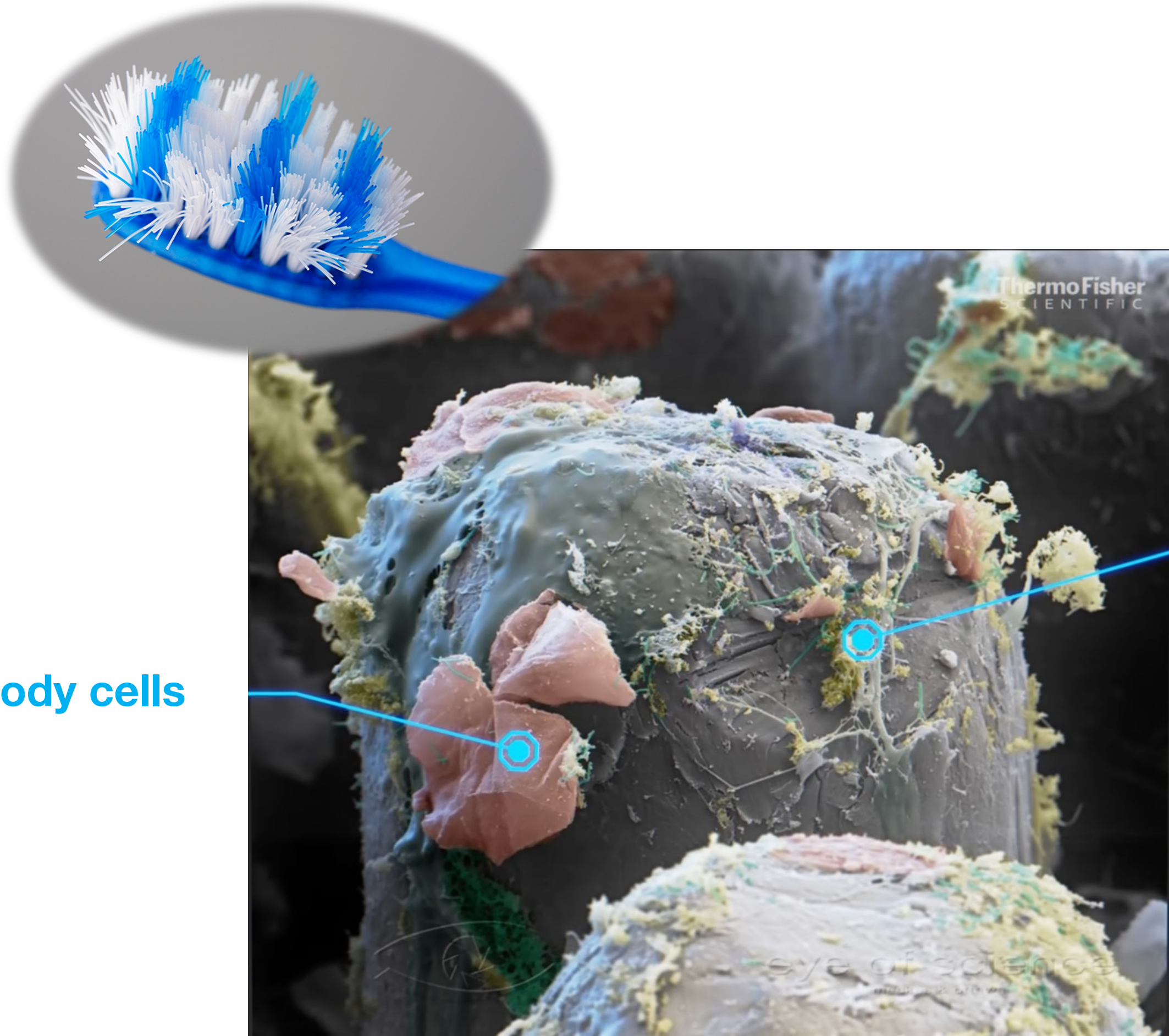
Scanning Electron Microscopy (SEM)

Transmission Electron Microscopy (TEM)



Electron Microscopy Techniques

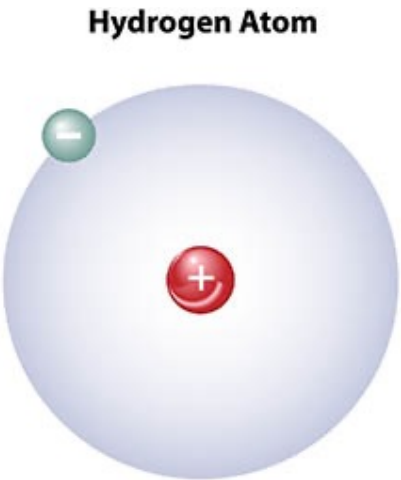
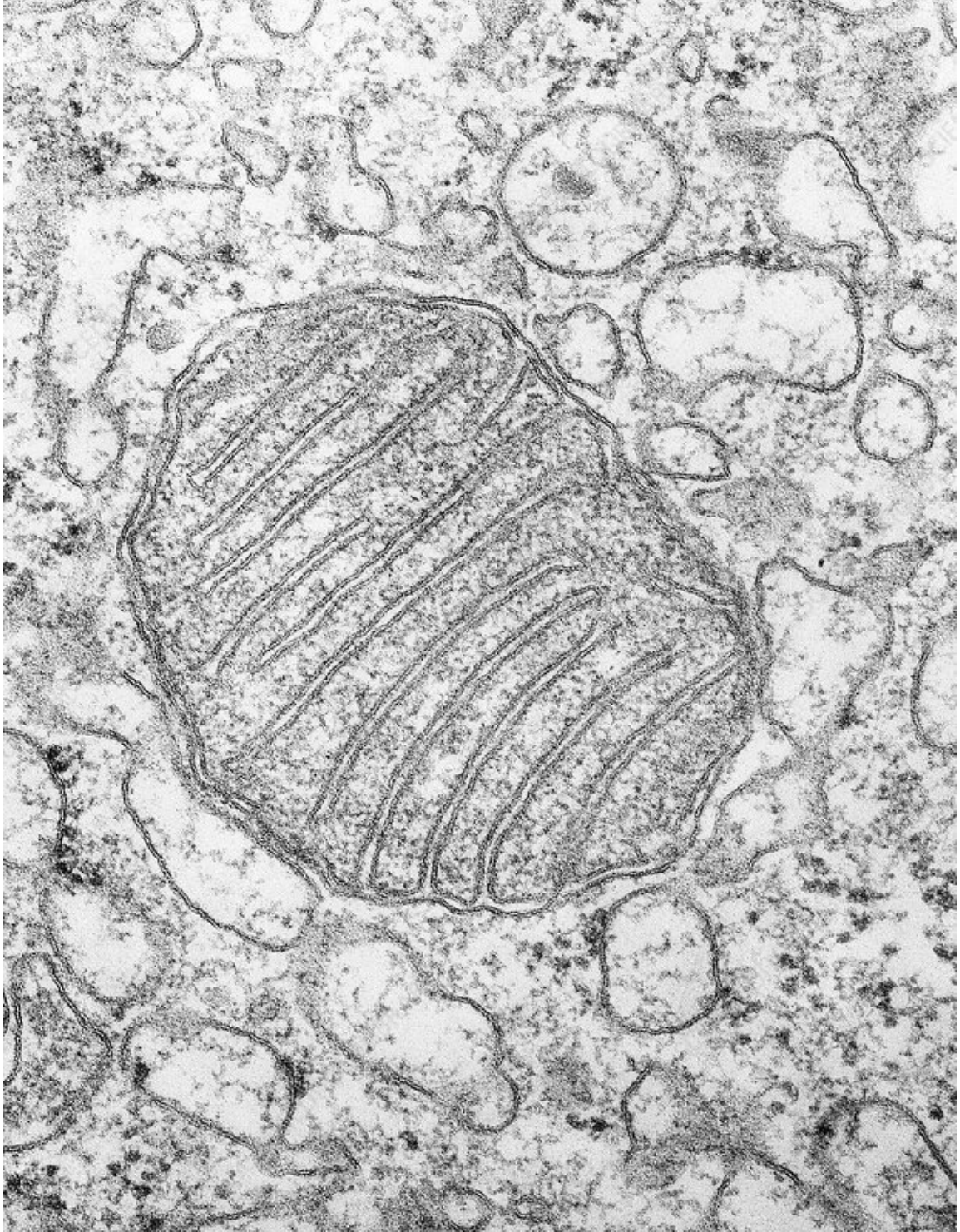
Scanning Electron Microscopy (SEM)



Bacteria

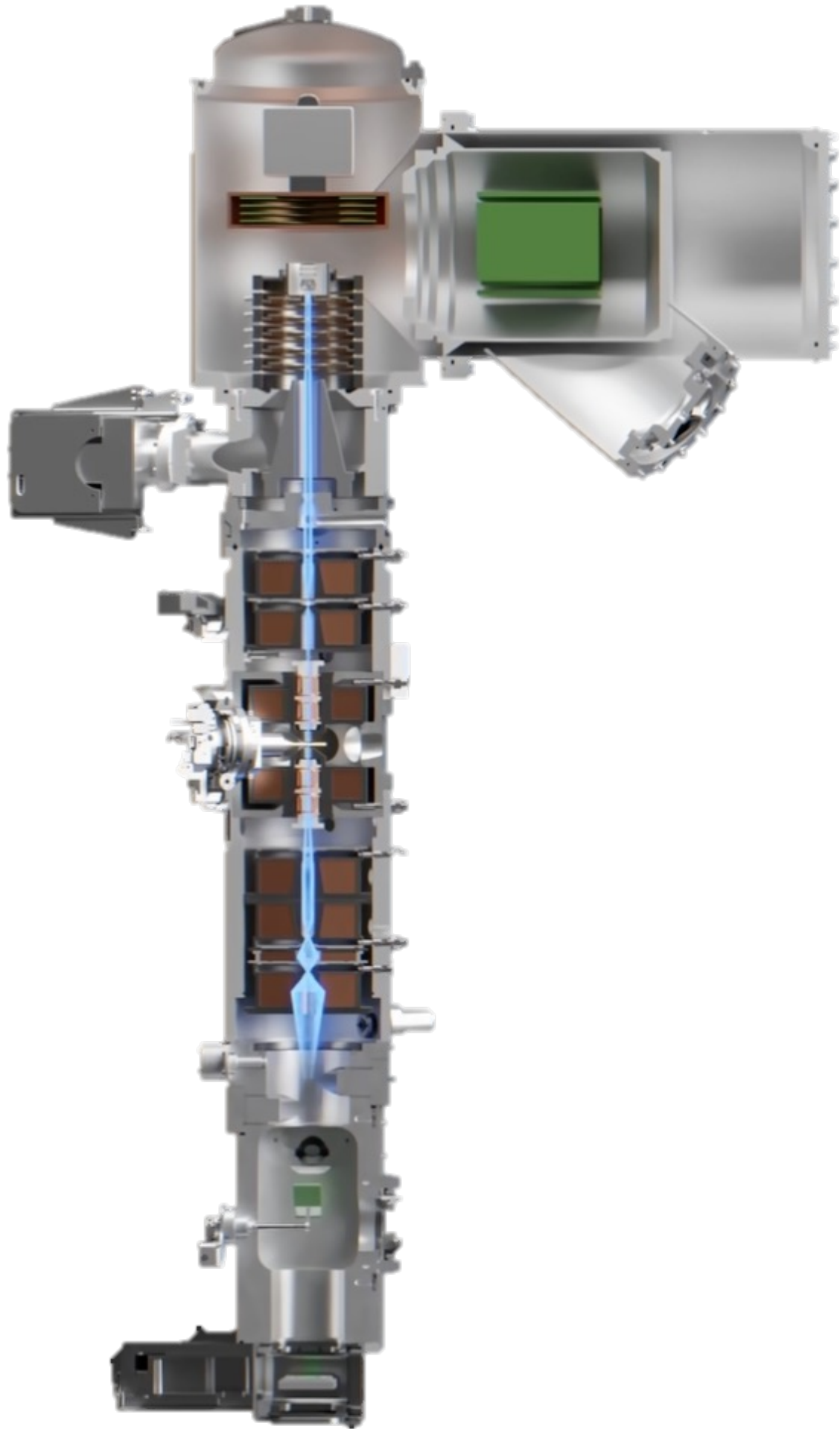
Max resolution: 1 nm

Transmission Electron Microscopy (TEM)

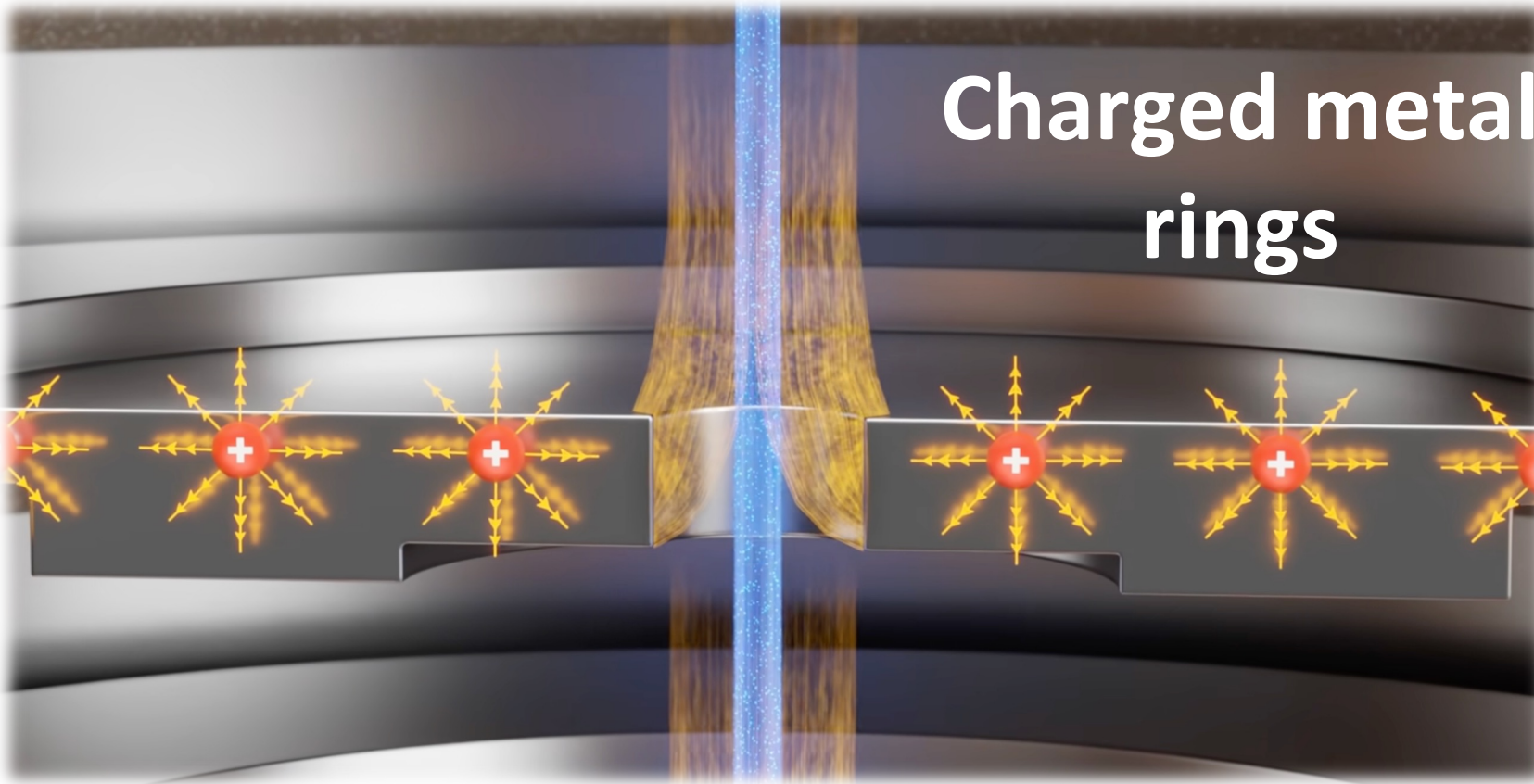
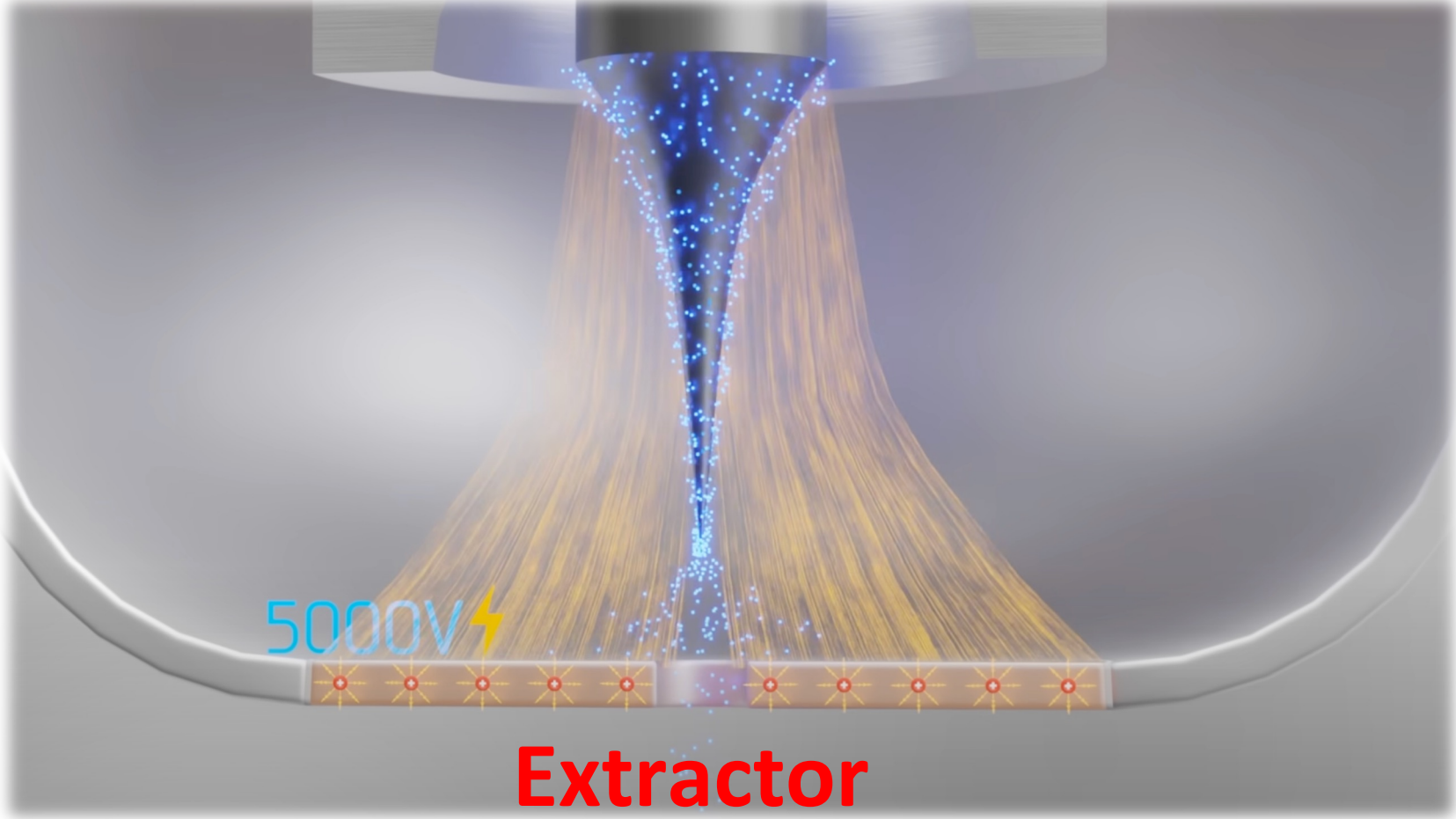


Max resolution: 50 pm

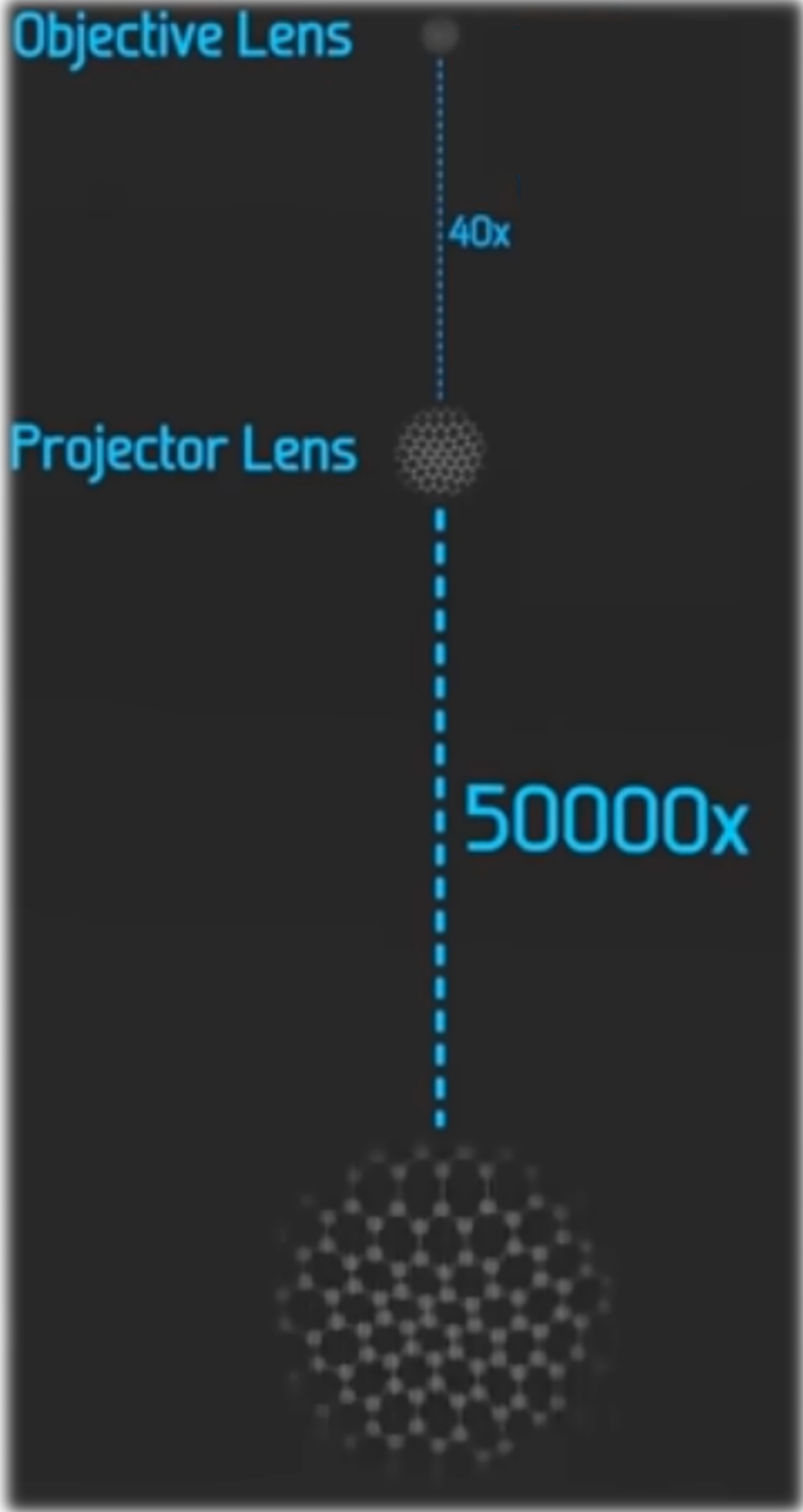
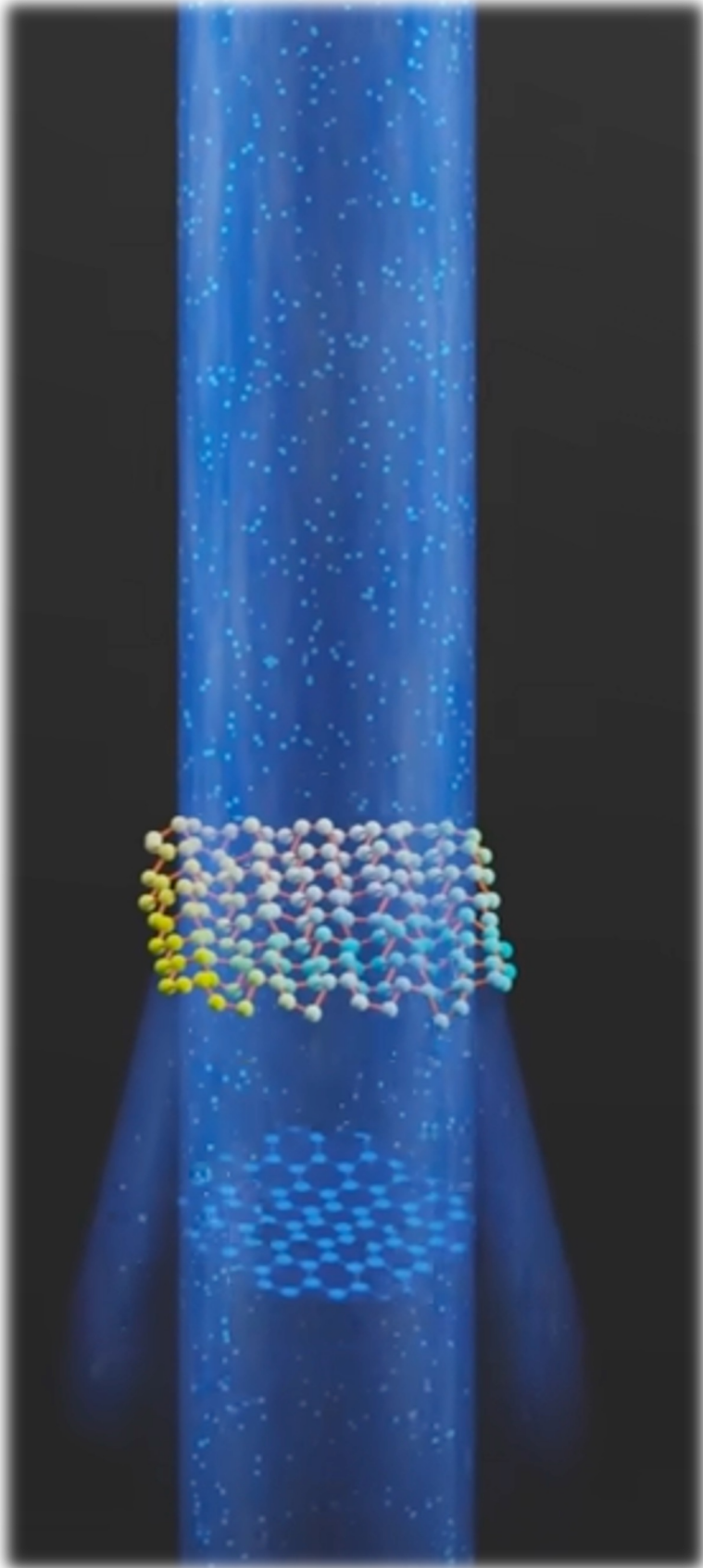
Transmission Electron Microscopy Recap



Tungsten crystal needle

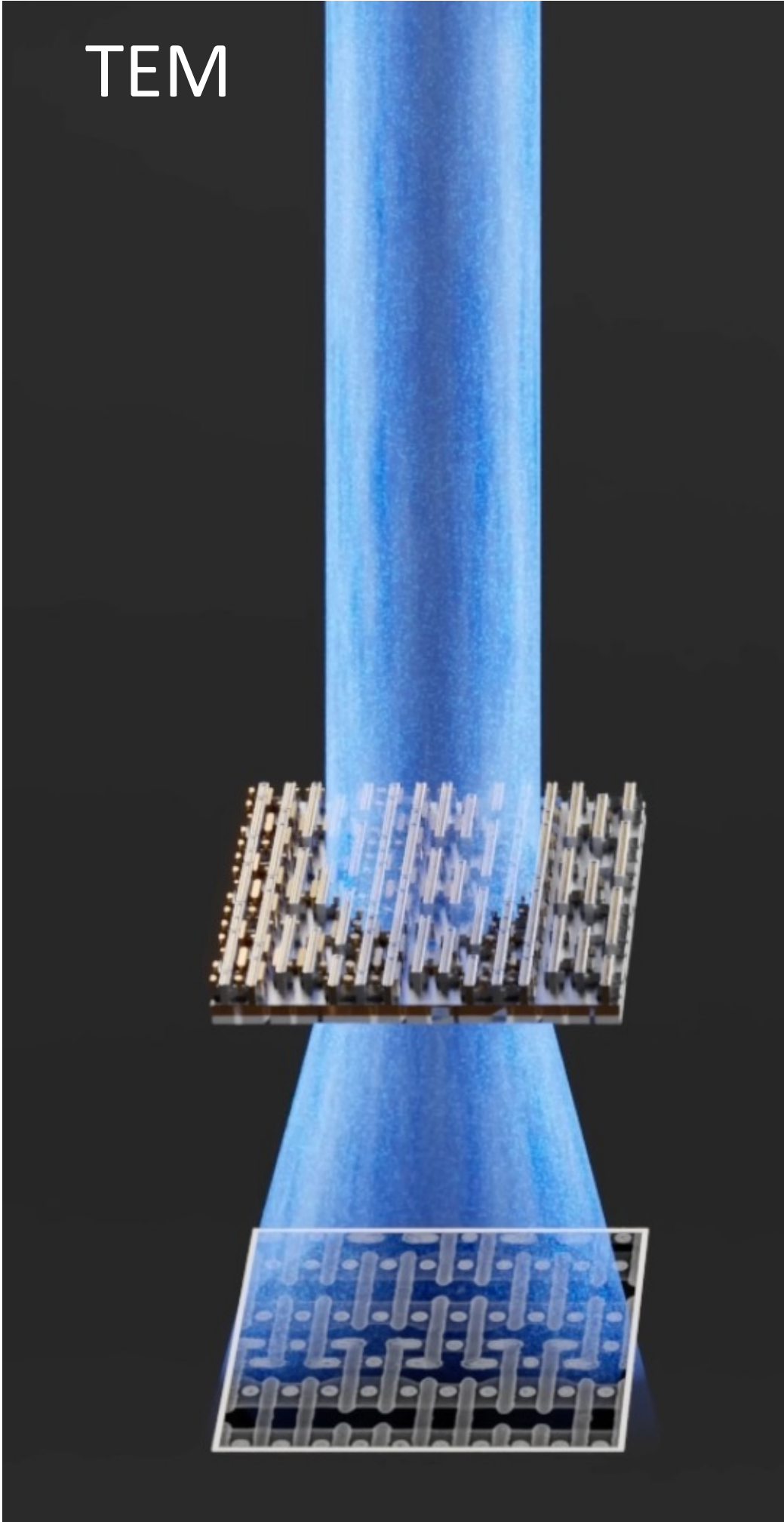
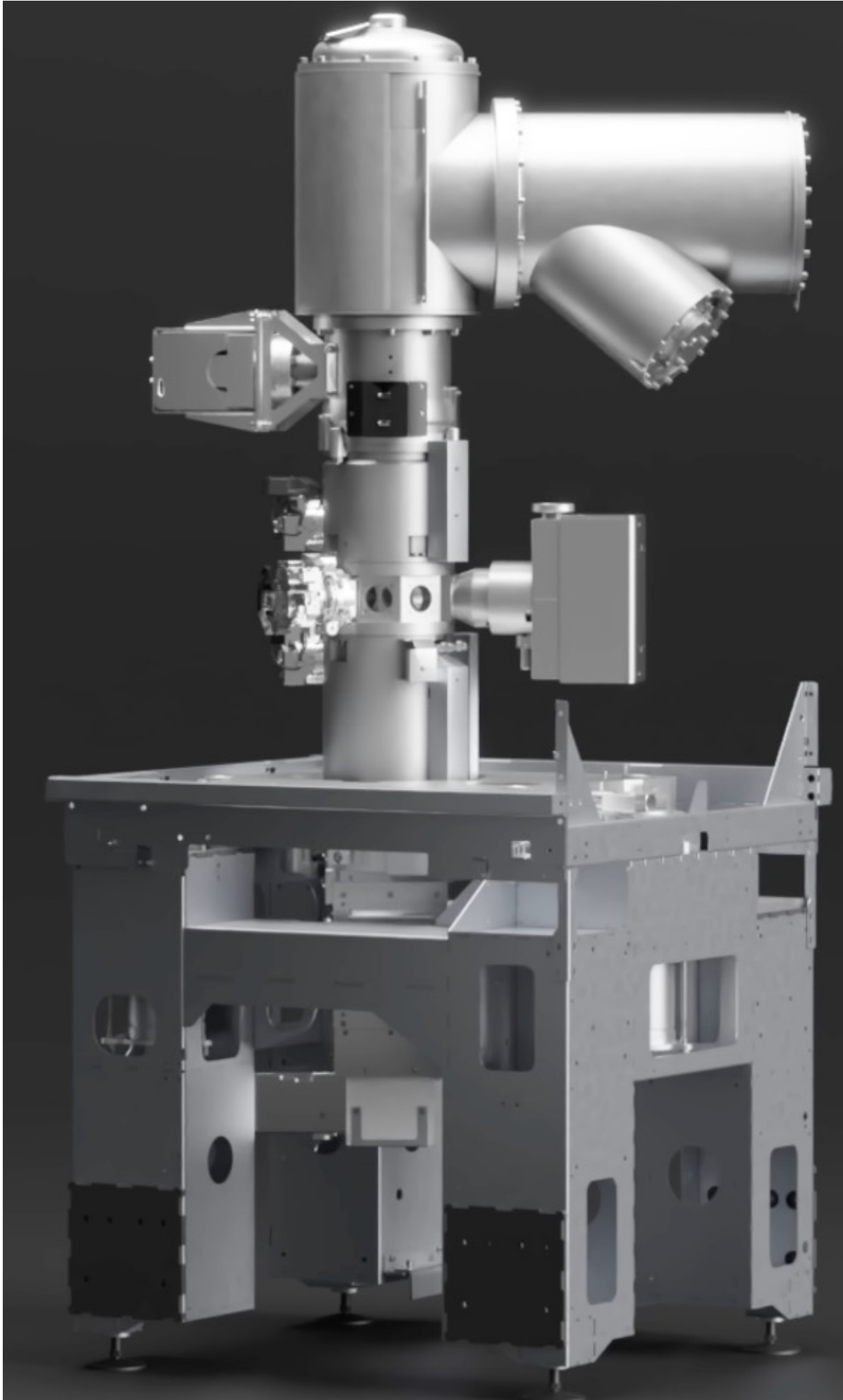


Accelerate electrons

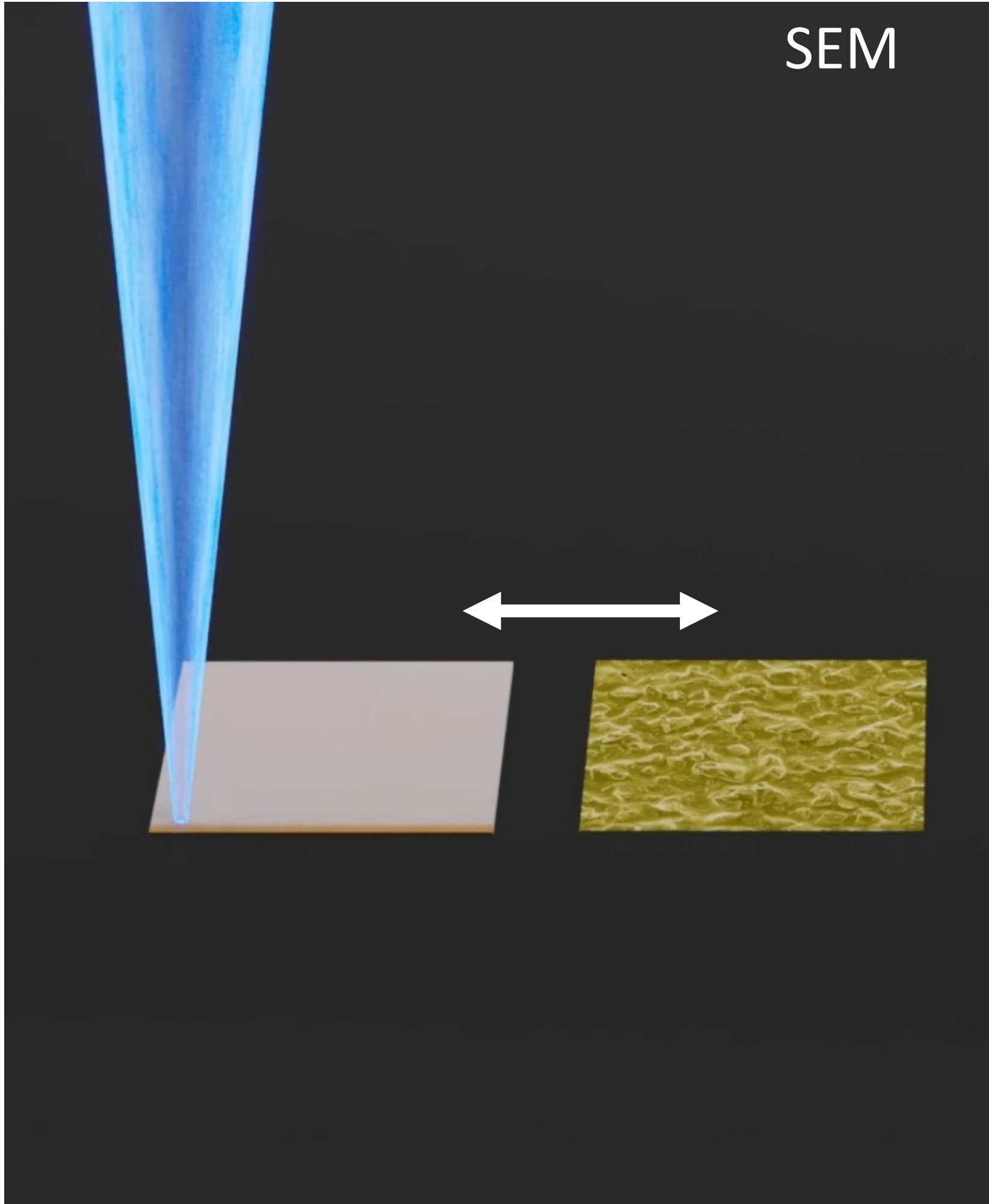


Imprint image of specimen on transmitted beam and amplify

Scanning Electron Microscopy



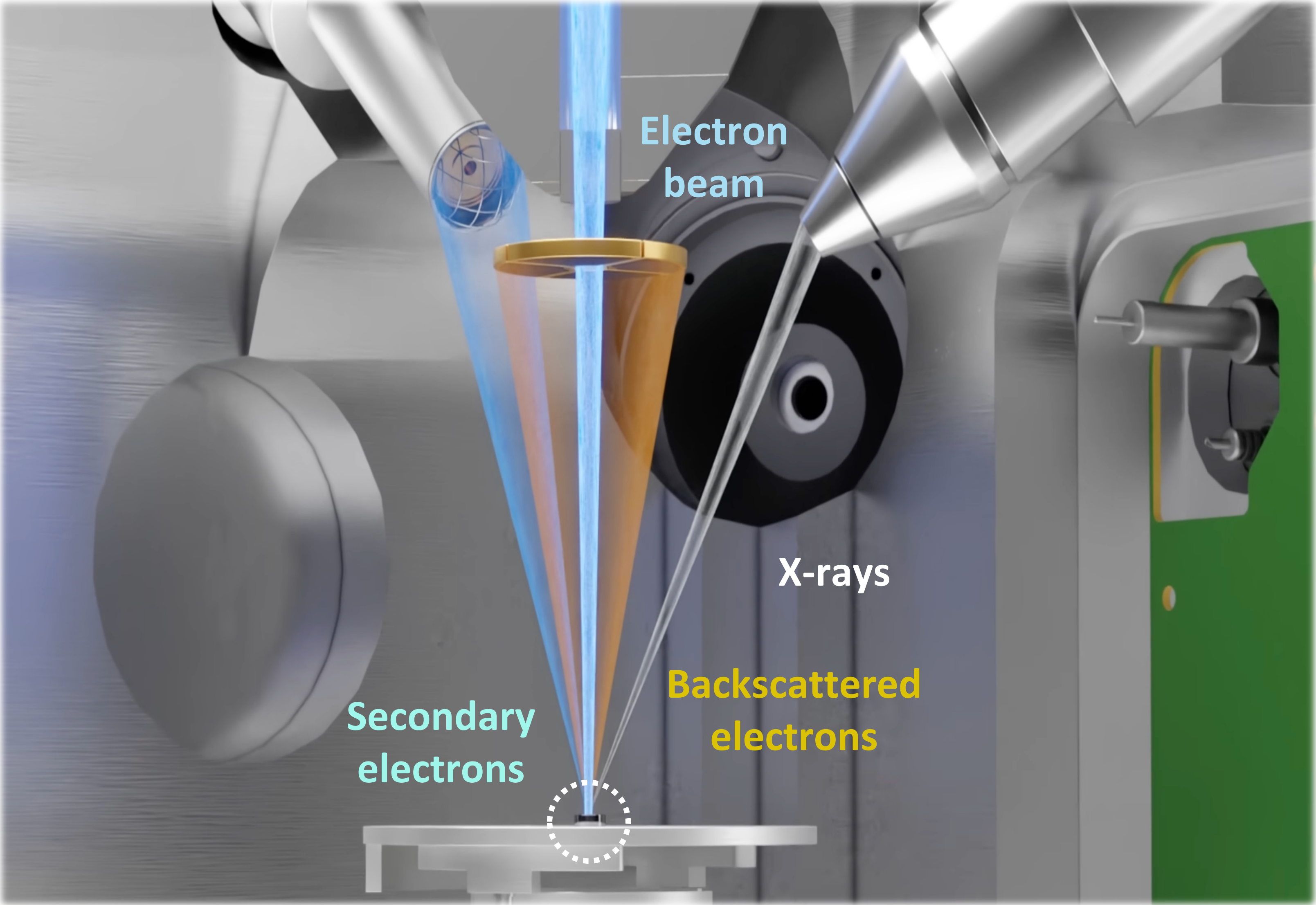
Illuminate specimen and imprint image



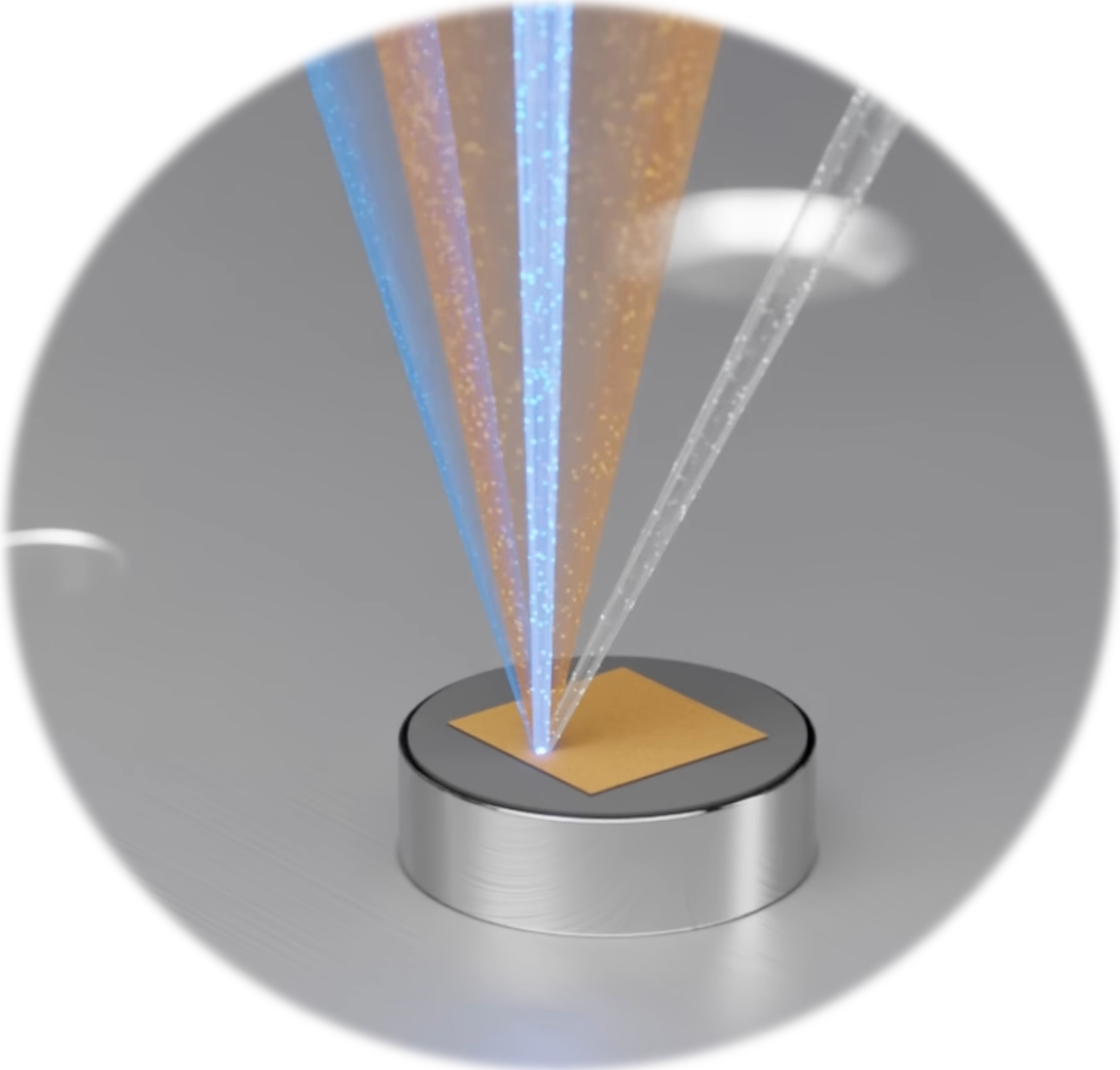
Create a focus spot and scan across the specimen



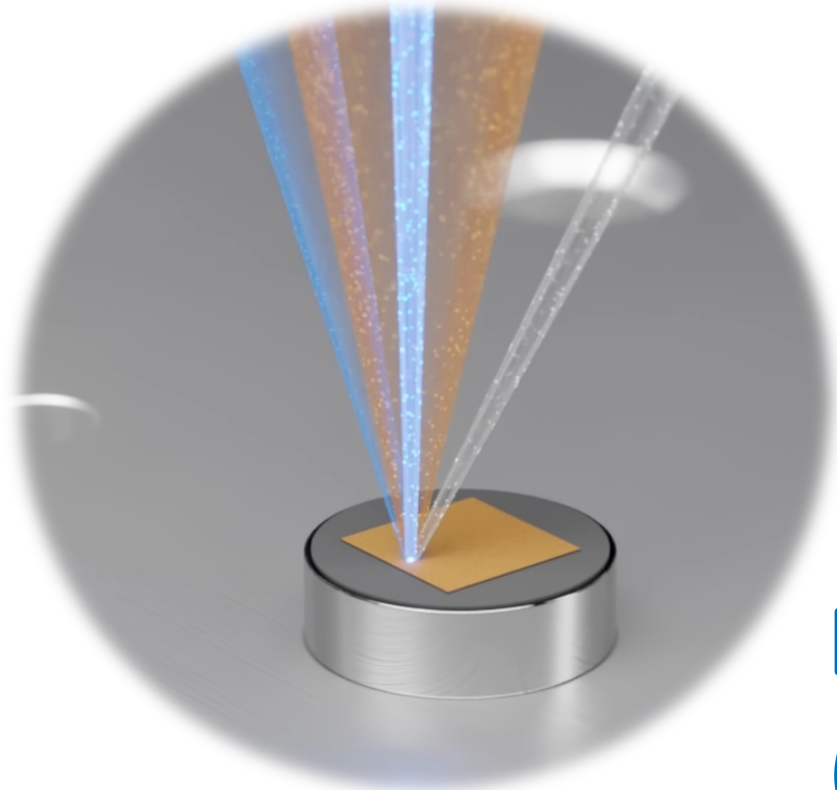
Scanning Electron Microscopy



Electrons accelerated at specified accelerating voltage (1-30 keV)



Scanning Electron Microscopy Spatial Resolution

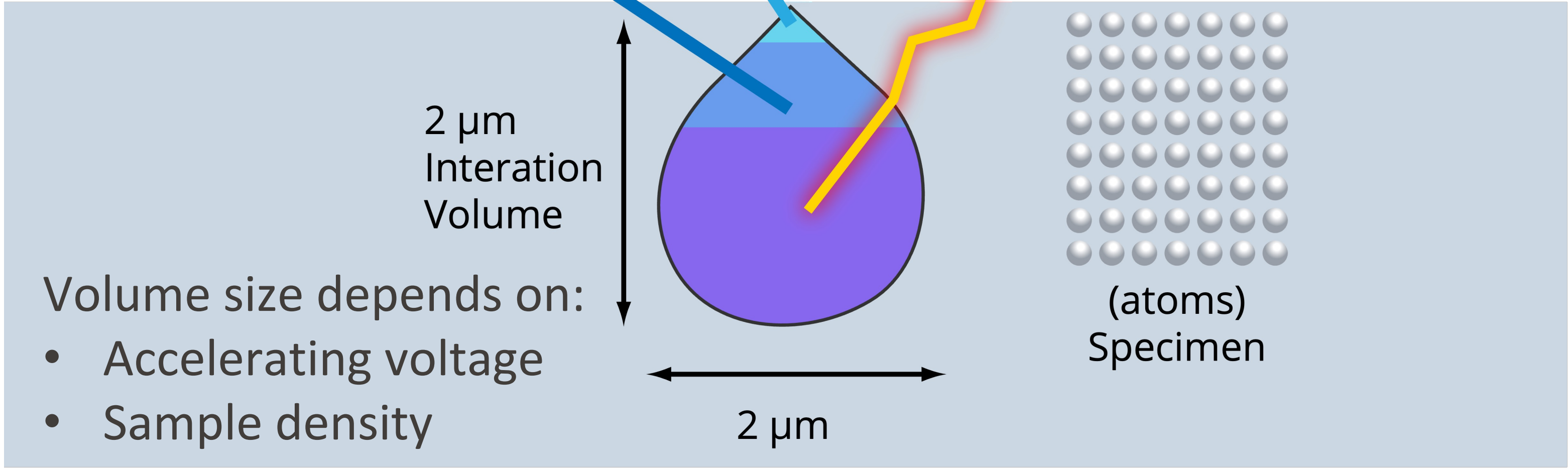


Secondary electrons
(shape information, 5 nm)

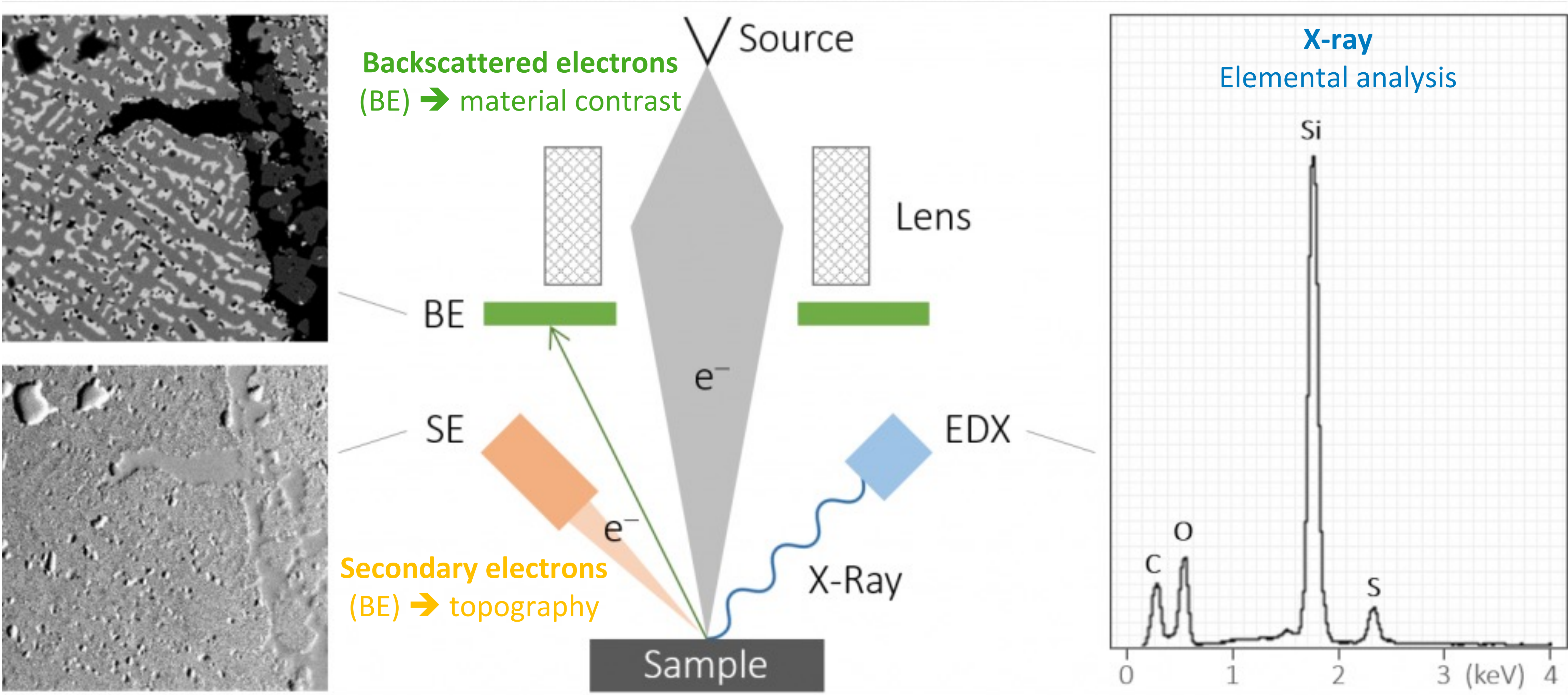
Backscattered electrons
(atomic number information, 400 nm)

Primary electron beam
(2-200 nm diameter)

X-rays
(microns)



Scanning Electron Microscopy Spatial Resolution



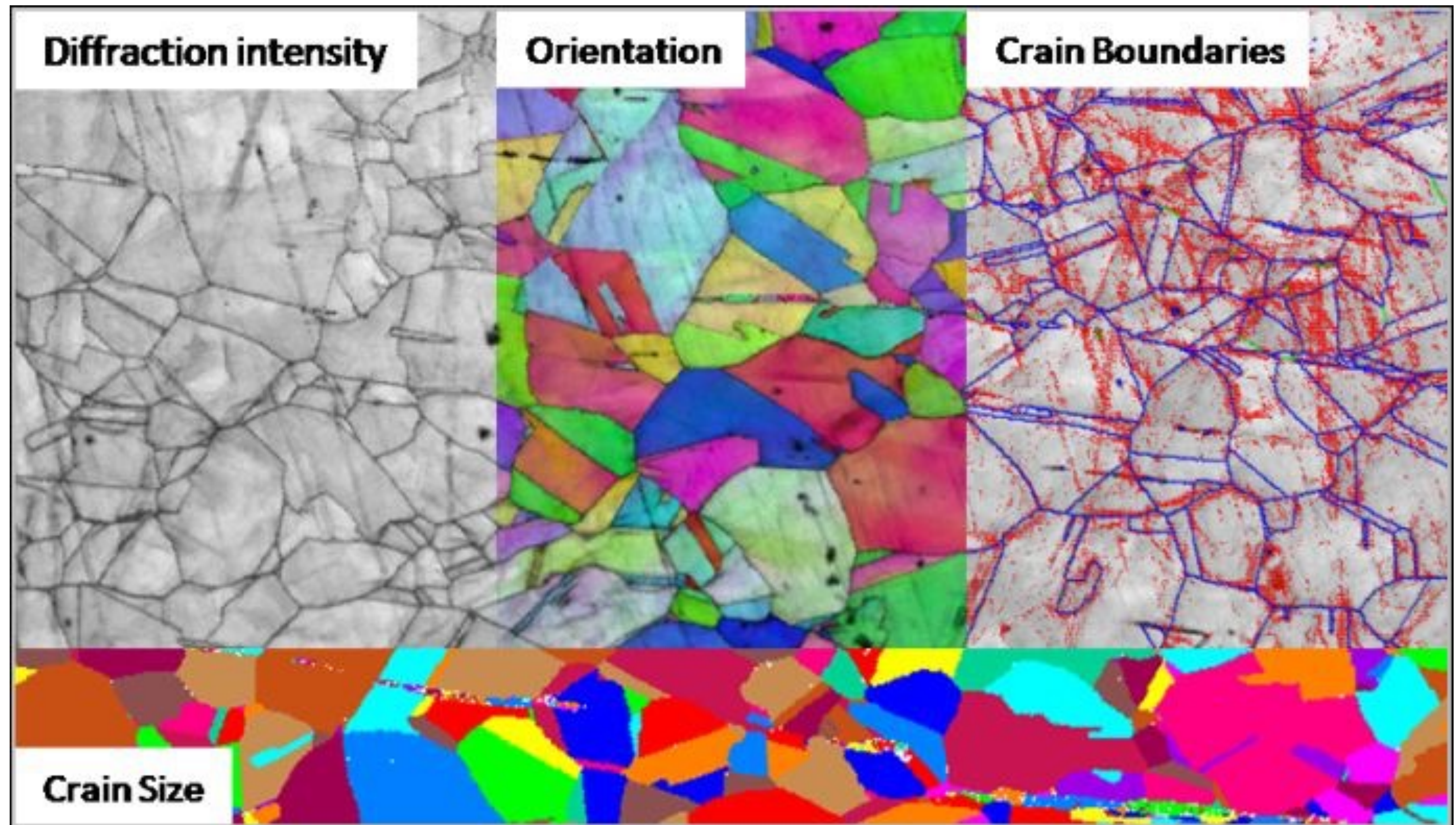
Scanning Electron Microscopy Spatial Resolution

Technique / Signal	Source of Signal	Information	Depth	Main Use
Secondary Electrons	Inelastic scattering of low-energy electrons	Surface topography, morphology	~1–5 nm	Image surface structure
Electron Backscatter Diffraction (EBDS)	Diffraction of backscattered electrons	Crystal orientation, phase, grain boundaries	~10–50 nm	How atoms are oriented
Energy-Dispersive X-Ray Spectroscopy (EDS/EDX)	X-rays emitted from atoms	Elemental composition (bulk)	~1–2 μm	What elements are present

Electron Backscatter Diffraction (EBSD)

Provides information on:

- Phase characterization (in combination with EDS)
- Boundary characterization
- Crystal orientations
- Texture
- Grain size



The EBSD Pattern is Due to Bragg Diffraction

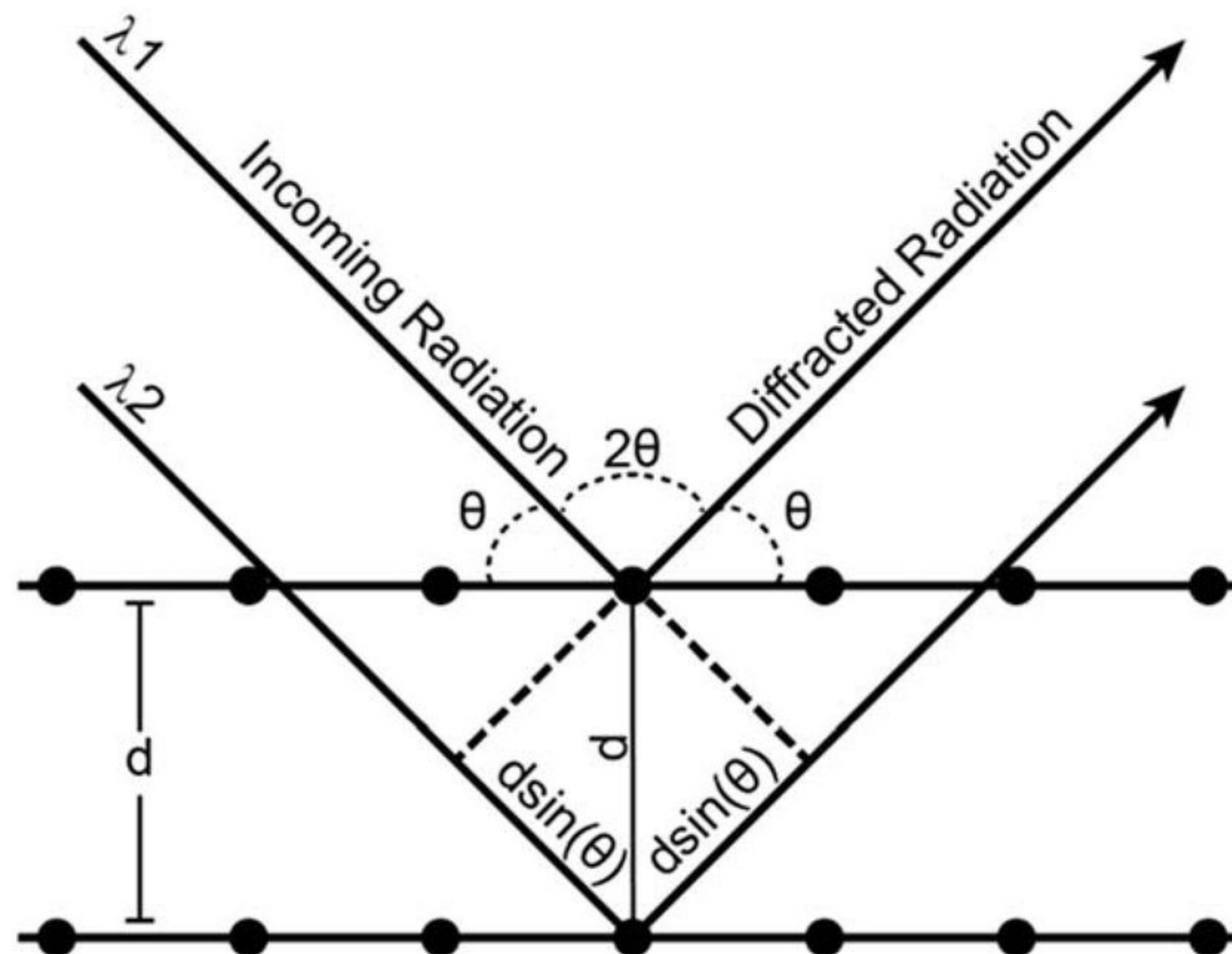
$$n\lambda = 2d \sin \theta$$

Bragg's Law

λ : the wavelength of the electron

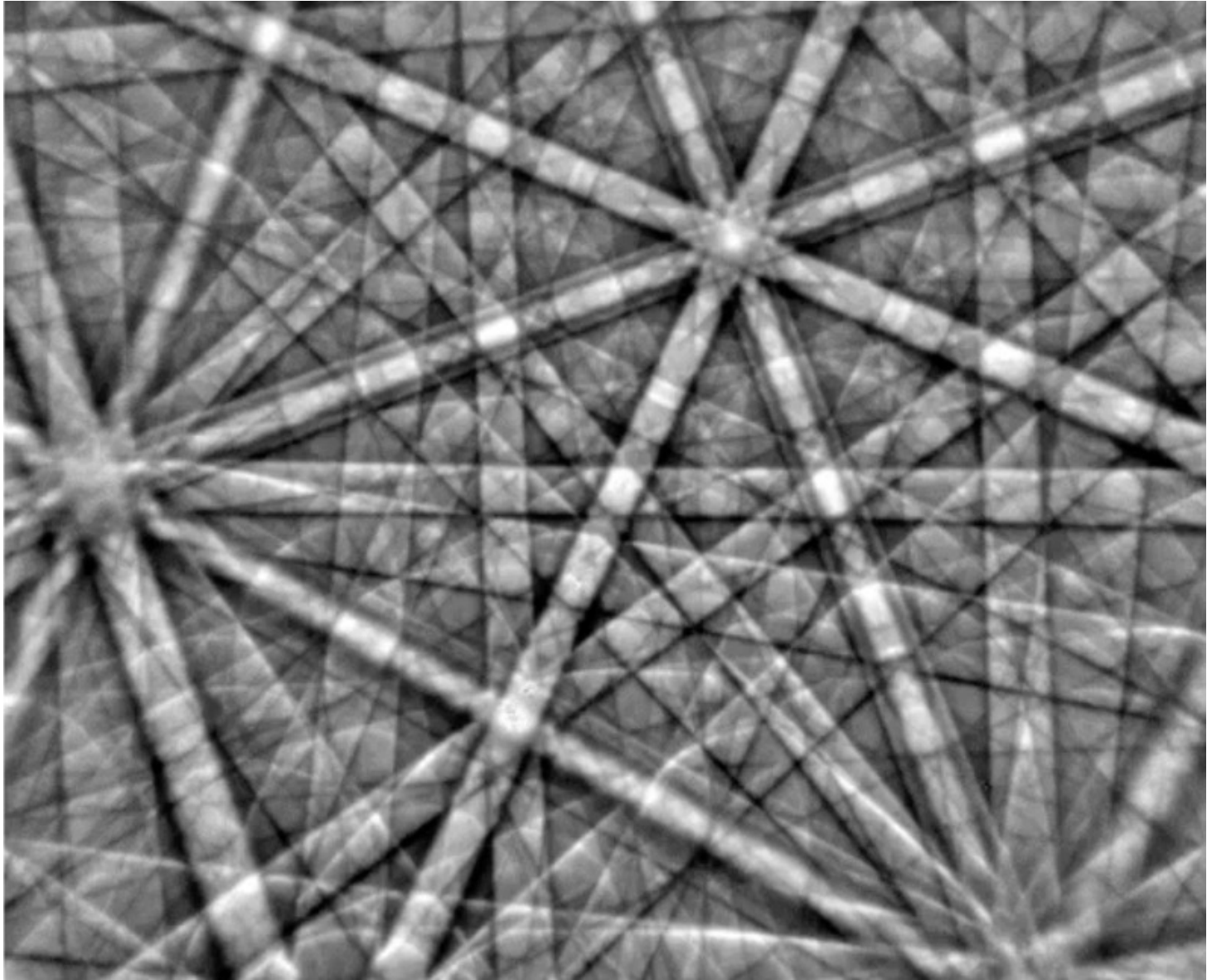
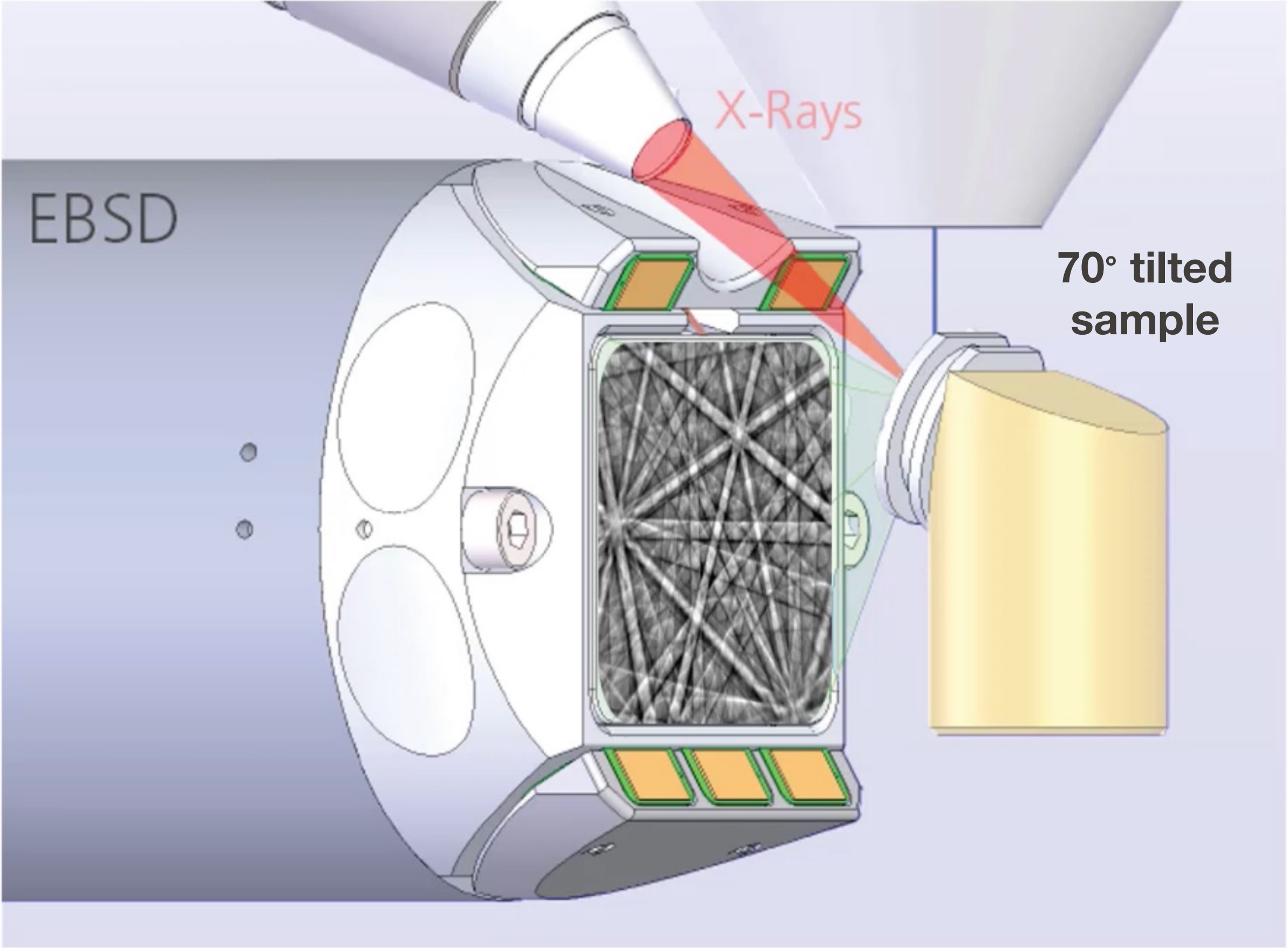
d : lattice spacing

θ : angle between incident ray and the scatter plane

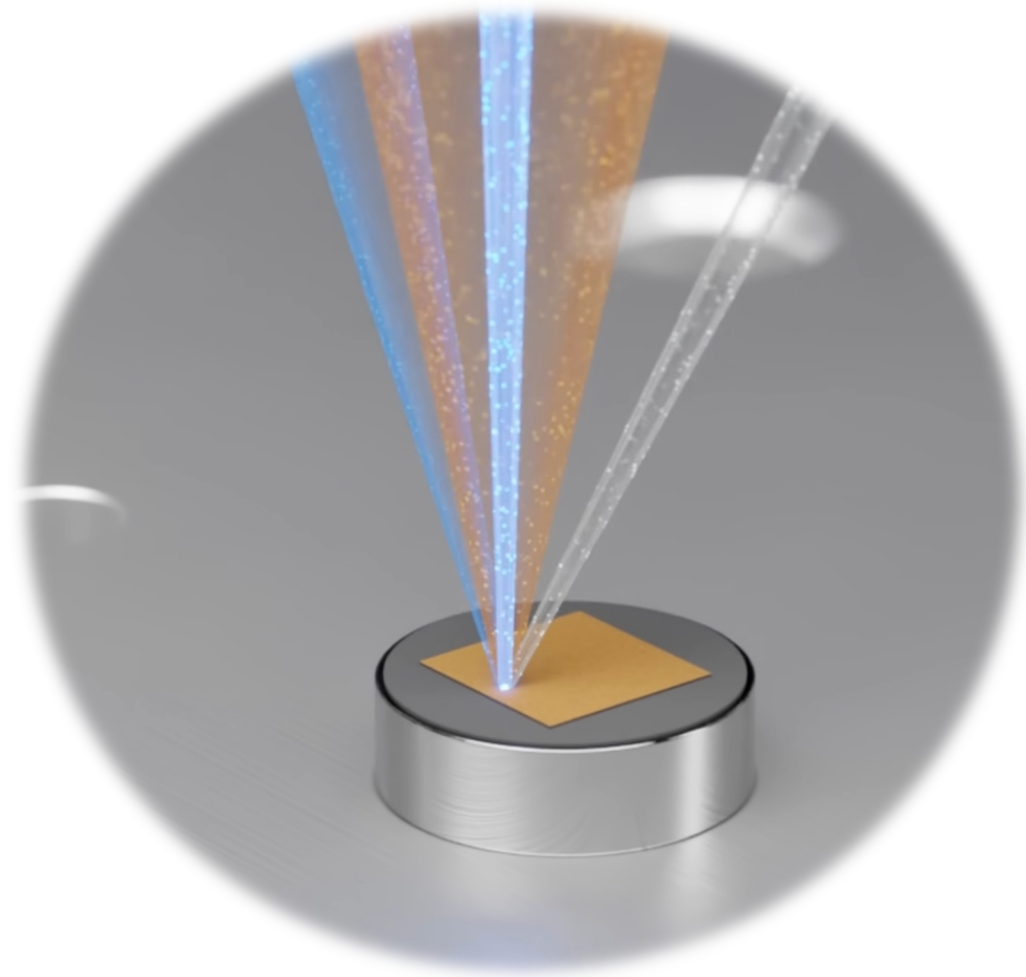


Electron Backscatter Diffraction (EBSD)

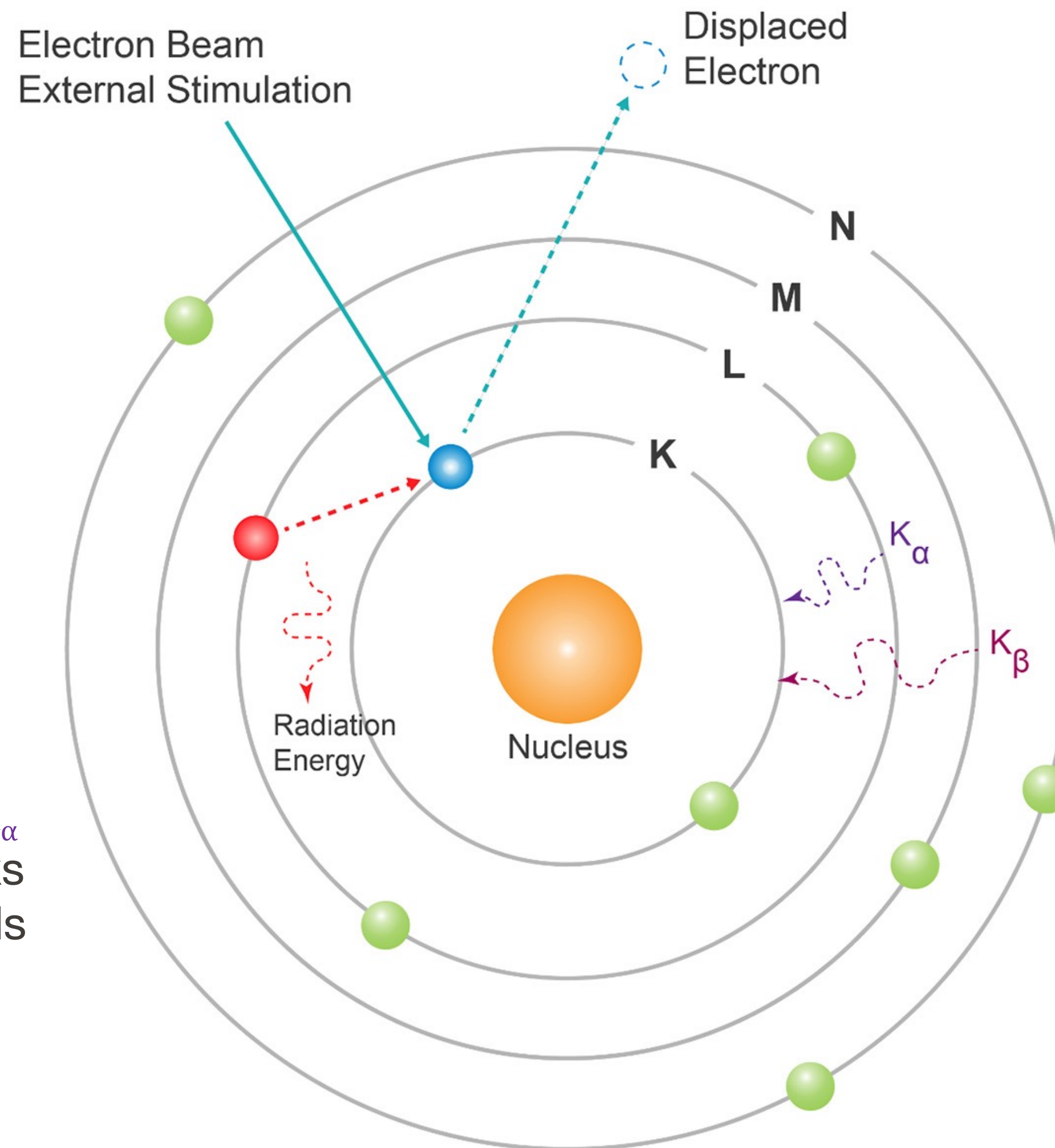
An SEM-based diffraction technique to measure crystalline materials



Energy Dispersive X-Ray Spectroscopy (EDS/EDX)



Characterizing the elemental composition on the microscale

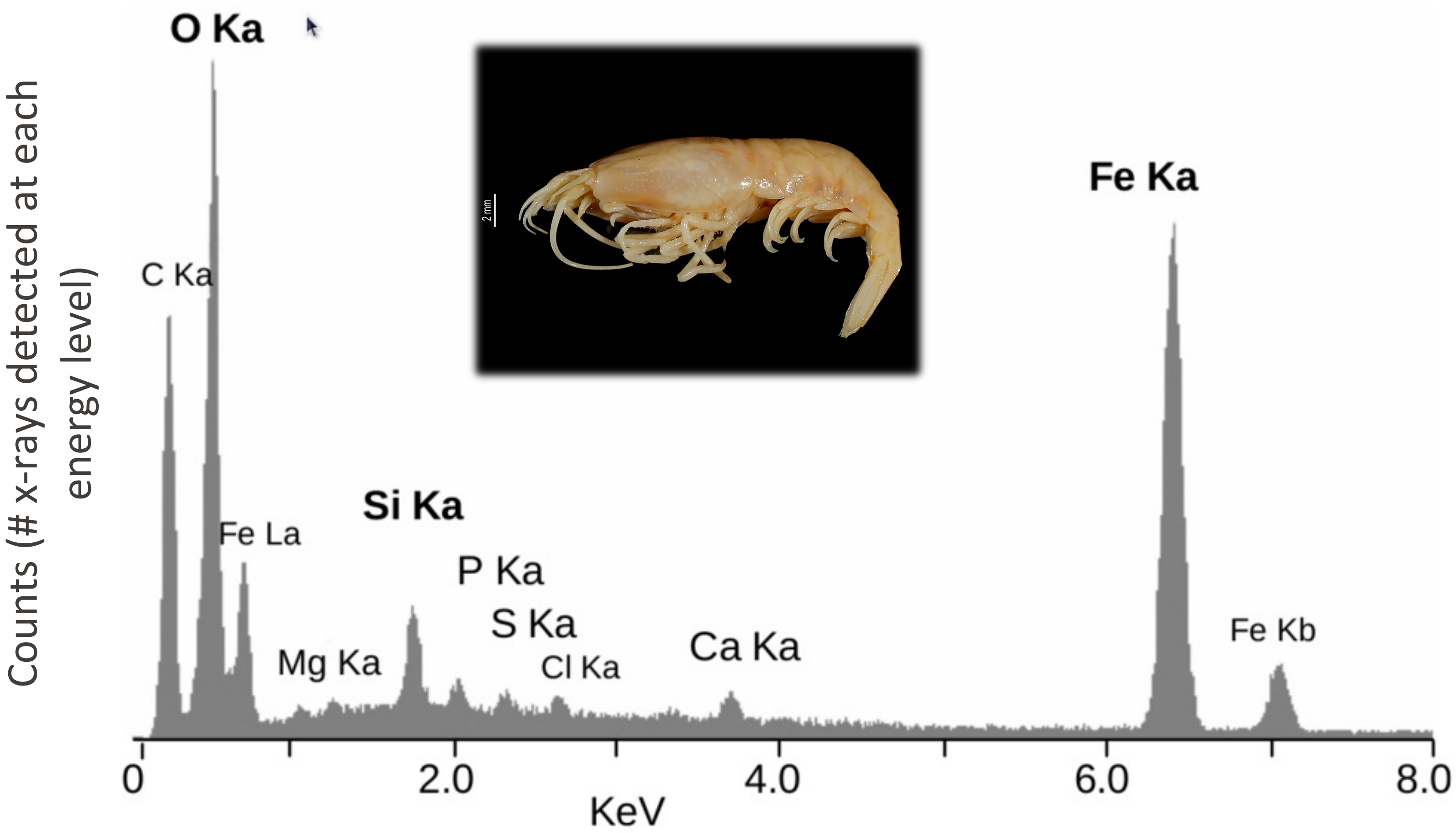
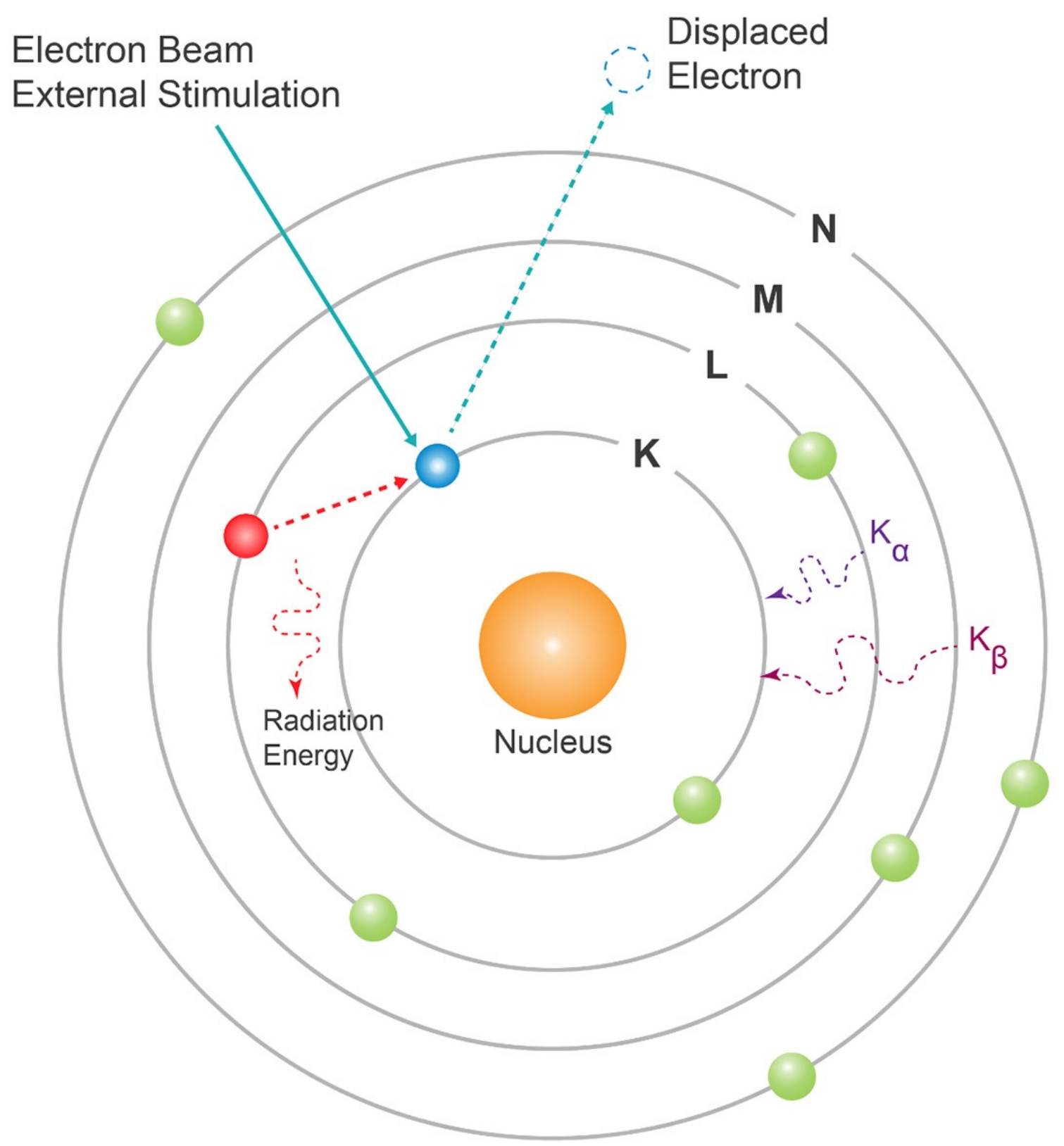


Each element has unique K_{α} and K_{β} energies (X-ray peaks produced when electron falls into lower energy shell)

1. Beam interacts with the atom, displaces electron out of its shell
2. Void filled by another electron from higher energy level
3. Energy released correlates to individual elements while proportional counts relate to the quantity of element

Energy Dispersive X-Ray Spectroscopy (EDS/EDX)

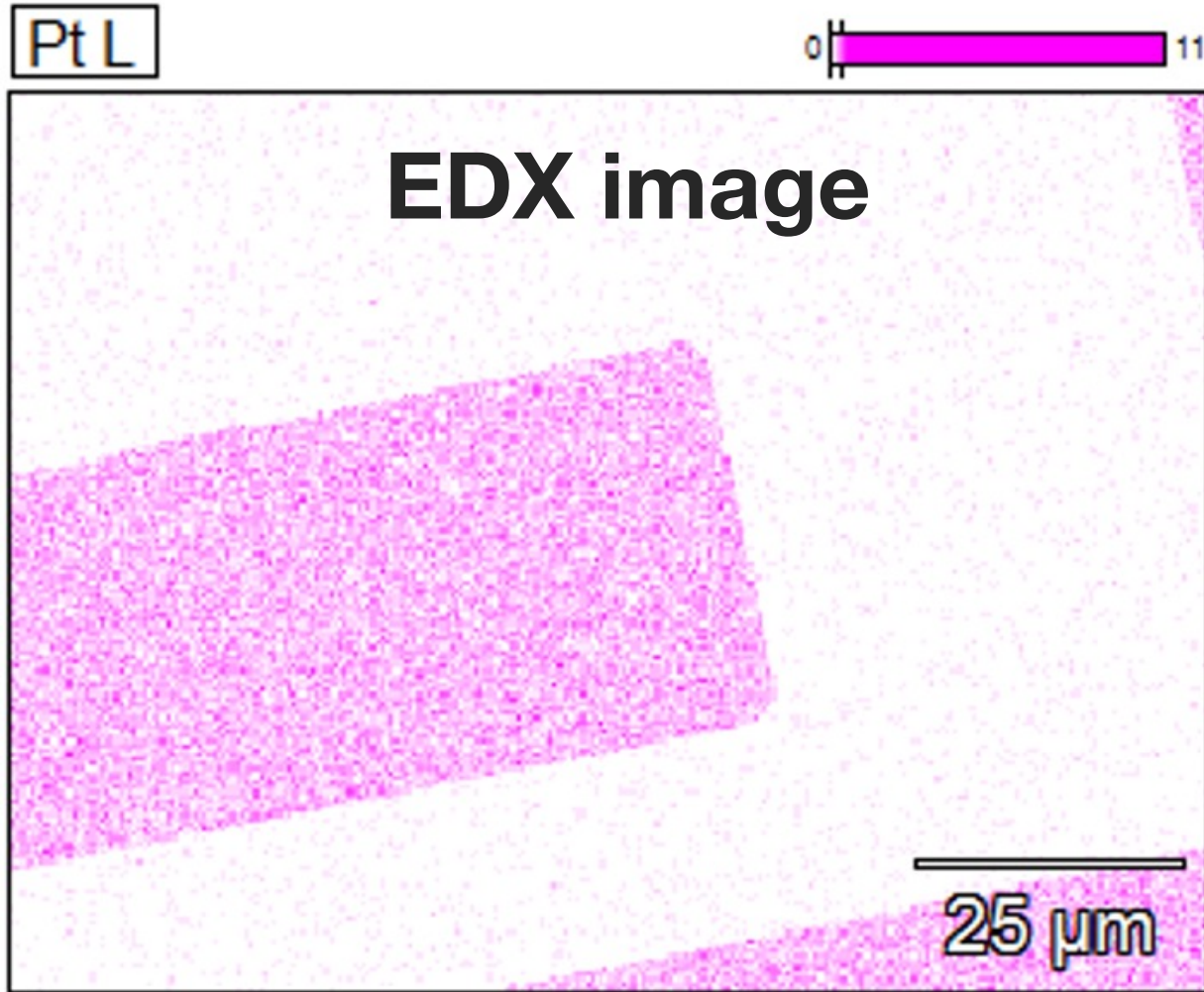
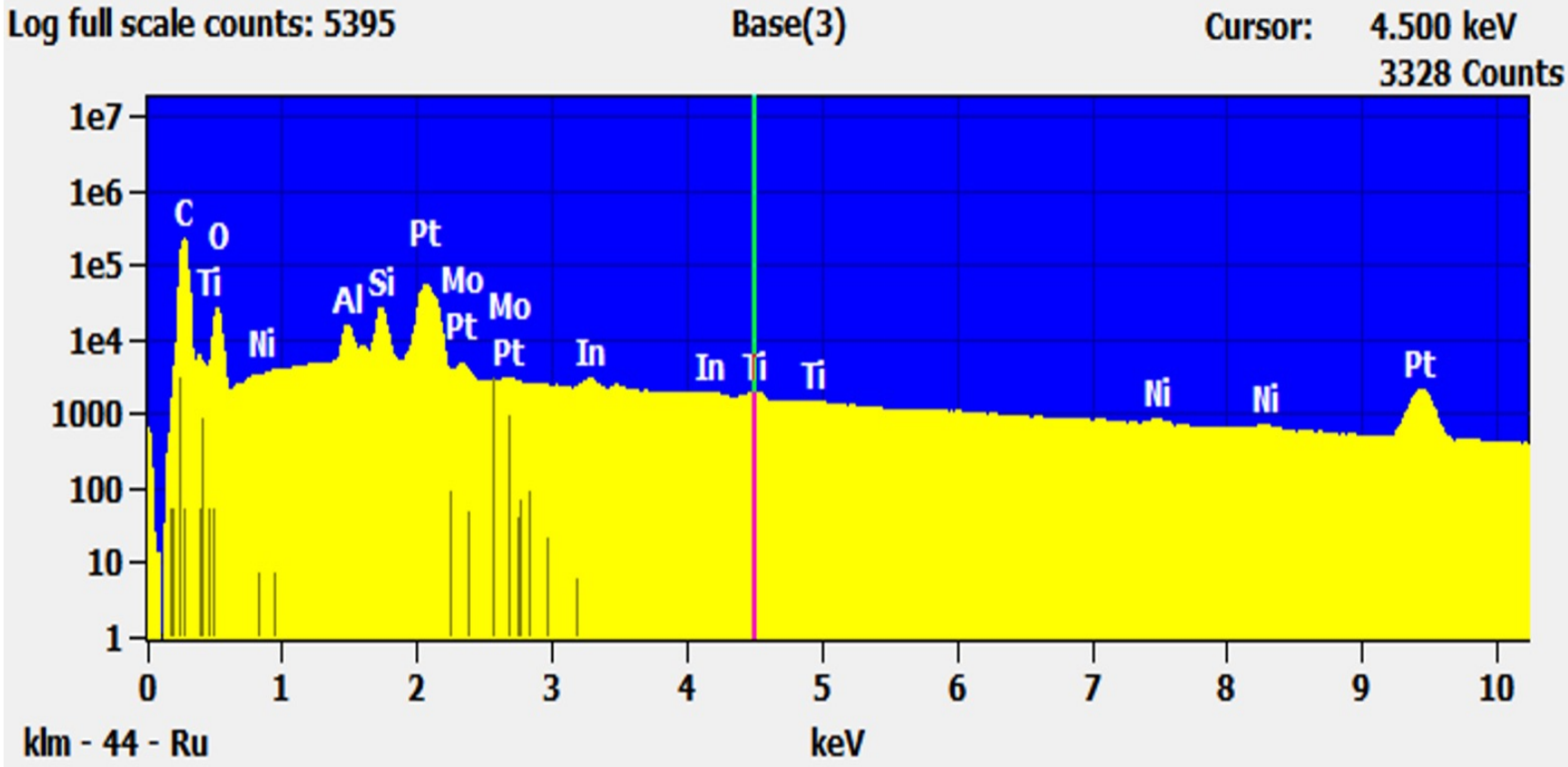
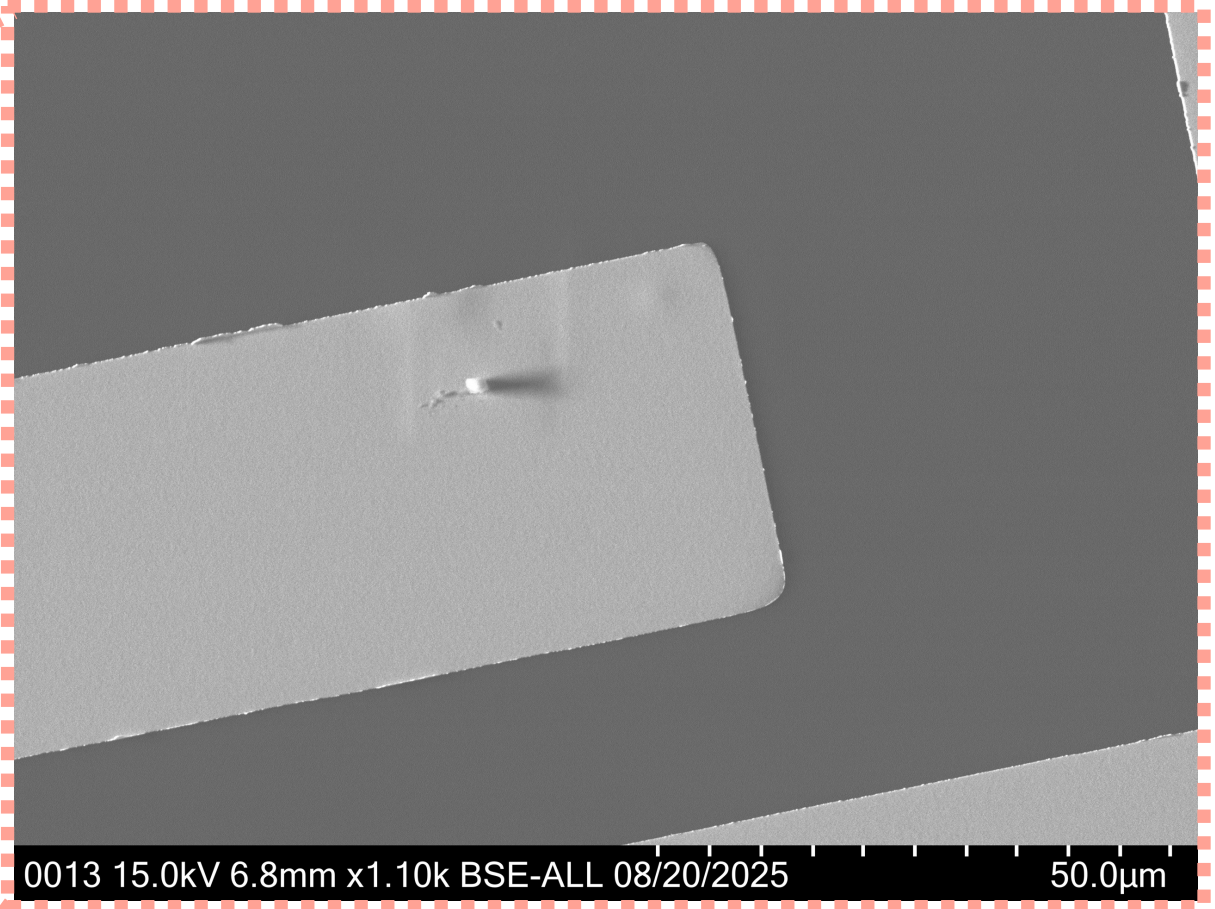
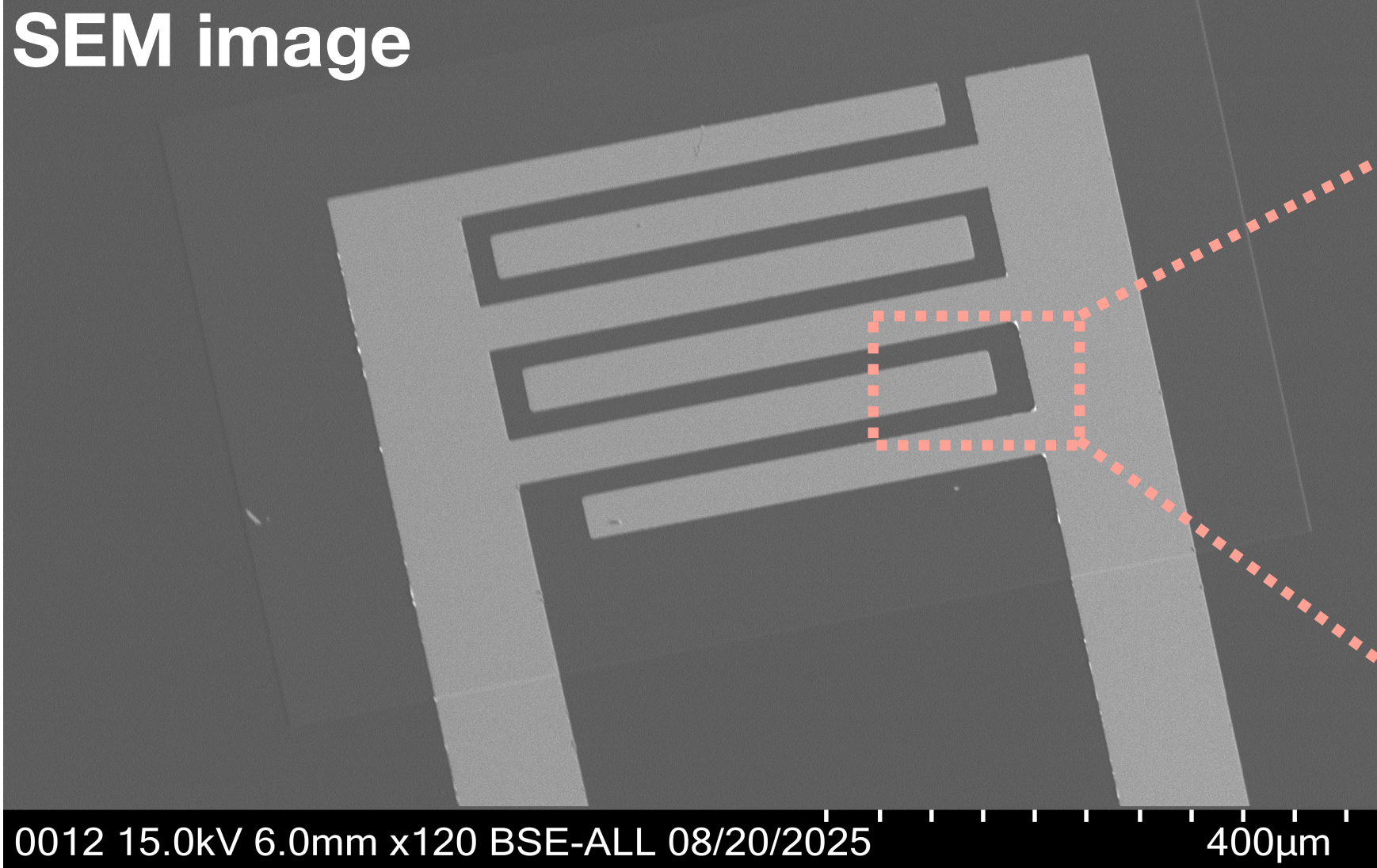
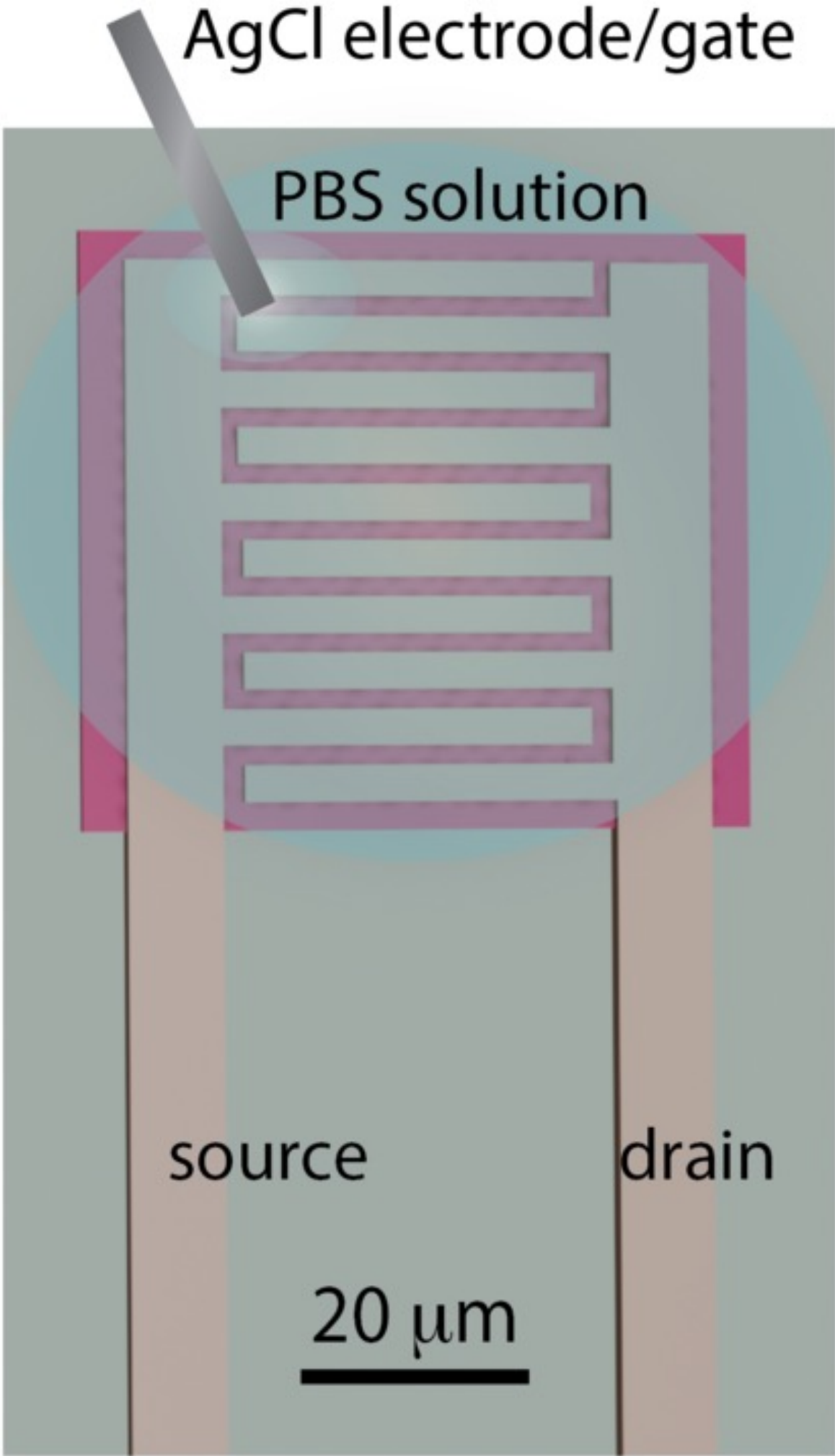
Characterizing the elemental composition on the microscale



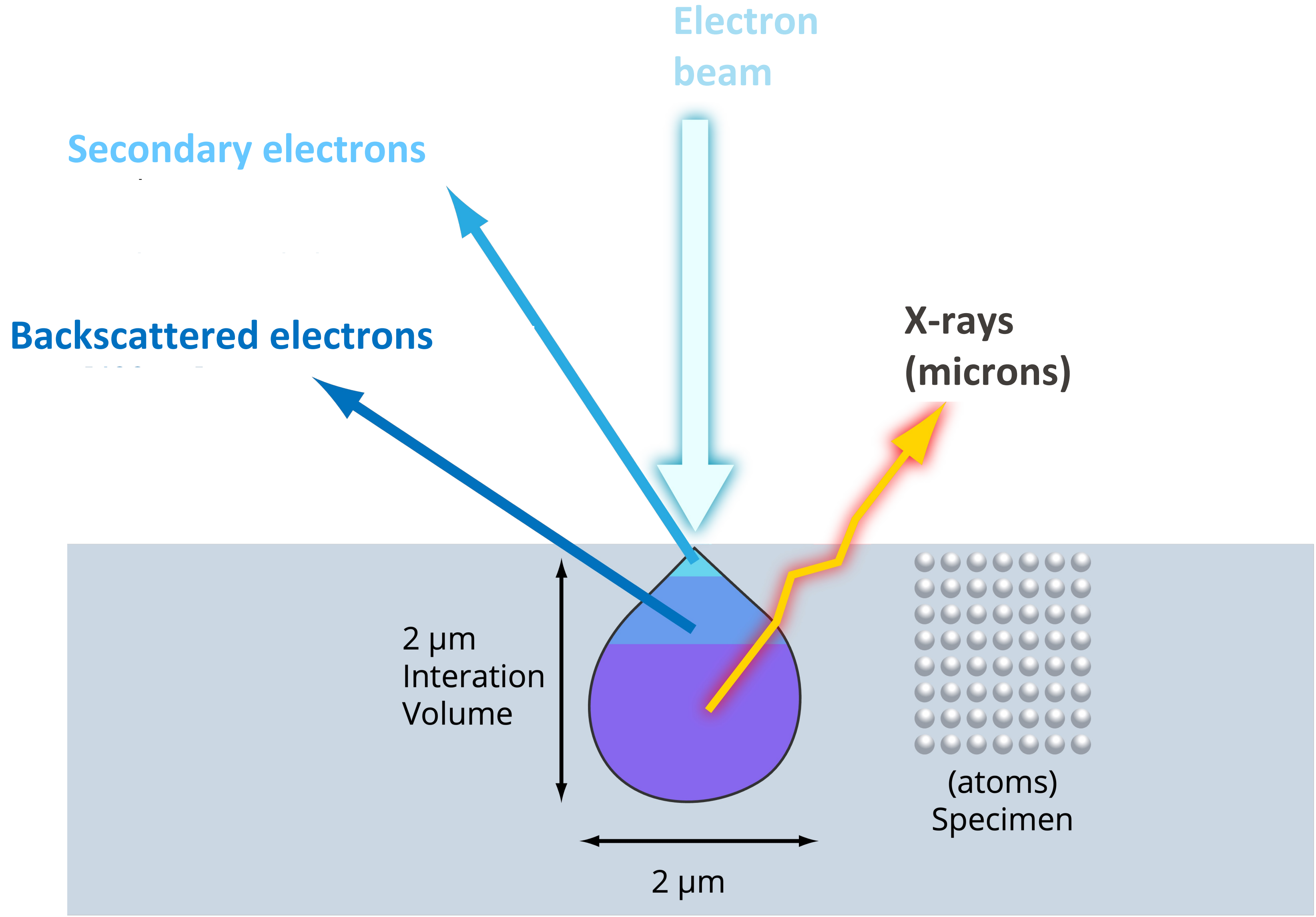
Transistor Imaging using SEM + EDX in Our Research



Sandra Hernandez Escobar



EDS/EDX is a Bulk Measurement, NOT Surface Measurement



Teardrop-shaped interaction volume much larger than the surface

1-2 μm penetration in metals/oxides

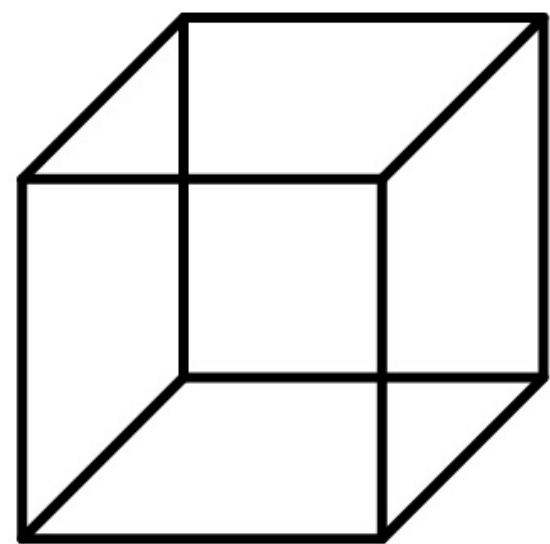
Several μm in light-element materials

Key Takeaways

- SEM results in different species (secondary/backscattered electrons, x-rays) that can subsequently be analyzed
- Scattering of secondary electrons provides image of surface topography characteristic of SEM
 - EBDS monitors the diffraction of backscattered electrons to provide information on grain boundaries/crystal orientation
- EDS/EDX monitors emitted x-rays to characterize elemental composition on the microscale (bulk measurement)

Challenges of Studying Surface Science

In general, difficult to analyze surface atoms without being overwhelmed with bulk signal



1 cm

Number of atoms in
a 1 cm³ cube

Bulk atoms = 10^{23}

Surface atoms = 10^{15}

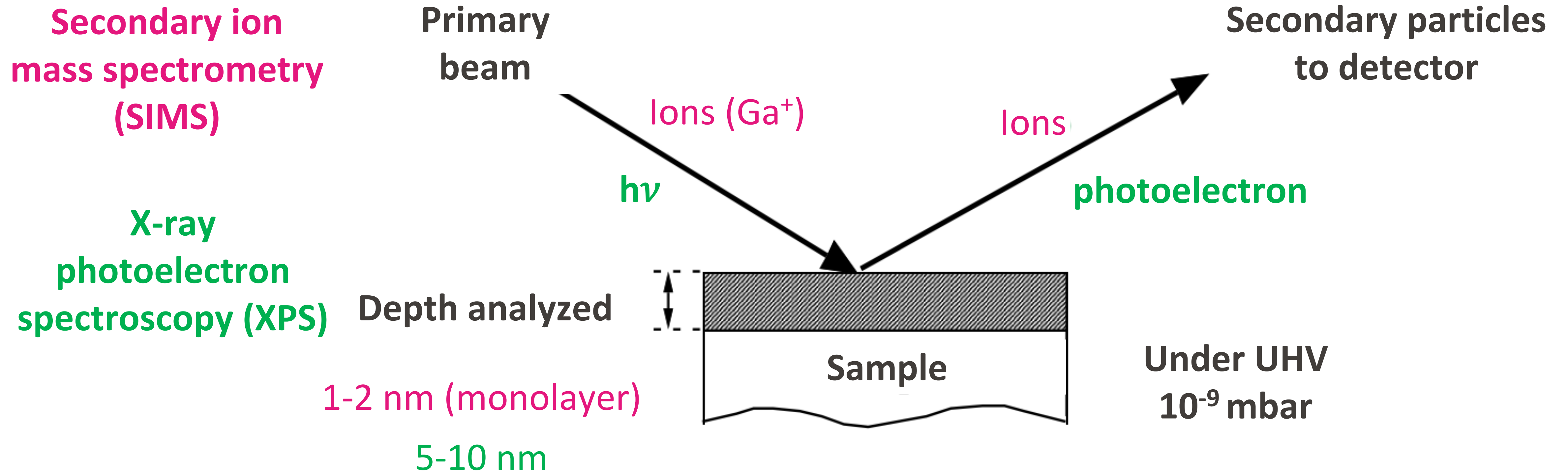


Tricks to overcome this
challenge

Ions: do not penetrate too much into the surface

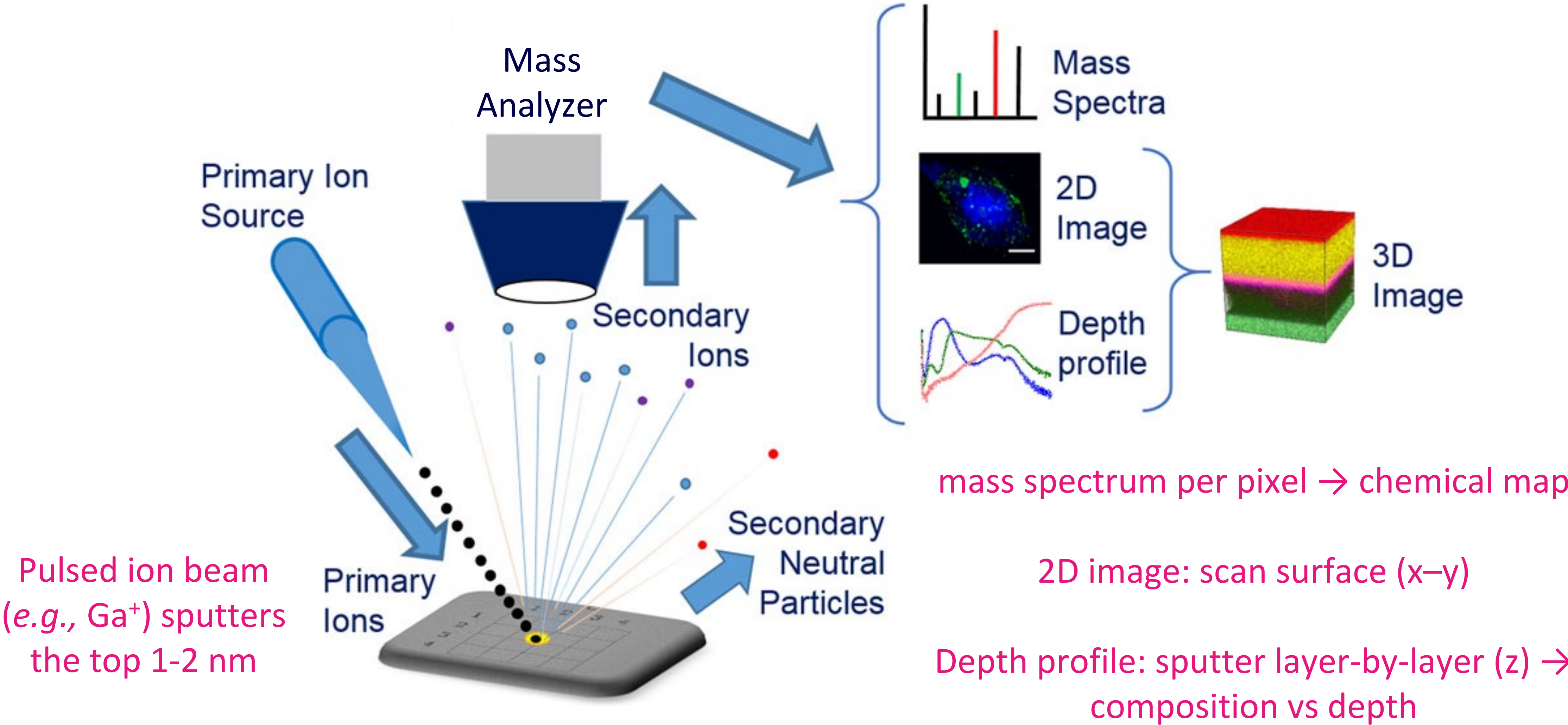
Low-energy electrons (10-20 eV): have a mean free path in the range of monolayers (5-10 nm)

Technologies to Monitor Surface Science: XPS and SIMS



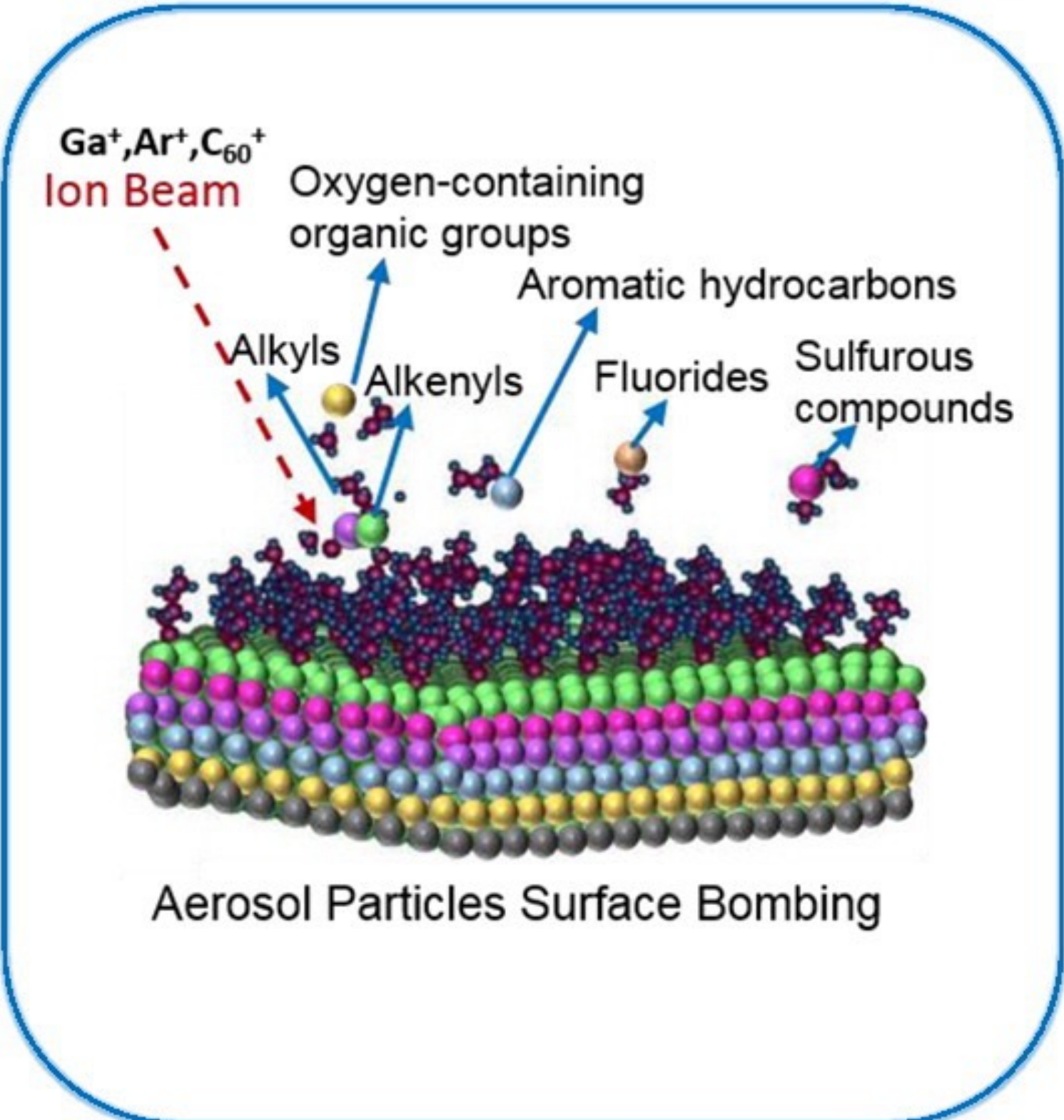
XPS is the more broadly useful technique for surface composition and chemical analysis

Secondary Ion Mass Spectrometry (SIMS)

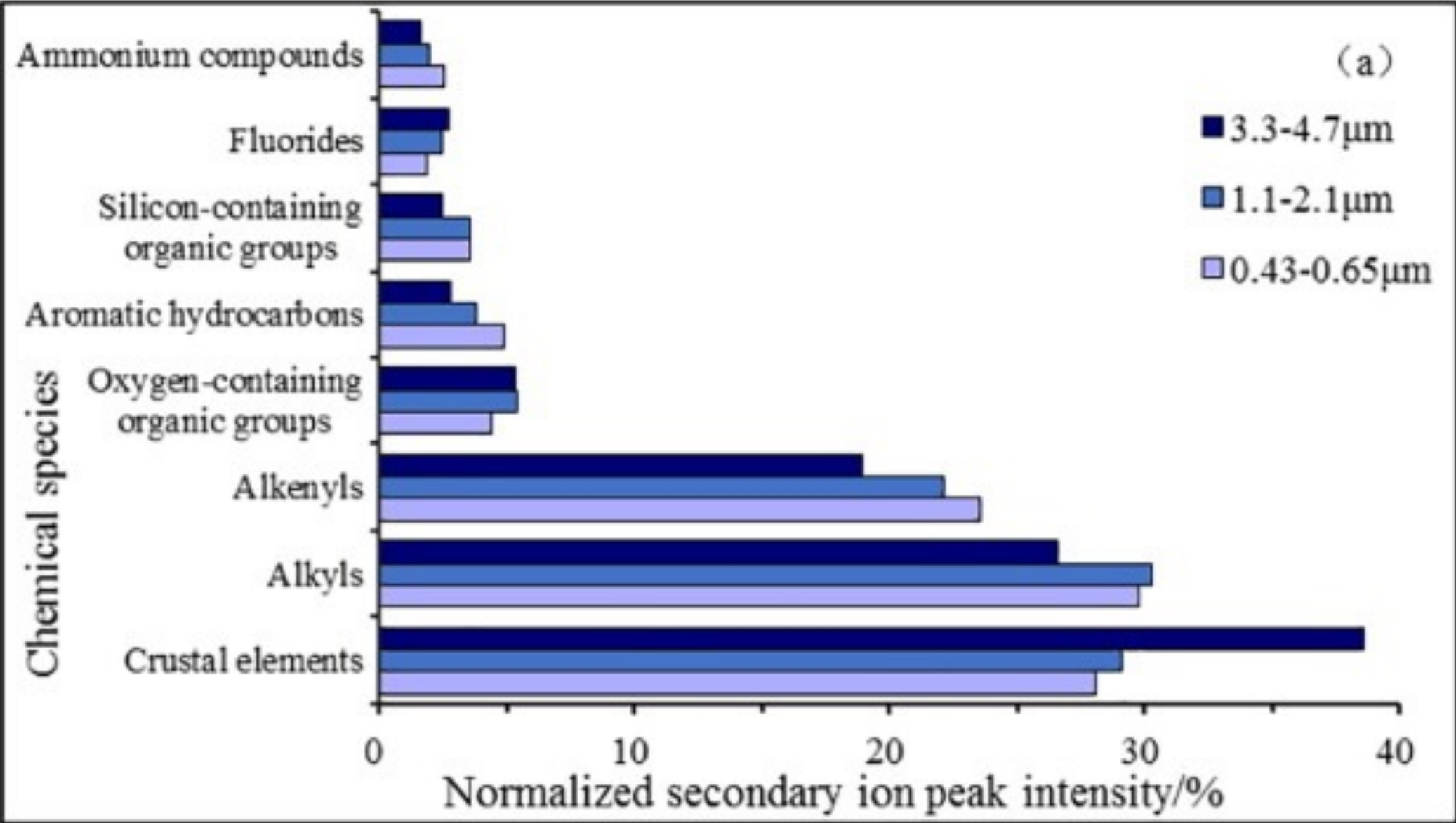
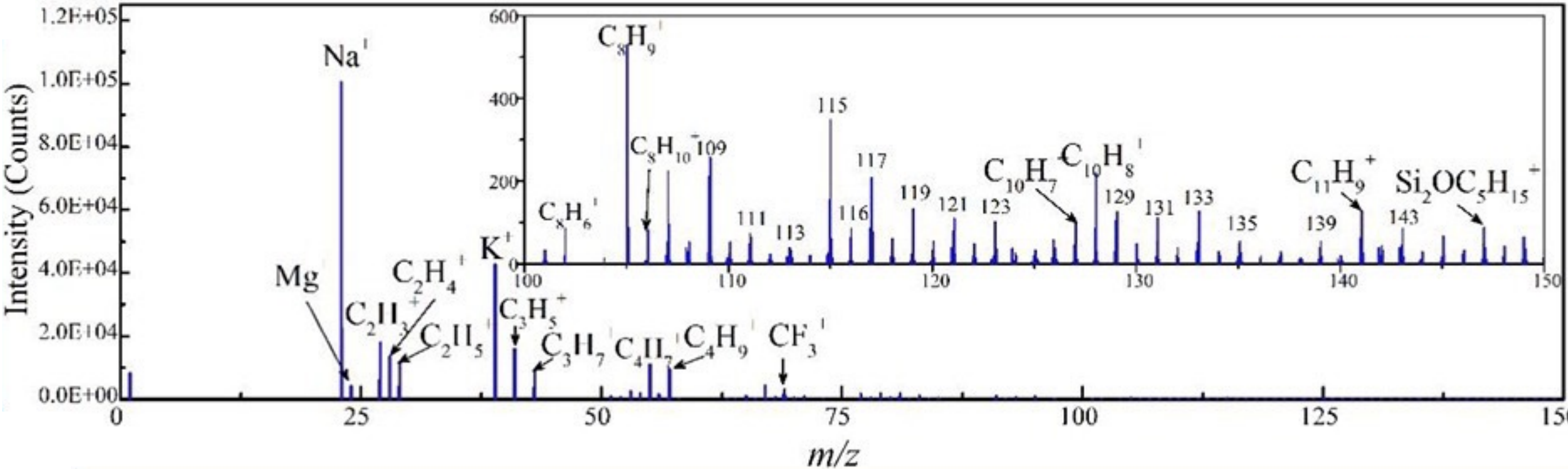


Secondary Ion Mass Spectrometry (SIMS) Used in Reality

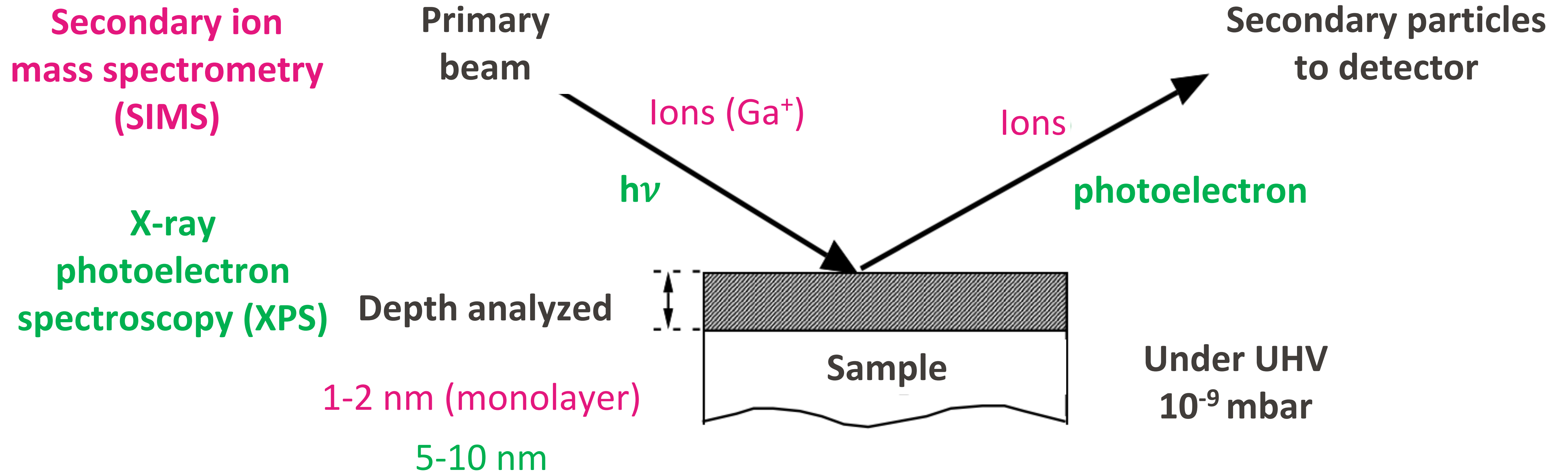
Quantifying atmospheric aerosol particles during heavy air pollution event in Beijing



Li et al. | J. Environ. Sci. | 2018



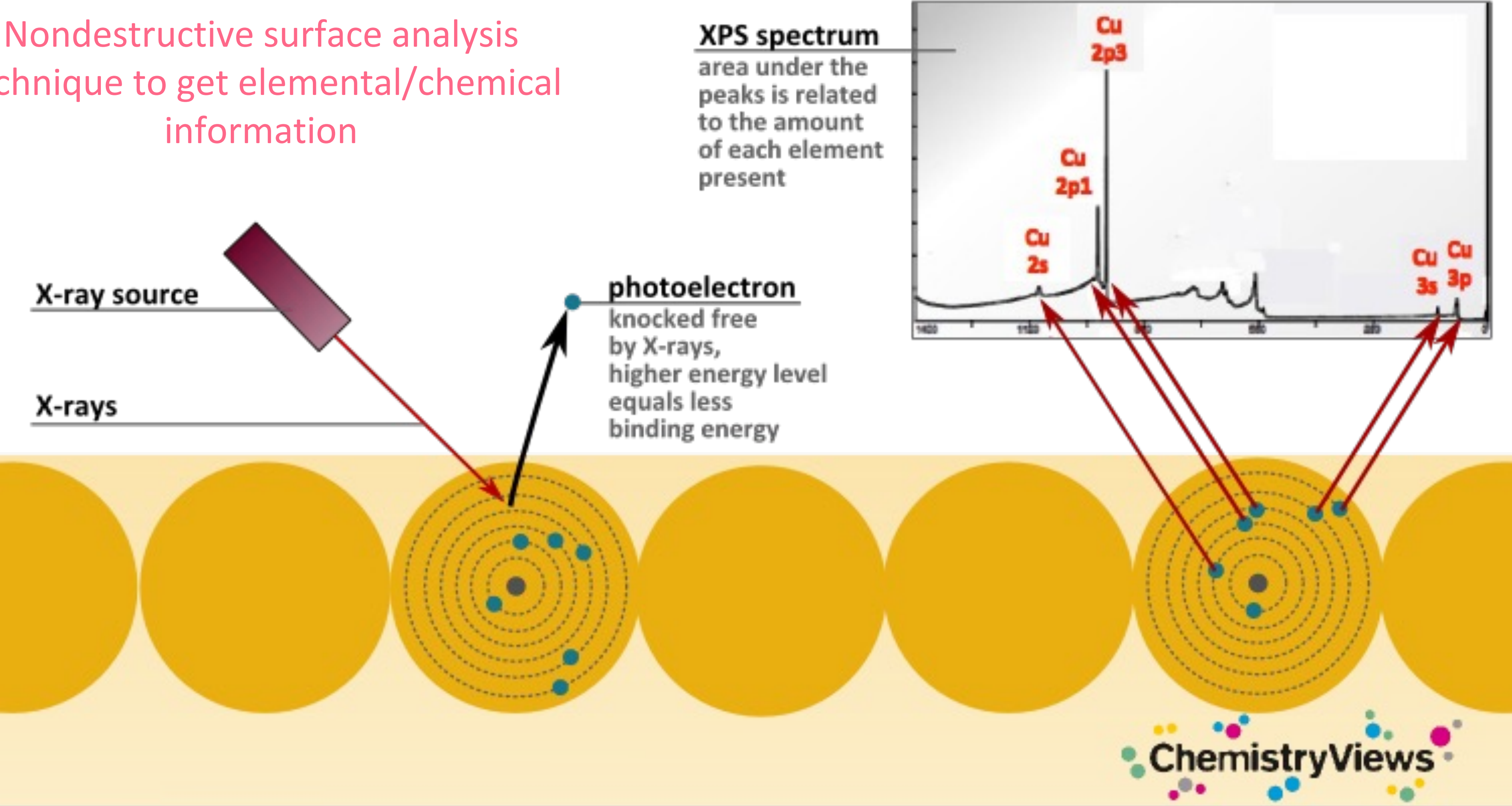
Technologies to Monitor Surface Science: XPS and SIMS



XPS is the more broadly useful technique for surface composition and chemical analysis

X-Ray Photoelectron Spectroscopy (XPS) to Monitor Surfaces

Nondestructive surface analysis technique to get elemental/chemical information



What Information Can XPS Provide?

Analytical capabilities of XPS:

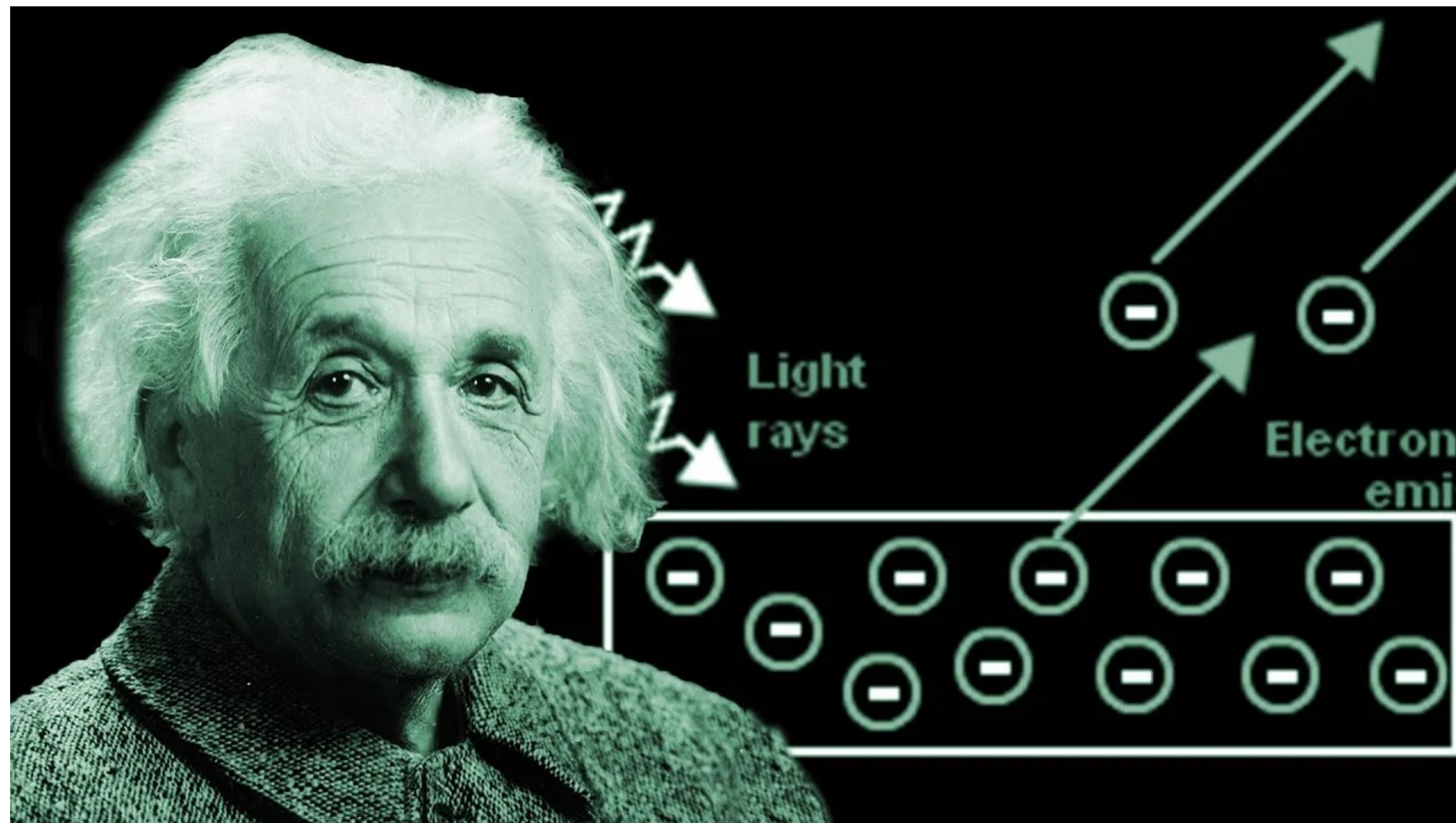
- Identification of elements on the surface
- Quantitative analysis – Chemical composition, film thickness
- Chemical state analysis – Oxidation state, chemical bonds
- Electronic band structure analysis

5 B BORON	6 C CARBON	7 N NITROGEN	8 O OXYGEN	9 F FLUORINE
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XPS Relies on the Photoelectric Effect

Photoelectric Effect



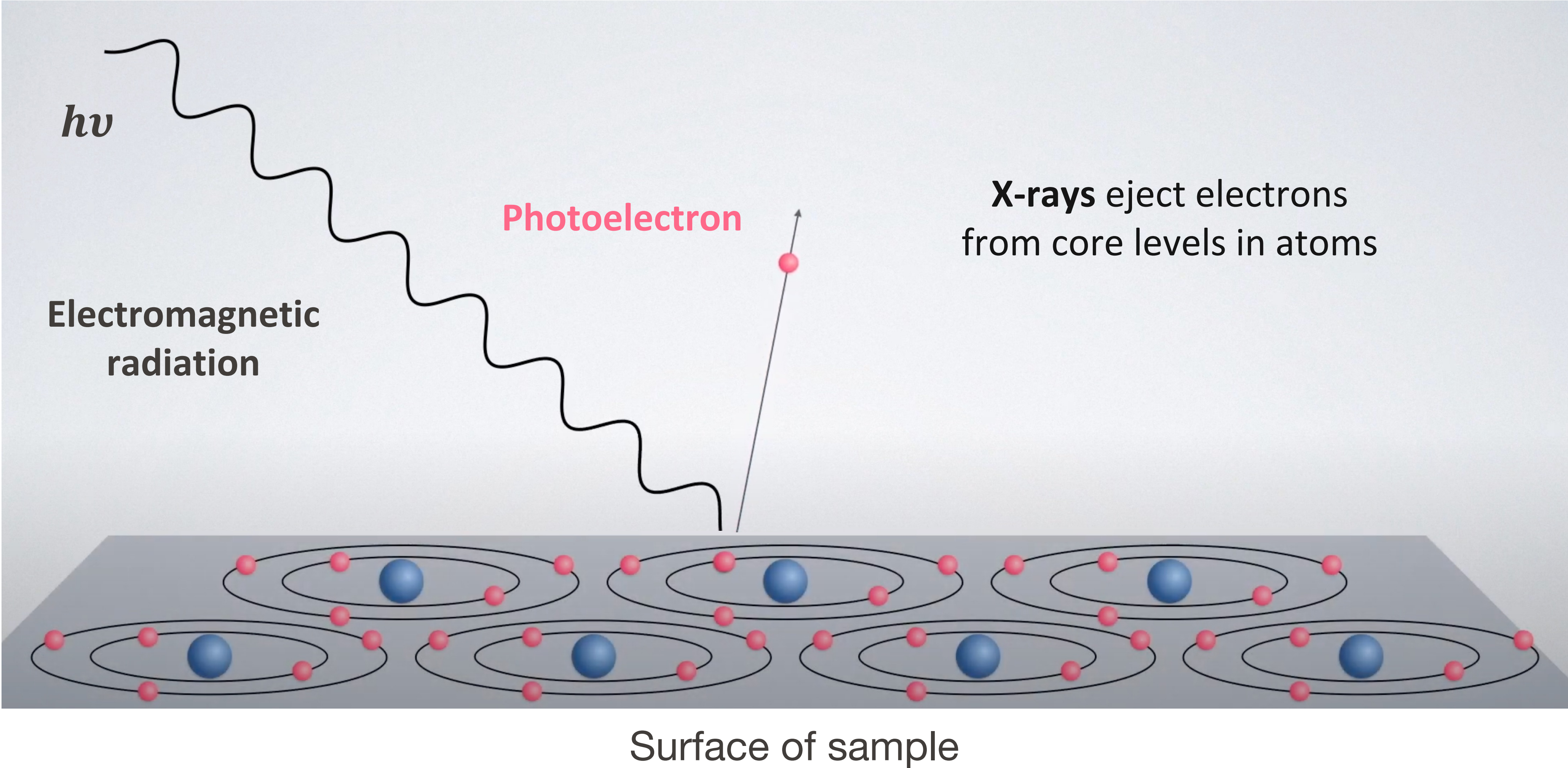
Albert Einstein

A **photoelectron** is an electron that is ejected from a material, typically a metal, when it absorbs a photon of sufficient energy

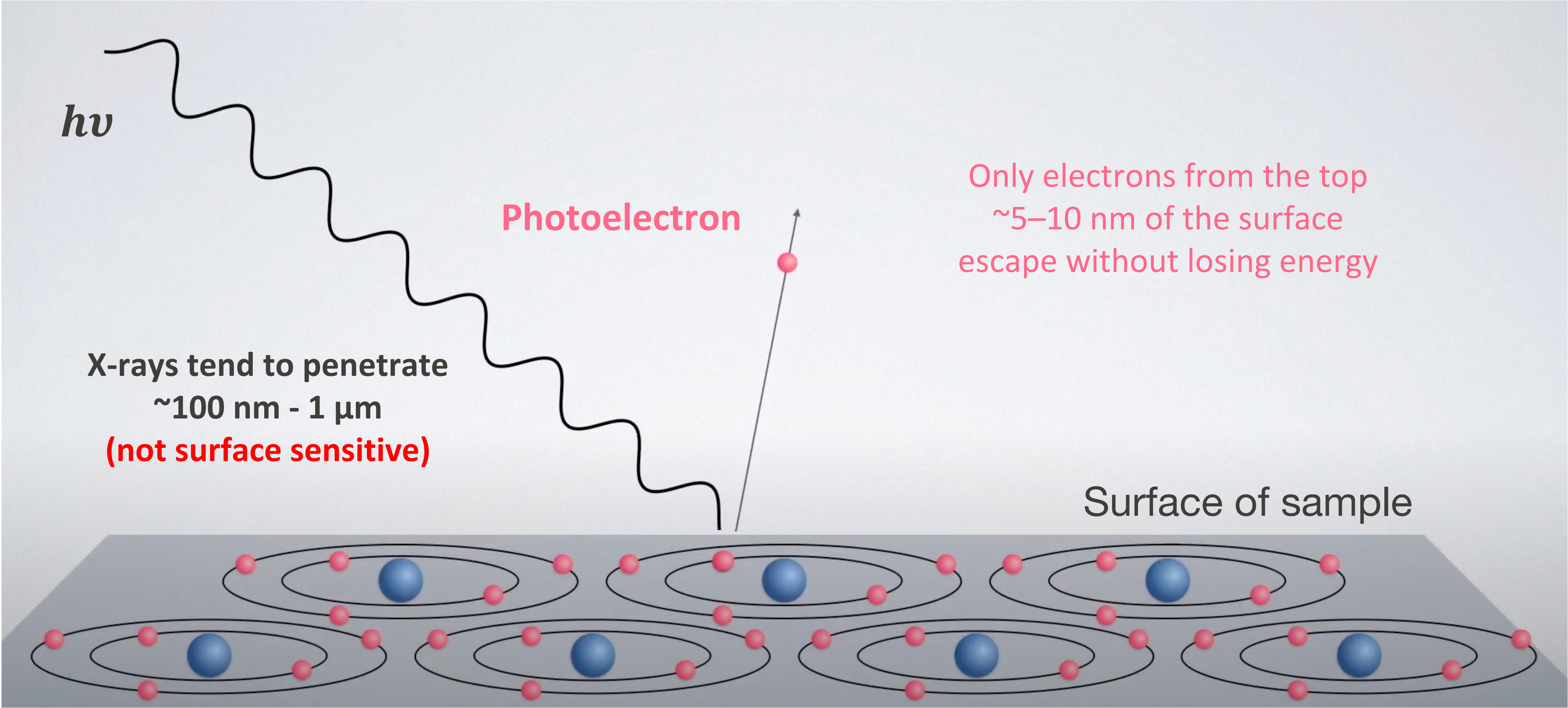


Nobel Prize in Physics for his discovery of the Photoelectric Effect (1921)

Photoelectric Effect



XPS Surface Sensitive Due to Escaping Electrons (Not X-Rays)



$h\nu$

Photoelectron

Only electrons from the top
~5–10 nm of the surface
escape without losing energy

X-rays tend to penetrate
~100 nm - 1 μm
(not surface sensitive)

Surface of sample

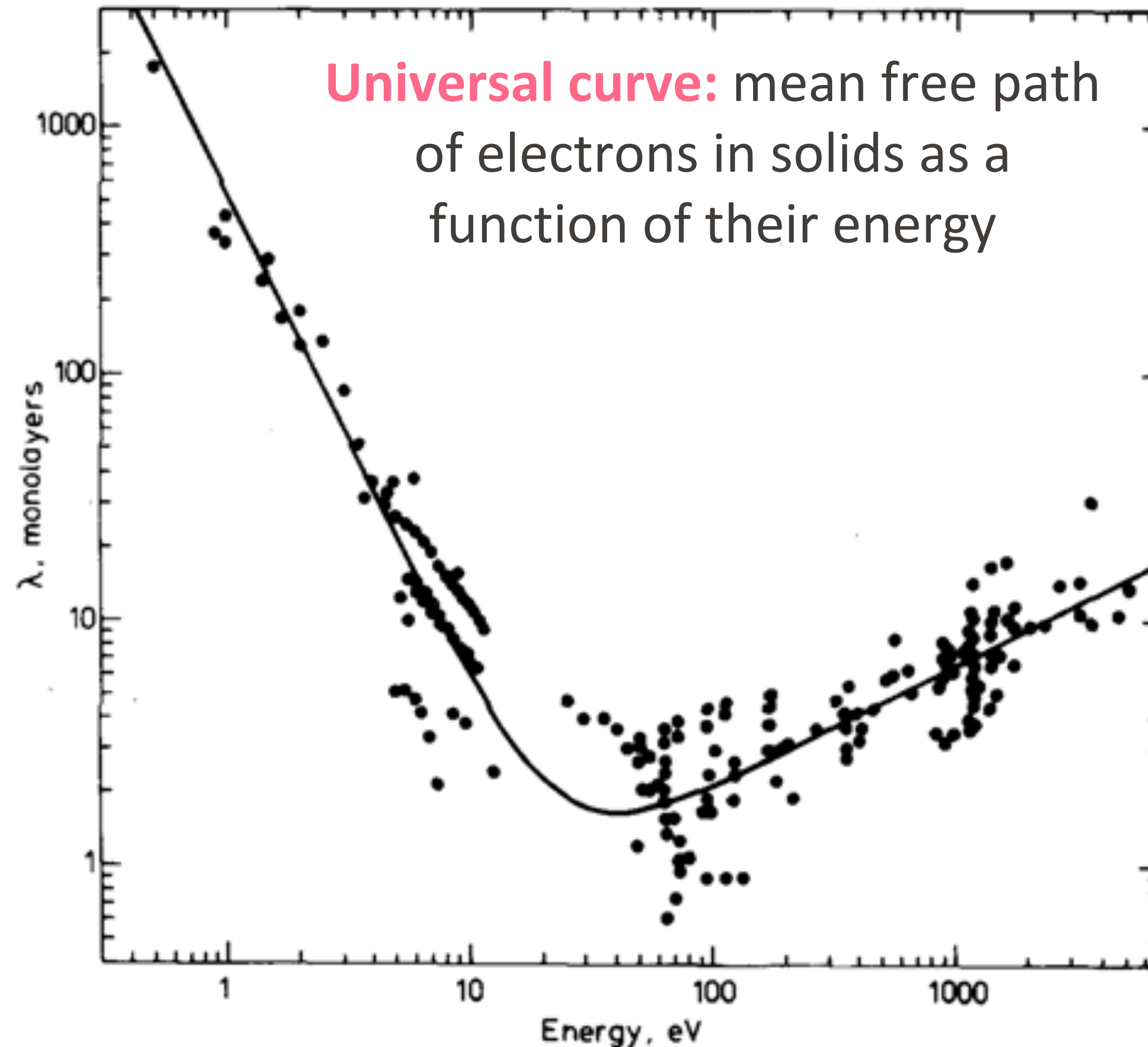
Electrons liberated down here do
not escape

XPS Surface Sensitive: Short Mean Free Path of Electrons in Solids

Inelastic mean free path of electrons in a solid:

how far electron can travel through material before losing energy

10 monolayers \sim 3 nm

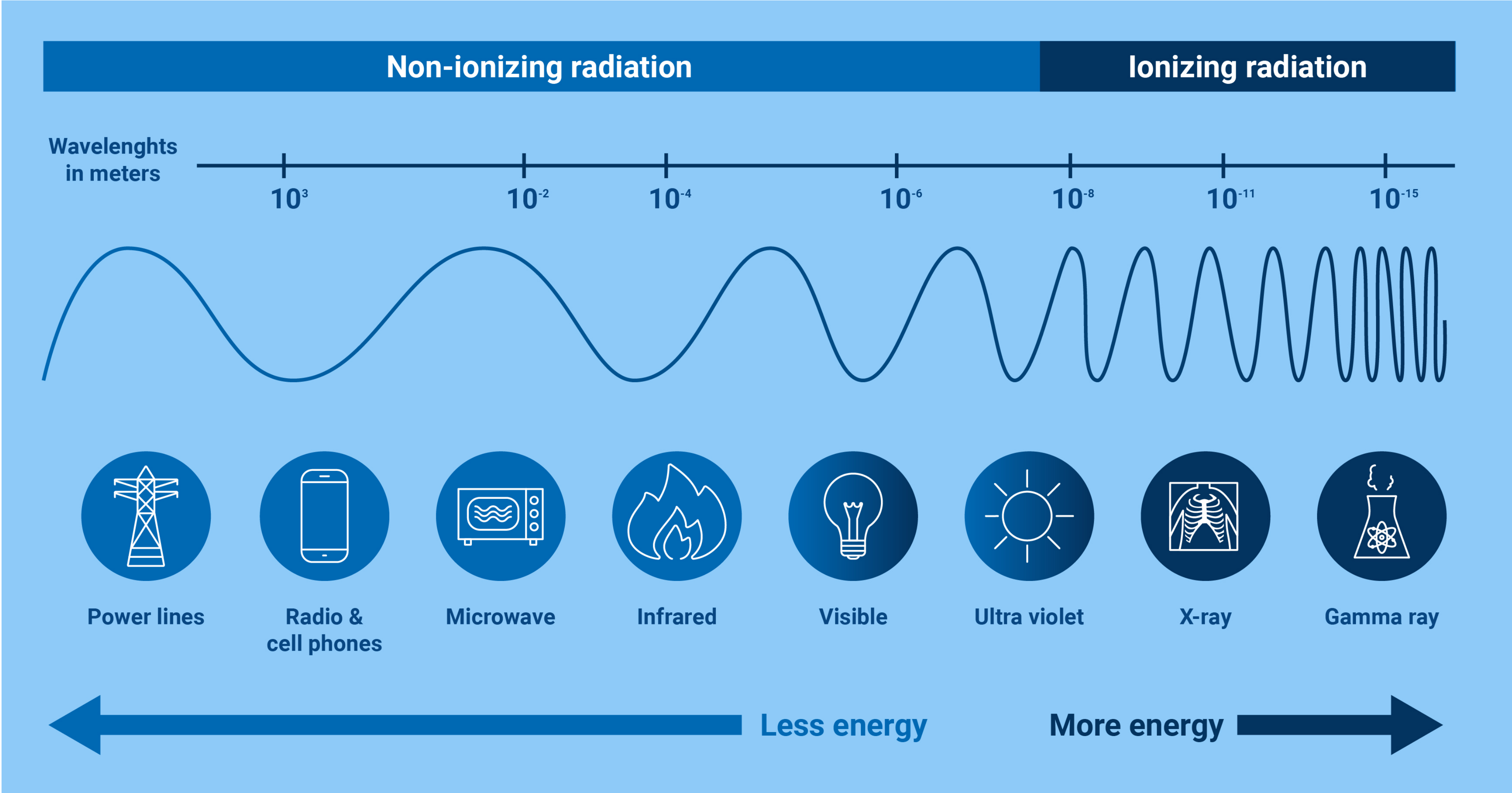


Each data point represents a measurement of the inelastic mean free path of electrons in some material at a particular kinetic energy

When We Talk About Mean Free Path in Gas vs. Solid Phases

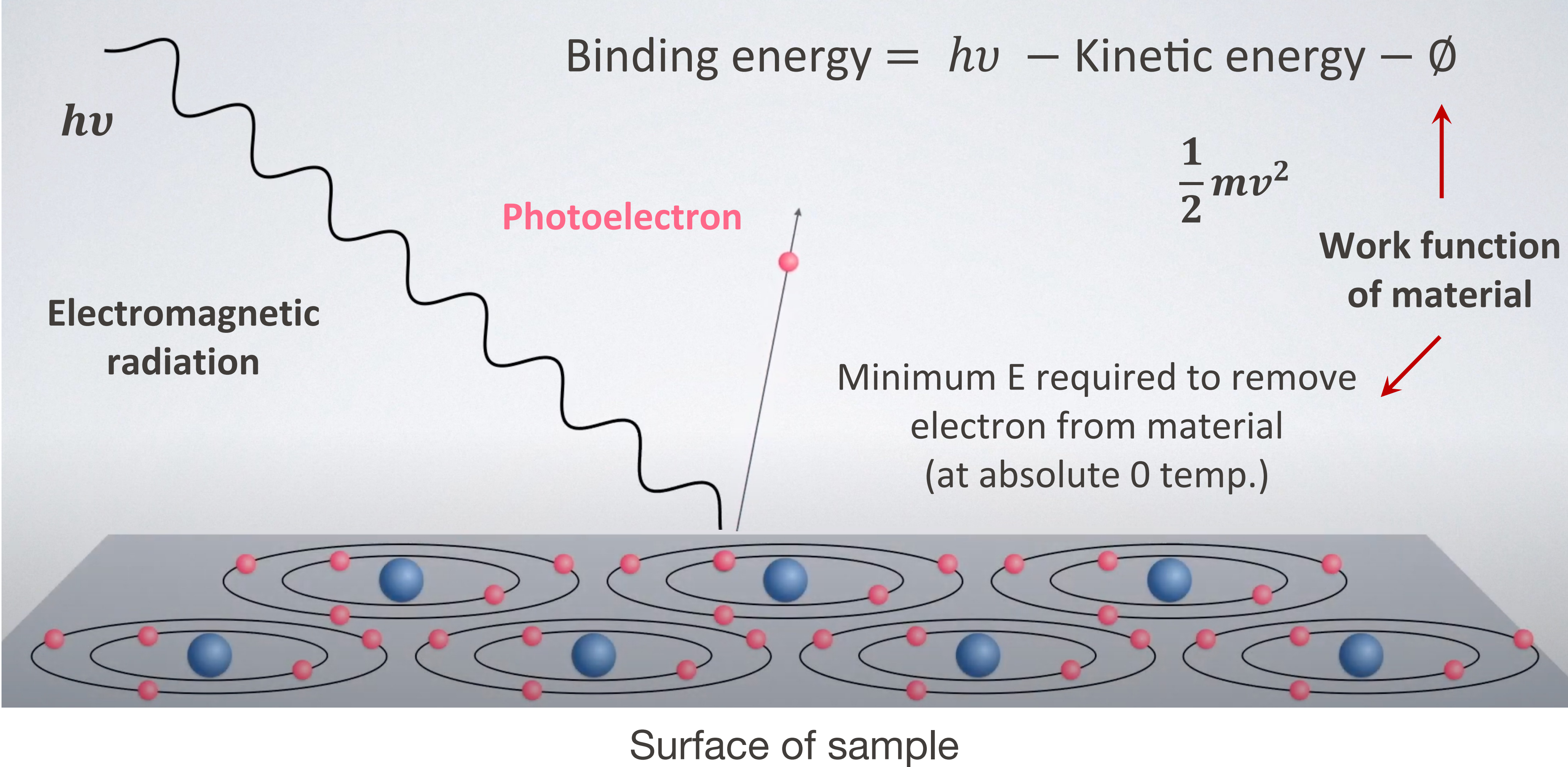
Property	Gas phase	Solid phase
Collisions with	Other molecules	Atoms, electrons, phonons in the lattice
Environment	Sparse	Dense
What happens at a “collision”	Deflection, possible energy loss	Energy loss (inelastic) or change in direction
Mean free path spatial scale	nm–m (depends on pressure)	Å–nm (depends on energy)

Electromagnetic Radiation – Ionizing Radiation for XPS

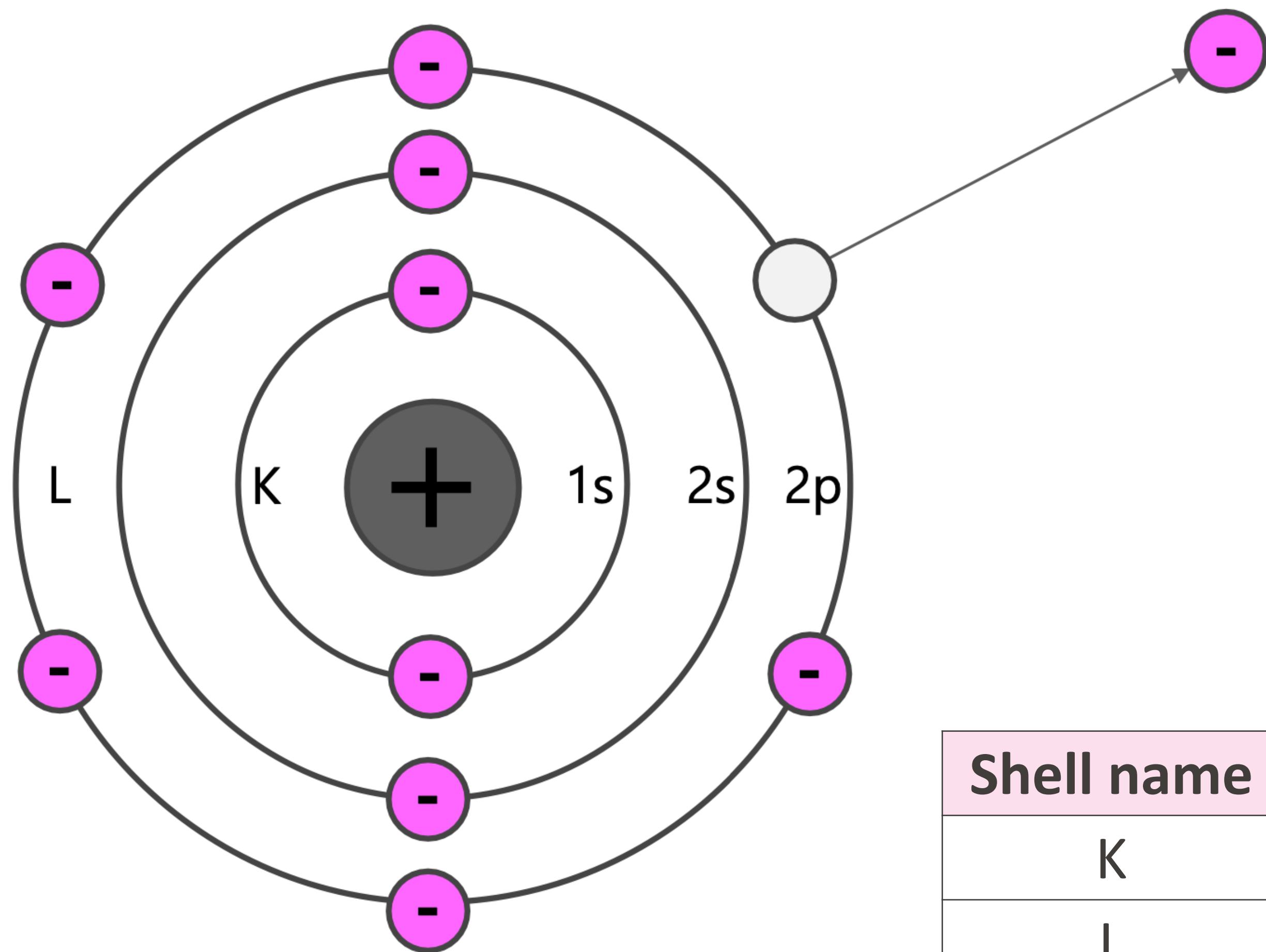


Valence electrons : UV light
Core electrons: X-rays

Photoelectric Effect Equation



What is Binding Energy?

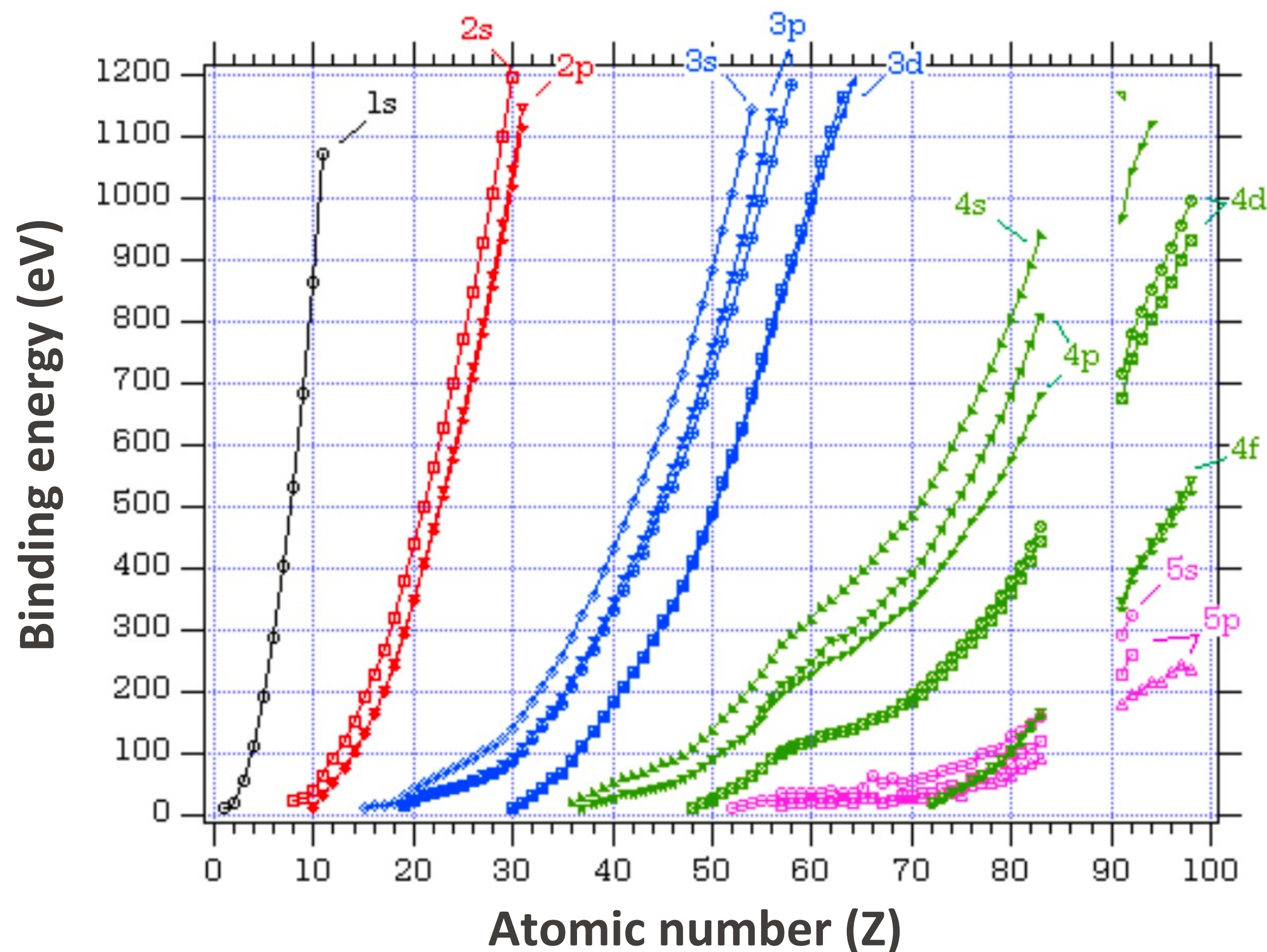


Binding energy = energy an electron needs to overcome the attraction of the nucleus

The presence of other electrons “screens” the nucleus charge → effective charge holding back the escaping electron is smaller

Shell name	Quantum number (n)	Example subshells
K	1	1s
L	2	2s, 2p

Core-Level Binding Energies are Element Specific



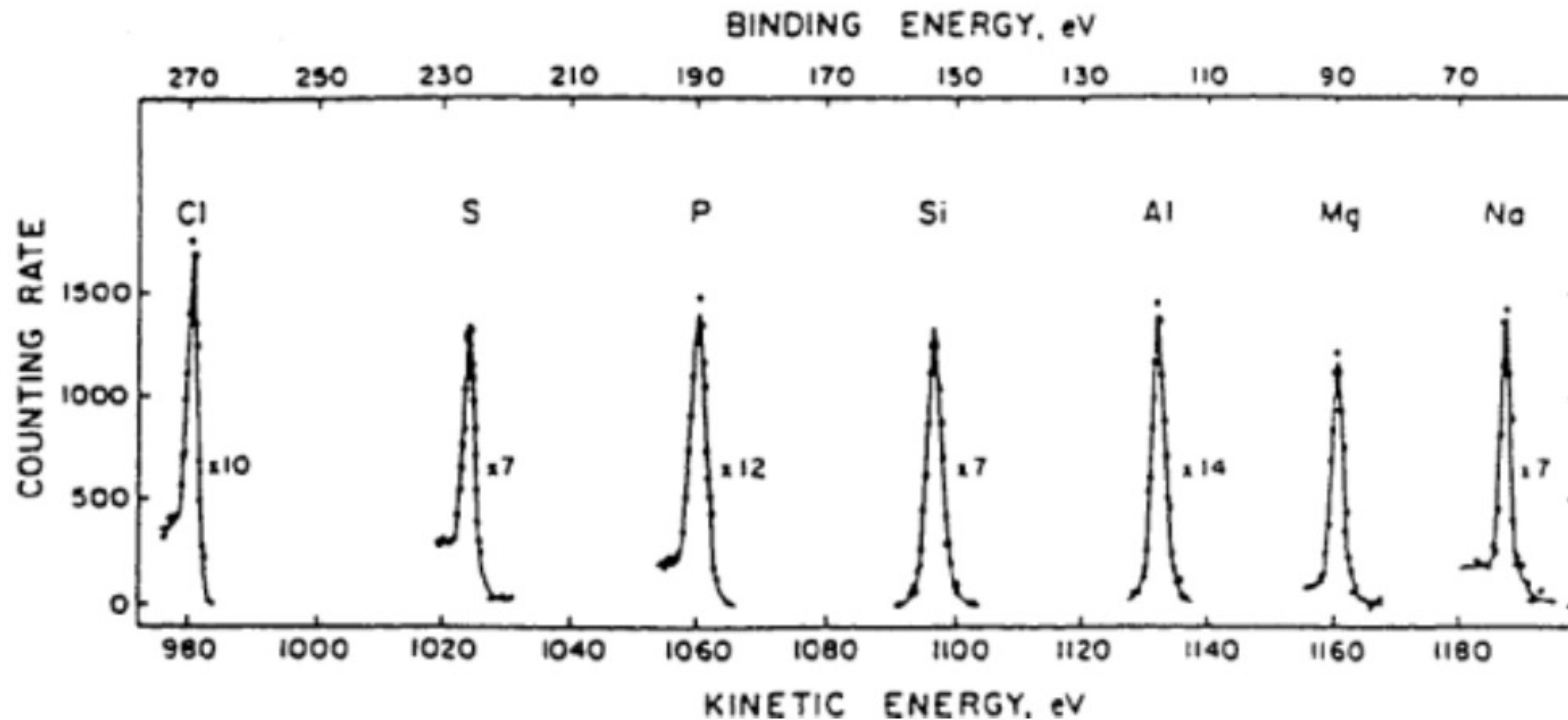
As you move to heavier elements (higher Z), core electrons (*e.g.*, 1s, 2s, 2p) are held more tightly by the nucleus → binding energies increase dramatically

Each element has a unique set of core levels, **binding energies can be used to fingerprint element**

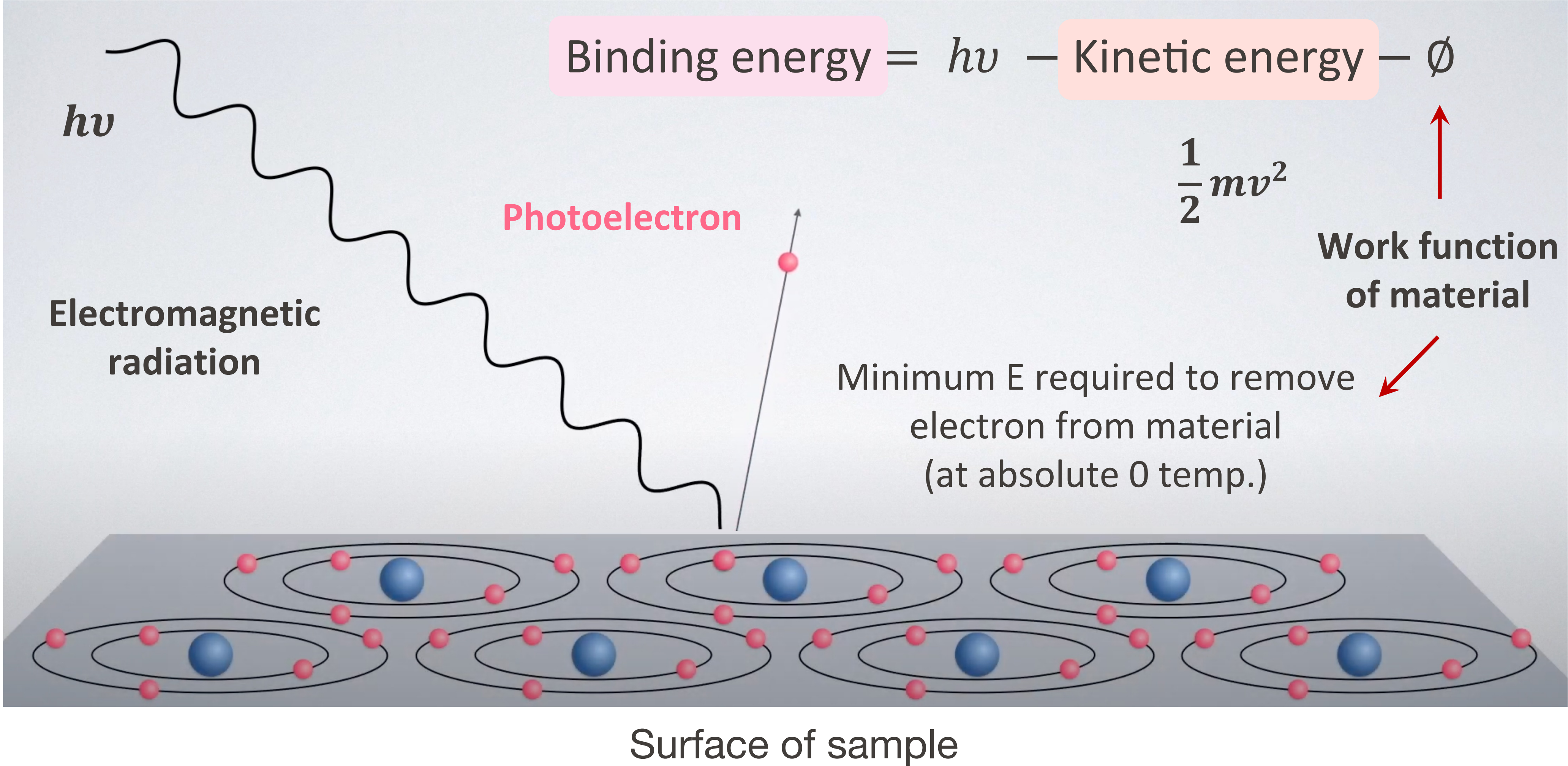
Core-Level Binding Energies are Element Specific

In XPS, higher binding energies correspond to lower kinetic energies and vice-versa

$$\text{Binding energy} = h\nu - \text{Kinetic energy} - \phi$$



Photoelectric Effect Equation

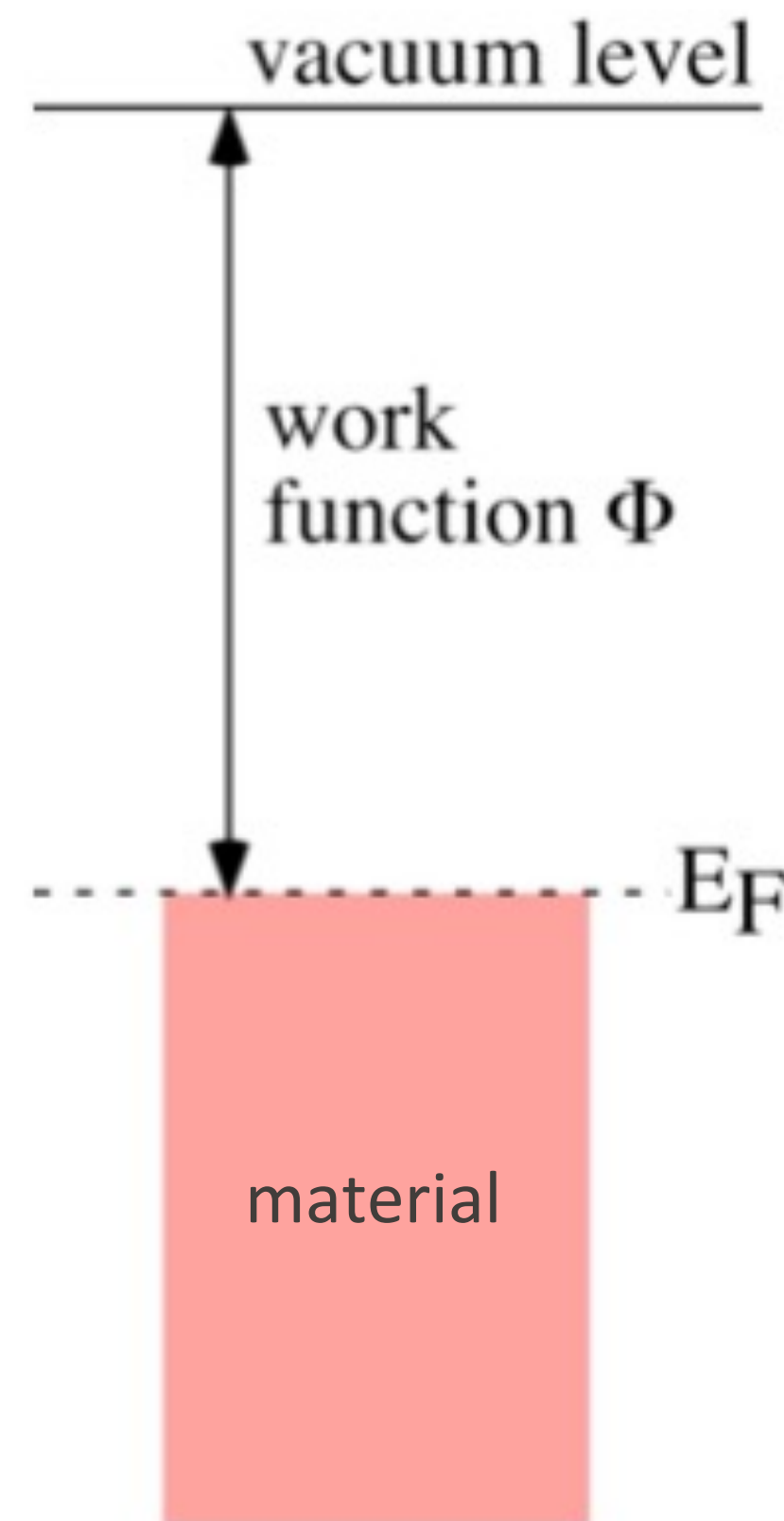


Work Function of Different Materials

Work function (Φ): difference between the potential energy of the electron in vacuum and Fermi level (E_F).

Represents the minimum energy required to eject an electron from the highest occupied level into vacuum

$$\Phi = E_{\text{vacuum}} - E_{\text{Fermi}}$$



~ 10 nm from the surface

Fermi level (E_F) can be regarded as the chemical potential of free electrons

Work Function of Different Materials

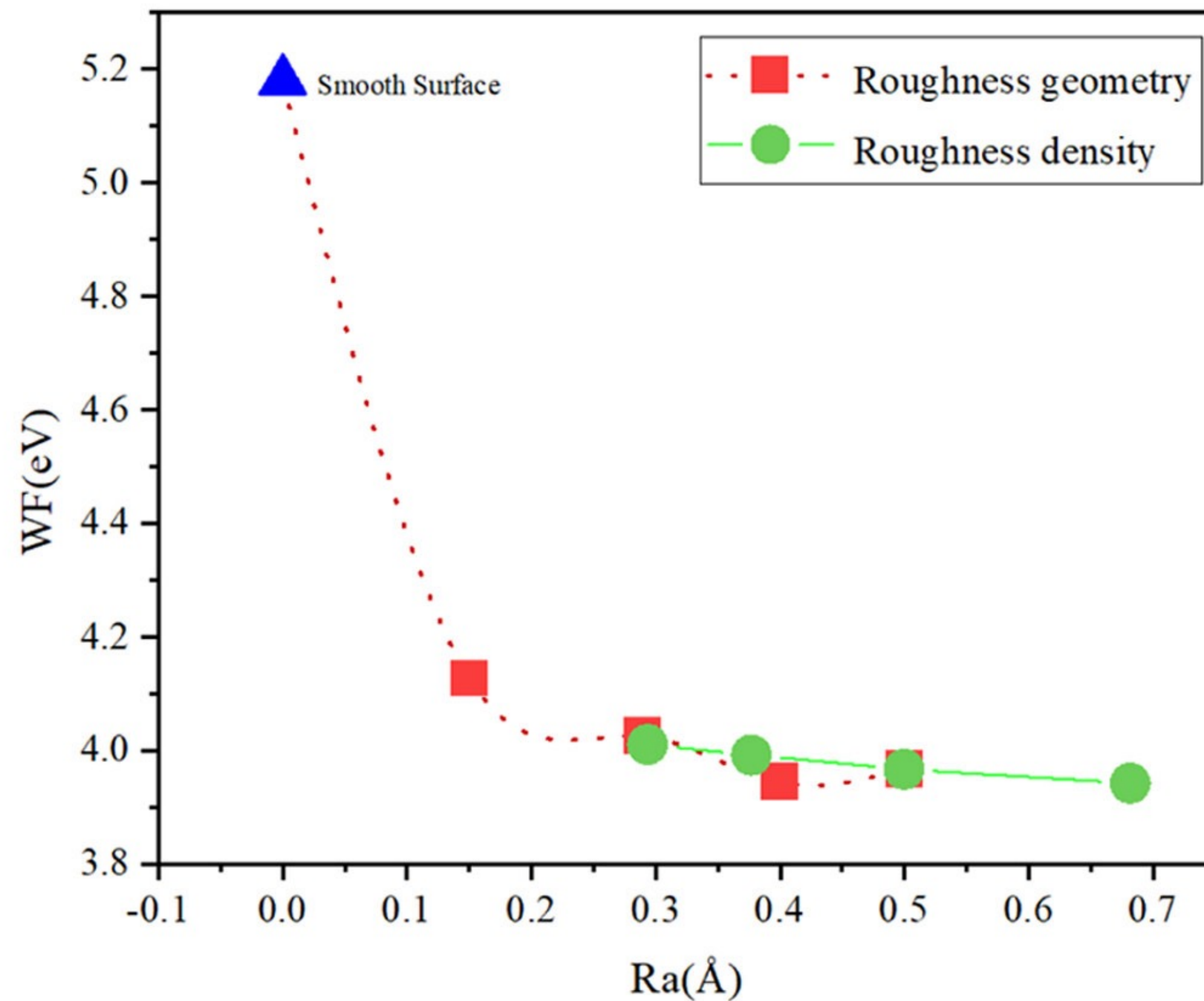
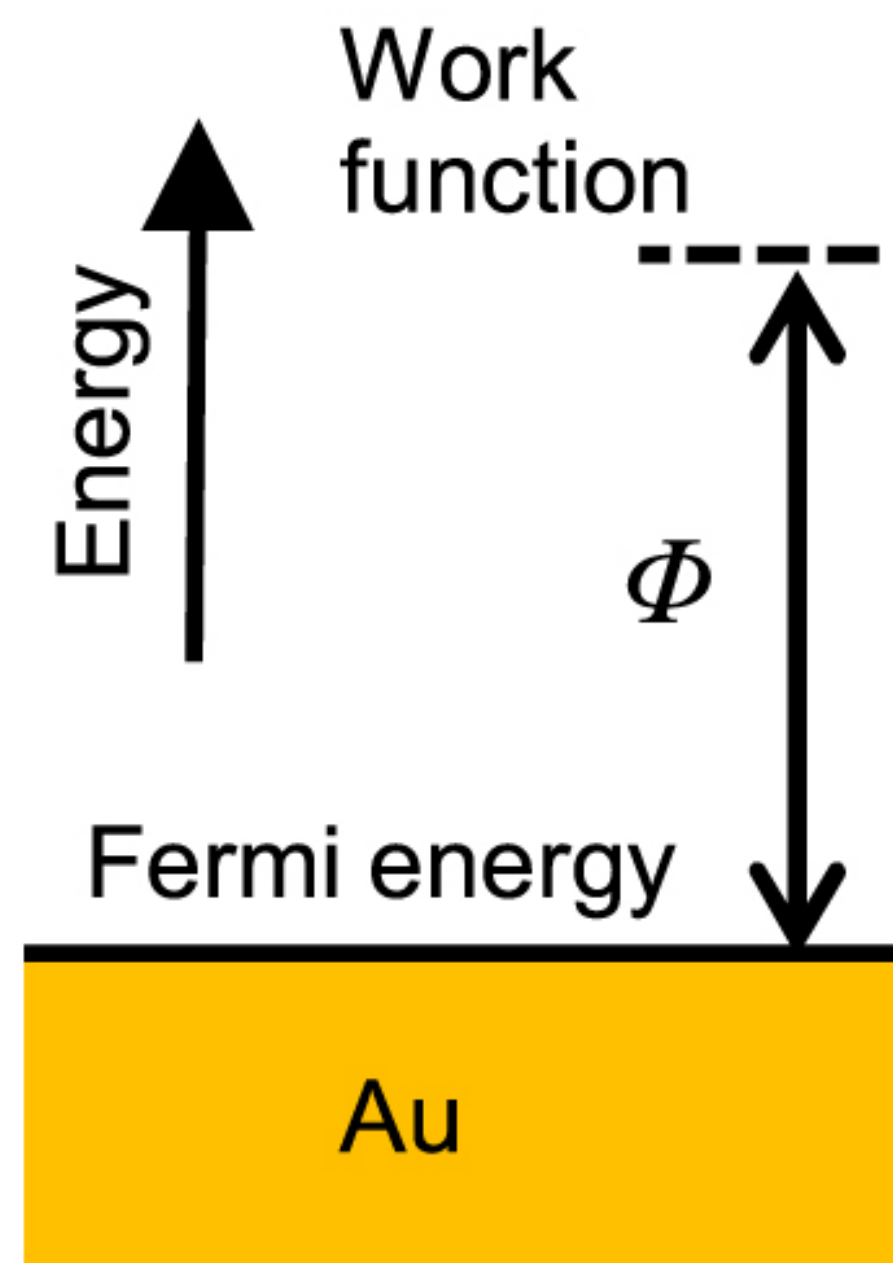
Φ is an inherent material property but it is not fixed – it strongly depends on the surface property of the material (crystallographic orientation/contamination)

Element	Surface plane	Work Function in eV
Ag	(110)	4.52
Ag	(100)	4.64
Ag	(111)	4.74
Cs	polycrystalline	2.14
Cu	(110)	4.48
Cu	(100)	4.59
Cu	(111)	4.98
Ge	(111)	4.80
Ni	(110)	5.04
Ni	(100)	5.22
Ni	(111)	5.35
W	(111)	4.47
W	(100)	4.63
W	(110)	5.25

Φ (eV)	Electron behavior	Chemical reactivity
Low	Electrons “loose” easily donated	Higher chemical reactivity (alkali metals)
High	Electrons are tightly bound	Lower reactivity (noble metals)

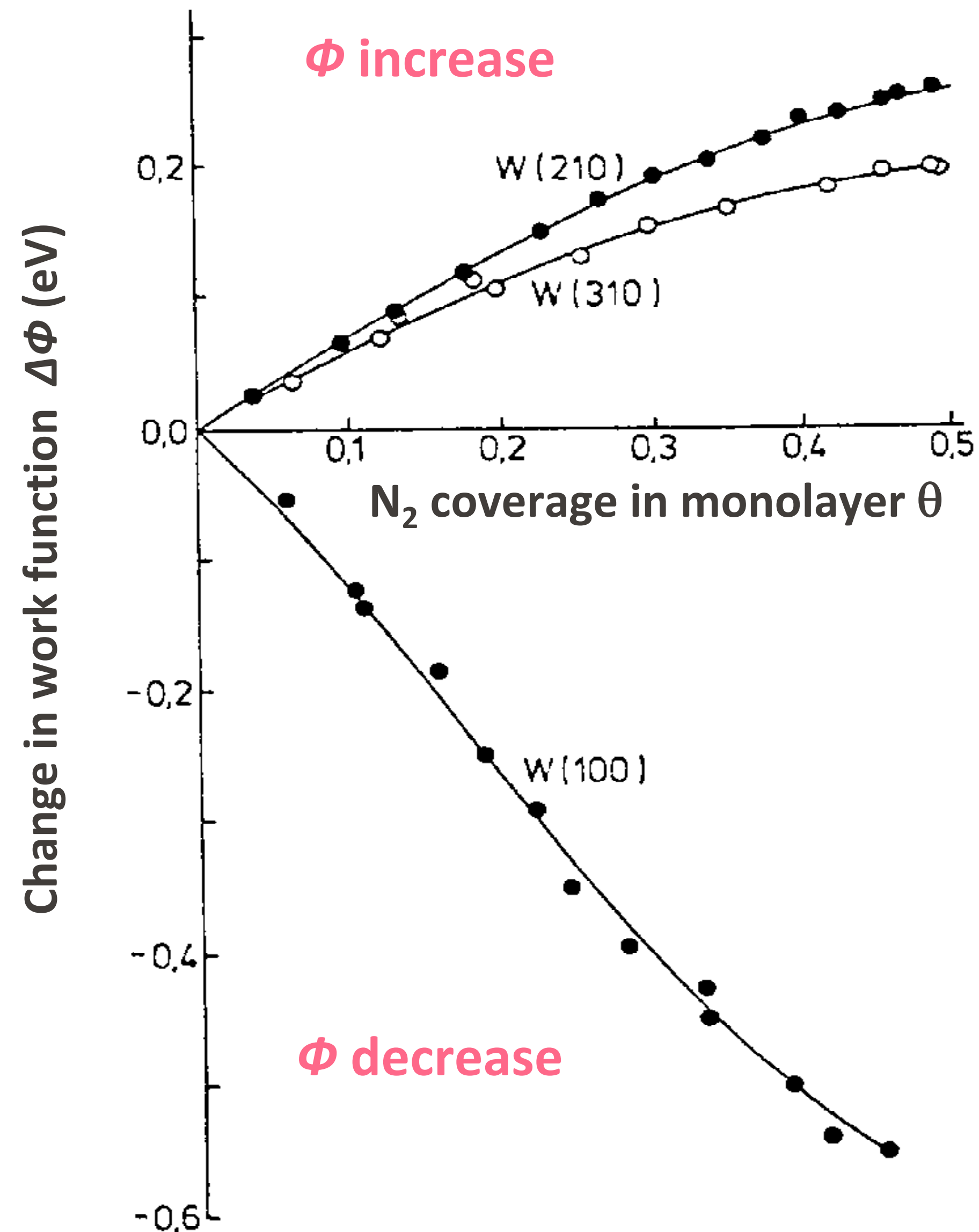
Surface Roughness Affects Work Function of Gold

Increasing surface roughness decreases the work function of gold and renders it chemically reactive



Aghili *et al.* | J. Phys. Chem. C | 2024

Adsorbates Alters the Work Function of Materials



W(210) rougher
↓
Adsorbate atoms located in same plane as metal atoms

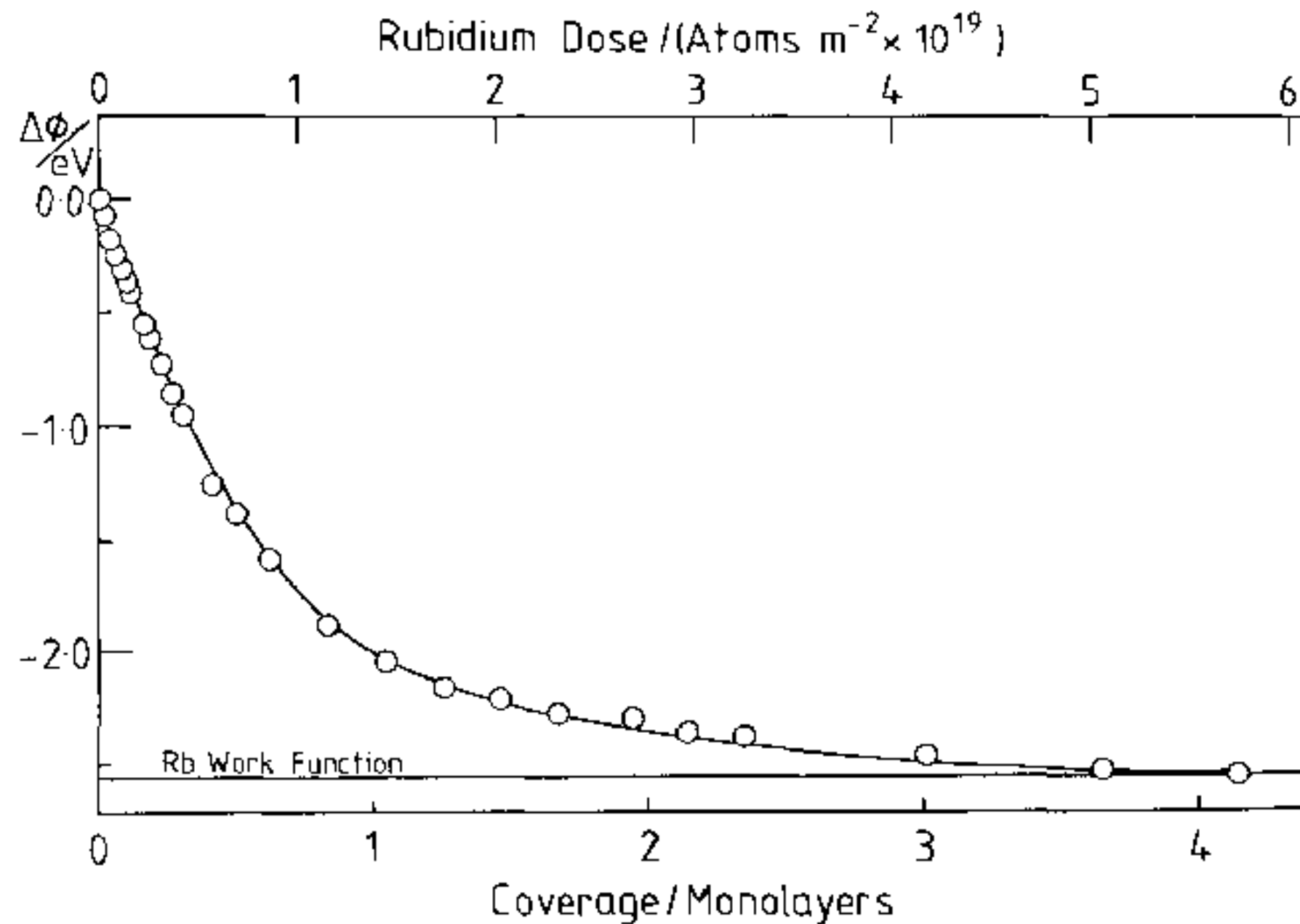
↓
Smoothing effect
↓
Work function increases

W(100) smoother
↓
Adsorbates stick out
↓
work function decreases upon adsorption

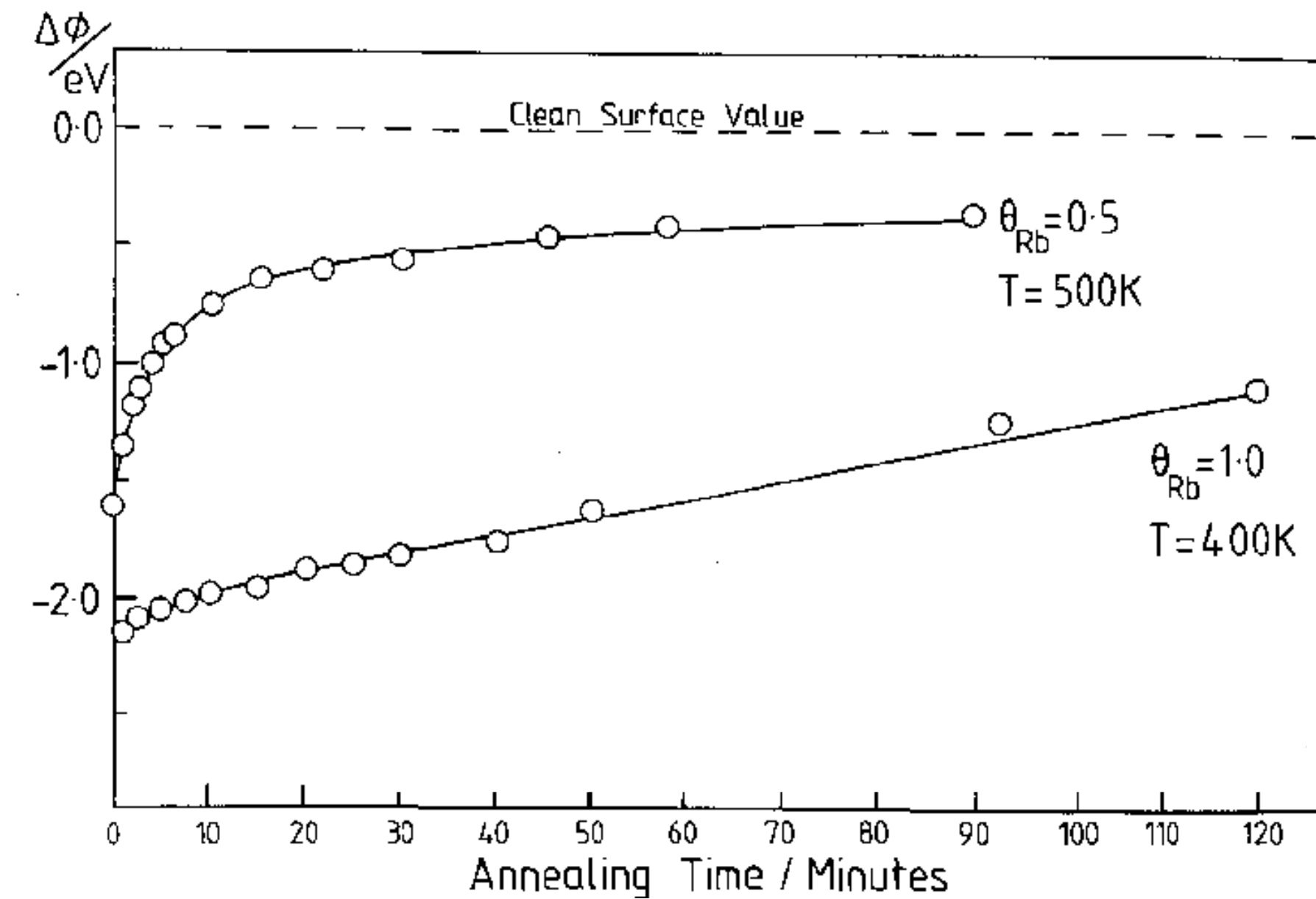
Source: Nic Spencer

Work Function Changes Reflect Surface Composition

The work function is highly sensitive to what is sitting on the surface



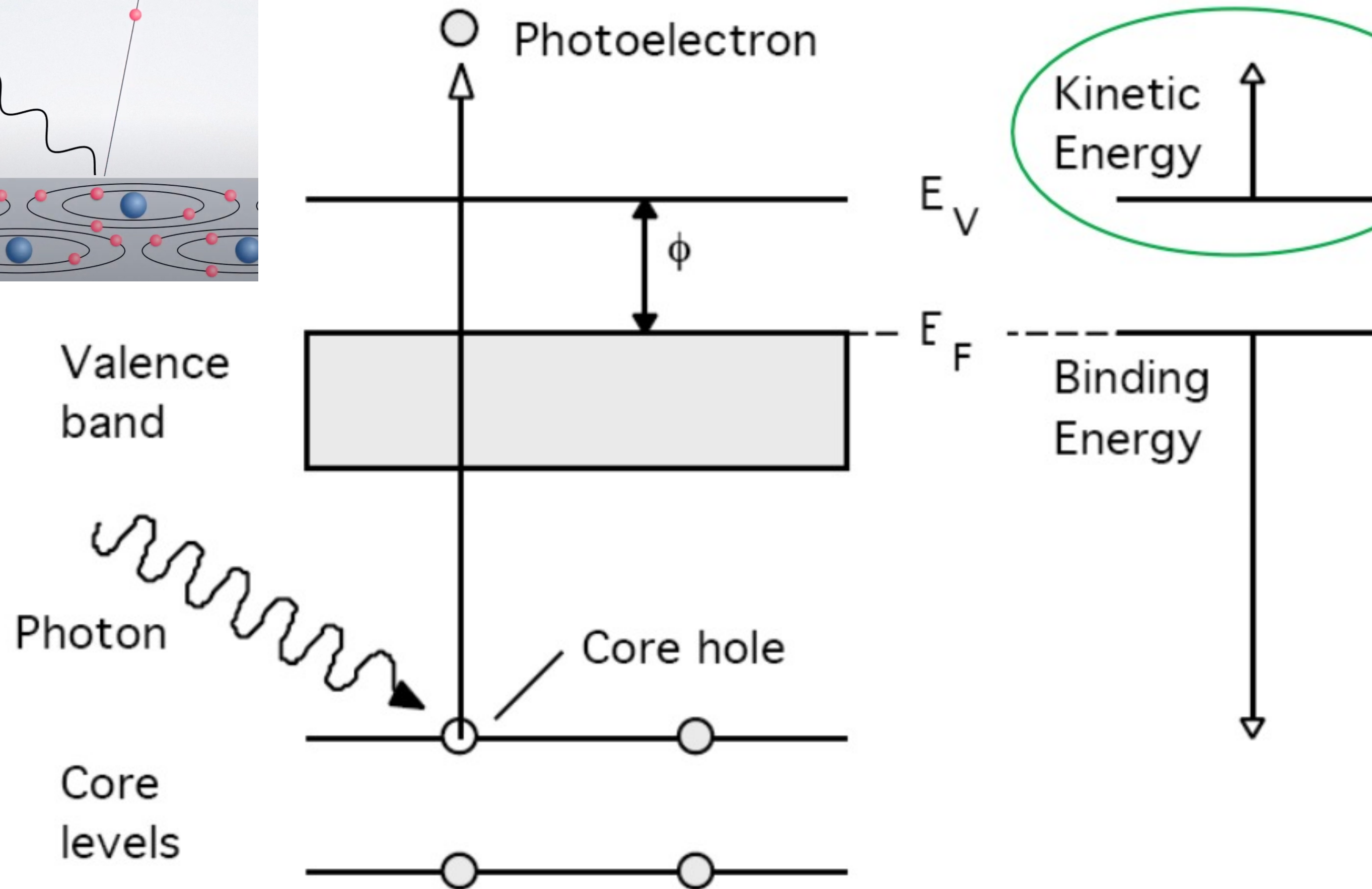
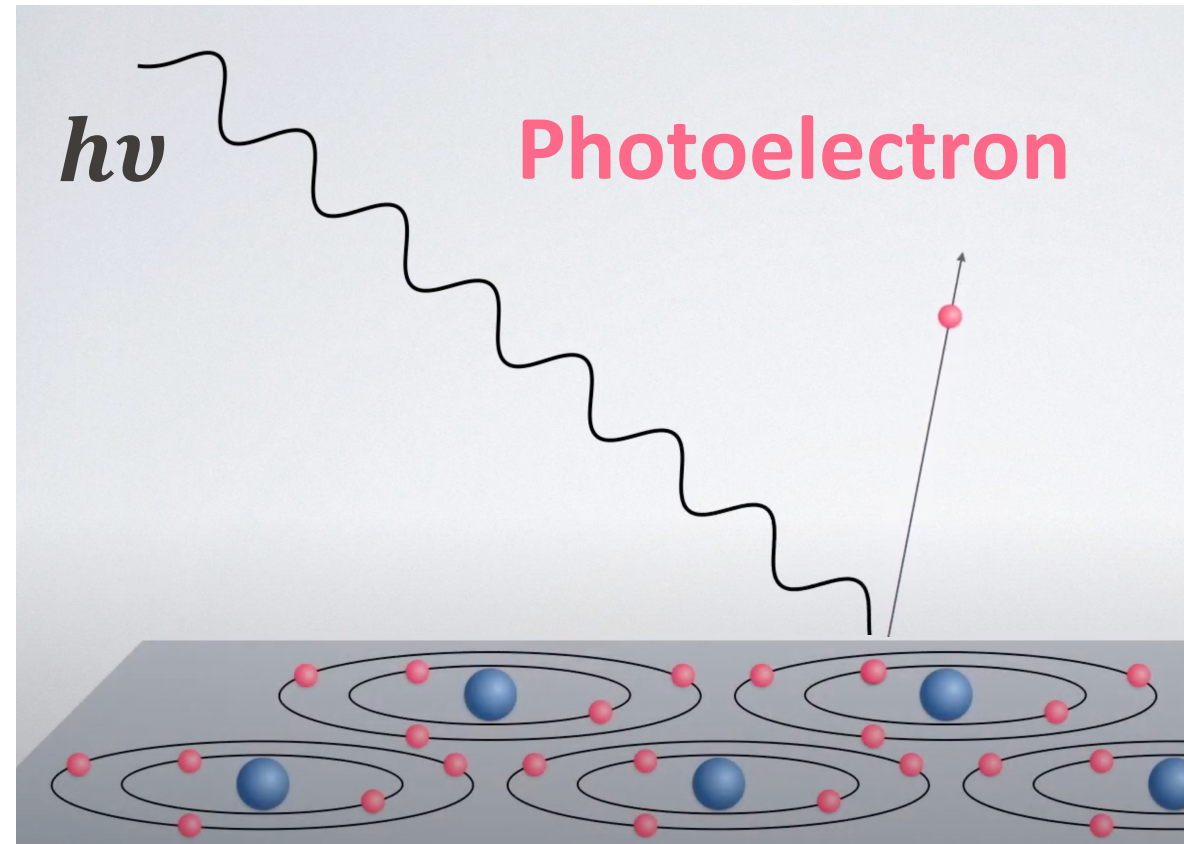
ϕ decrease of Ag(111) surface by adsorption of Rb atoms (donates electrons to metal)



$\Delta\phi$ increase upon annealing Rb-covered surface

→ Rb atoms diffuse into bulk of Ag crystal and no longer sit on surface
Eventually, reaches ϕ of clean silver

Relating the Work Function and Fermi Level to XPS

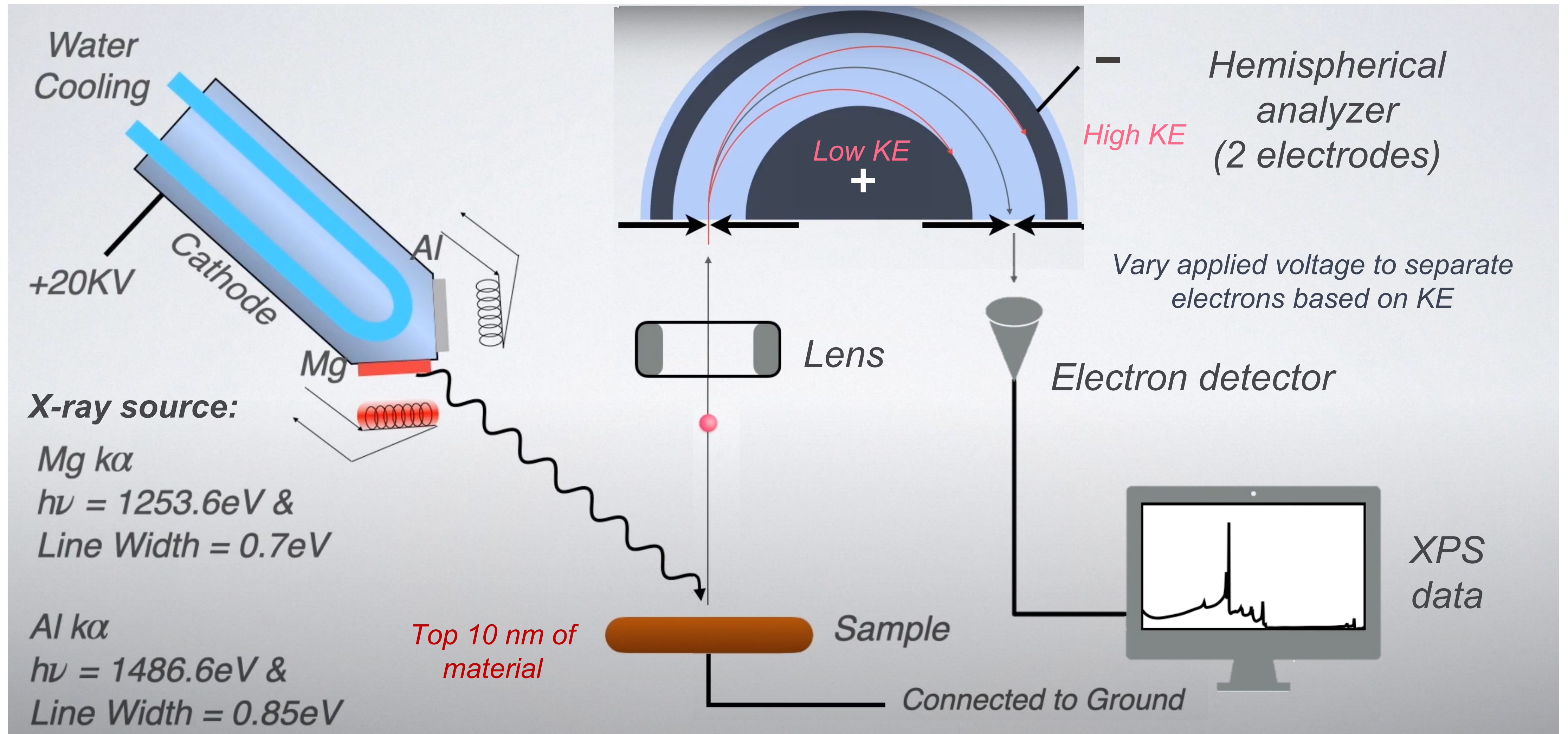


Photoelectron kinetic energy can be measured

No photoemission for $h\nu < \phi$

Kinetic energy of photoelectron increases as binding energy decreases

How Does XPS Analyze Surface Elements?



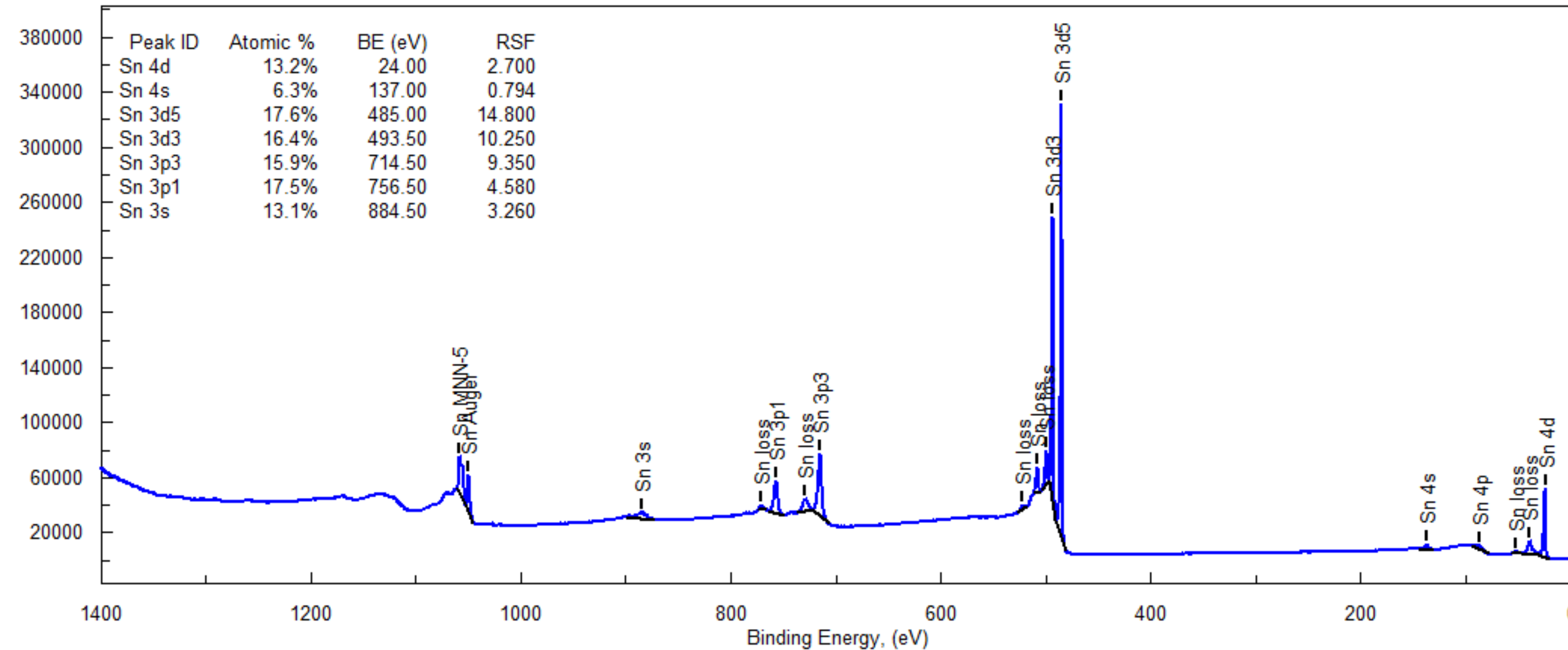
Binding Energy (eV) vs. Number of Electrons Counted

Kinetic energy of ejected electrons is related to the binding energy of the electron in the atom, which is unique to each element

$$\text{Binding energy} = h\nu - \text{Kinetic energy} - \phi$$

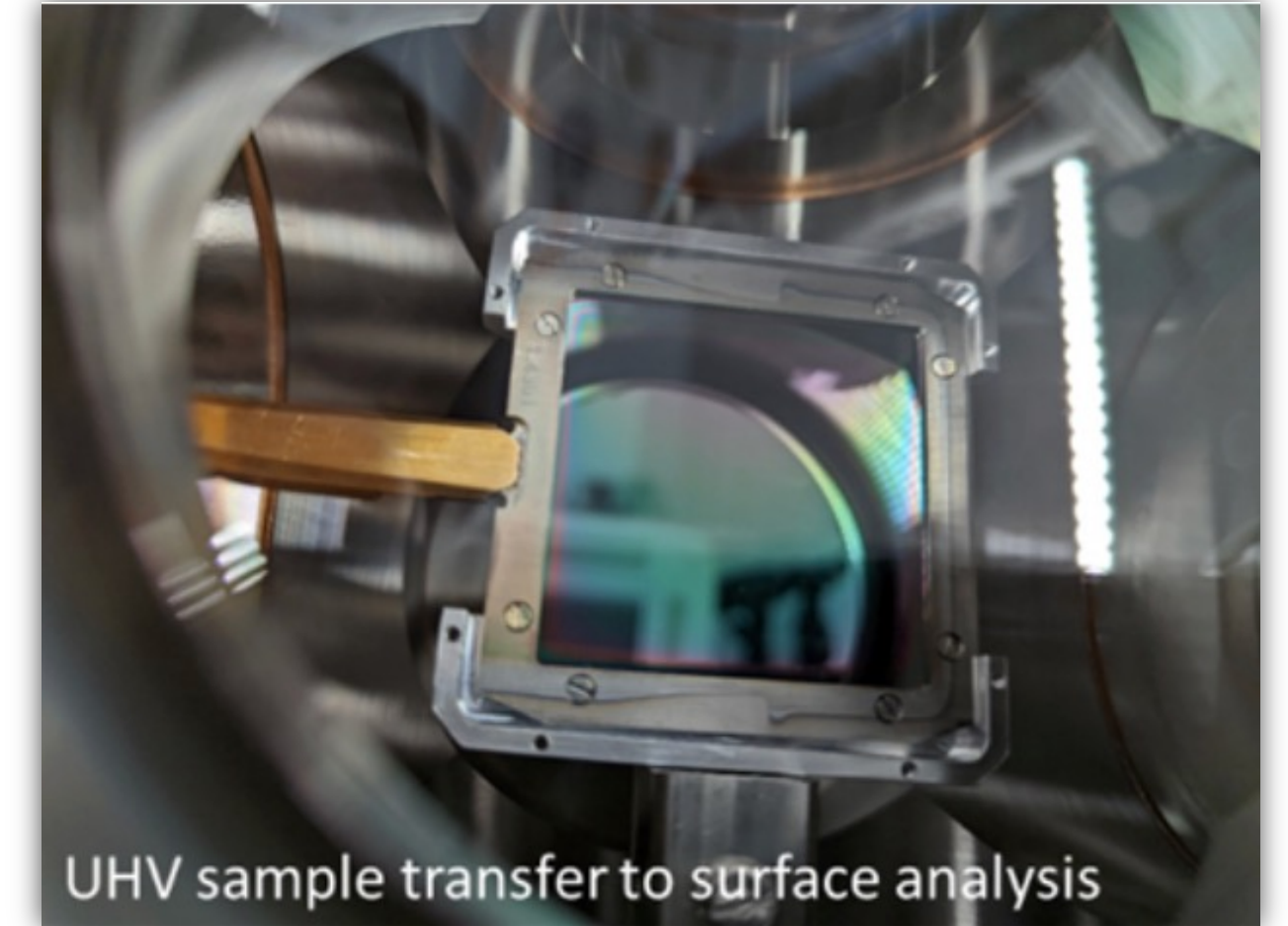
Sample Description: Sn, tin

Counts



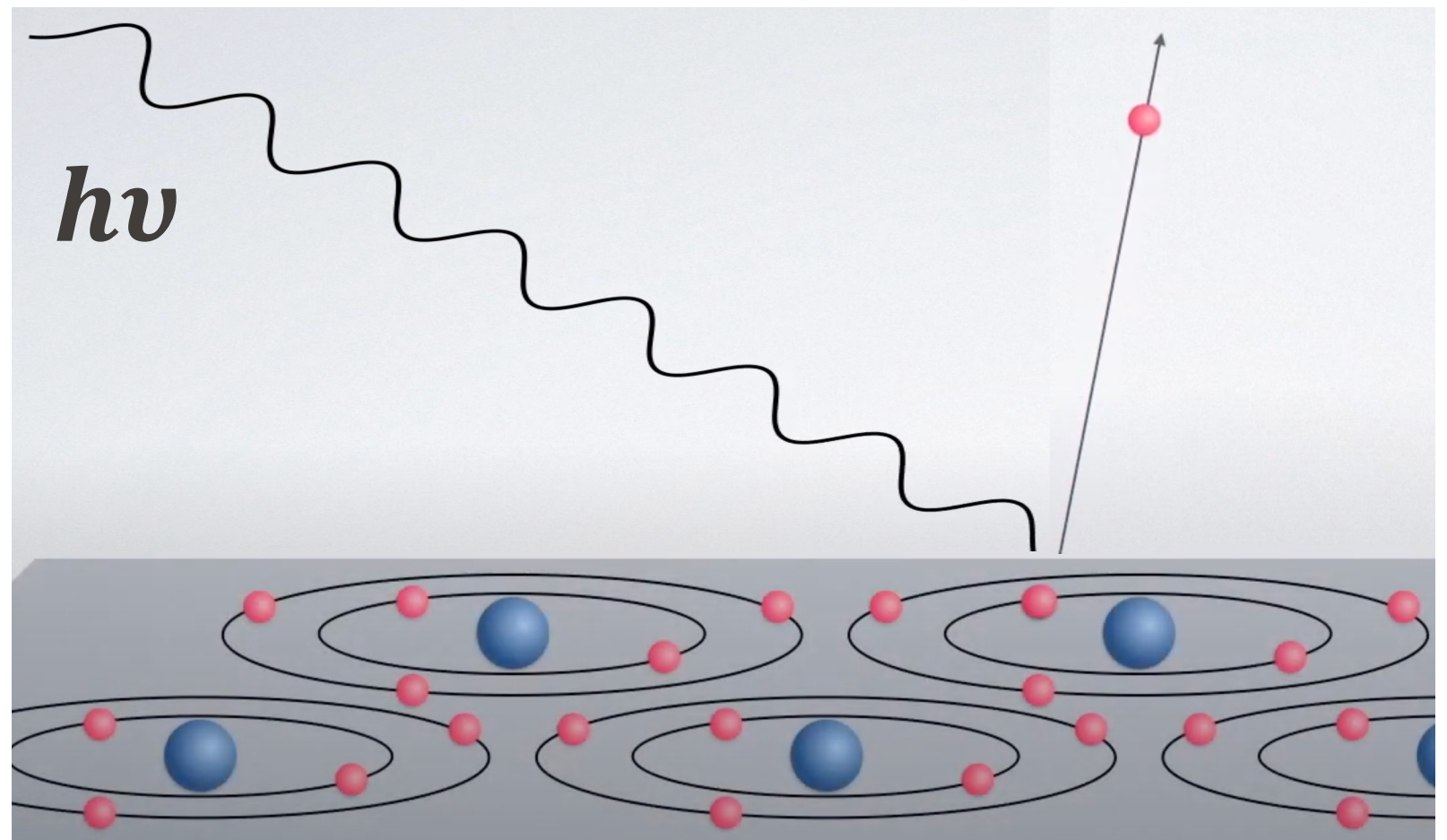
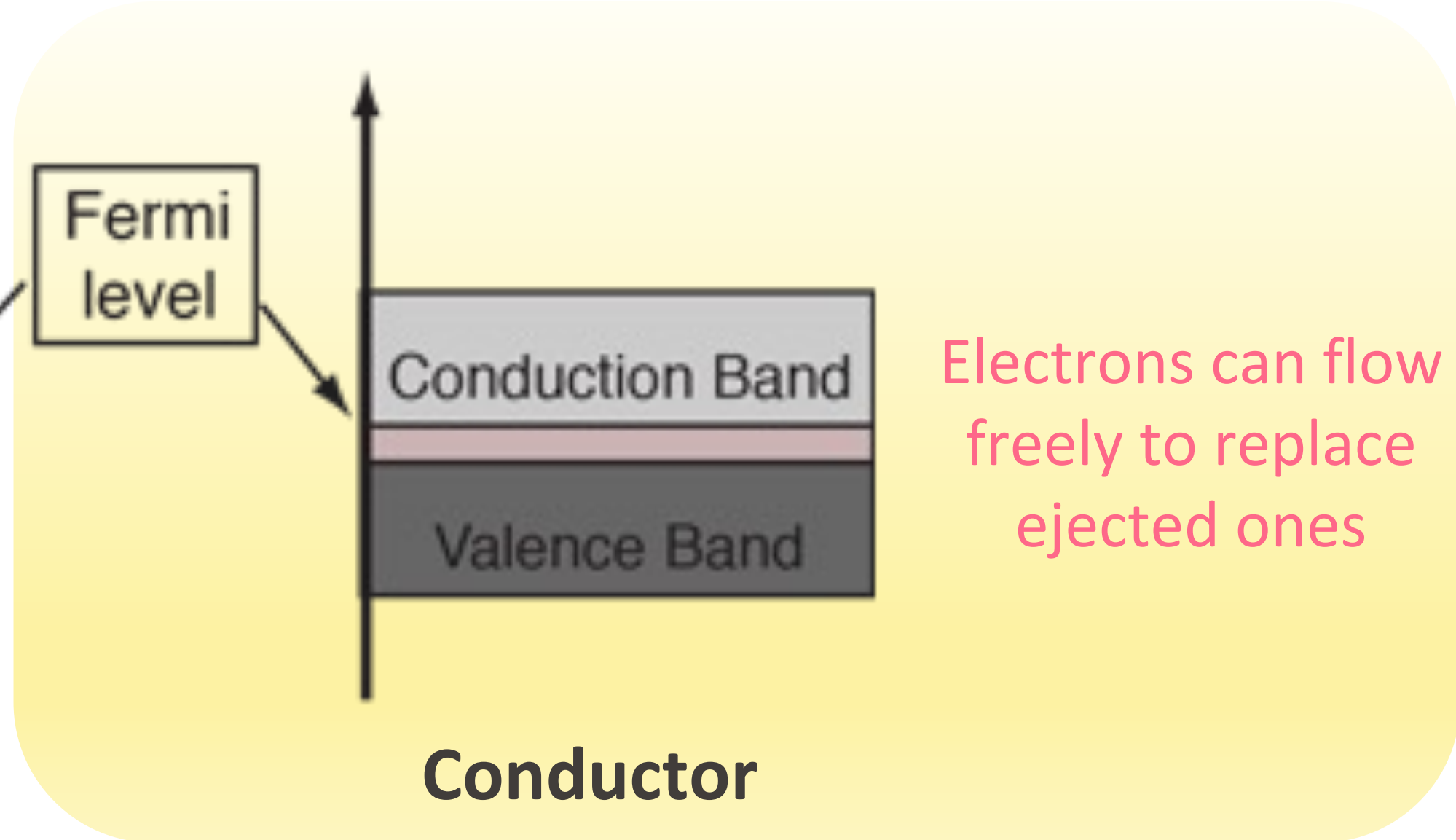
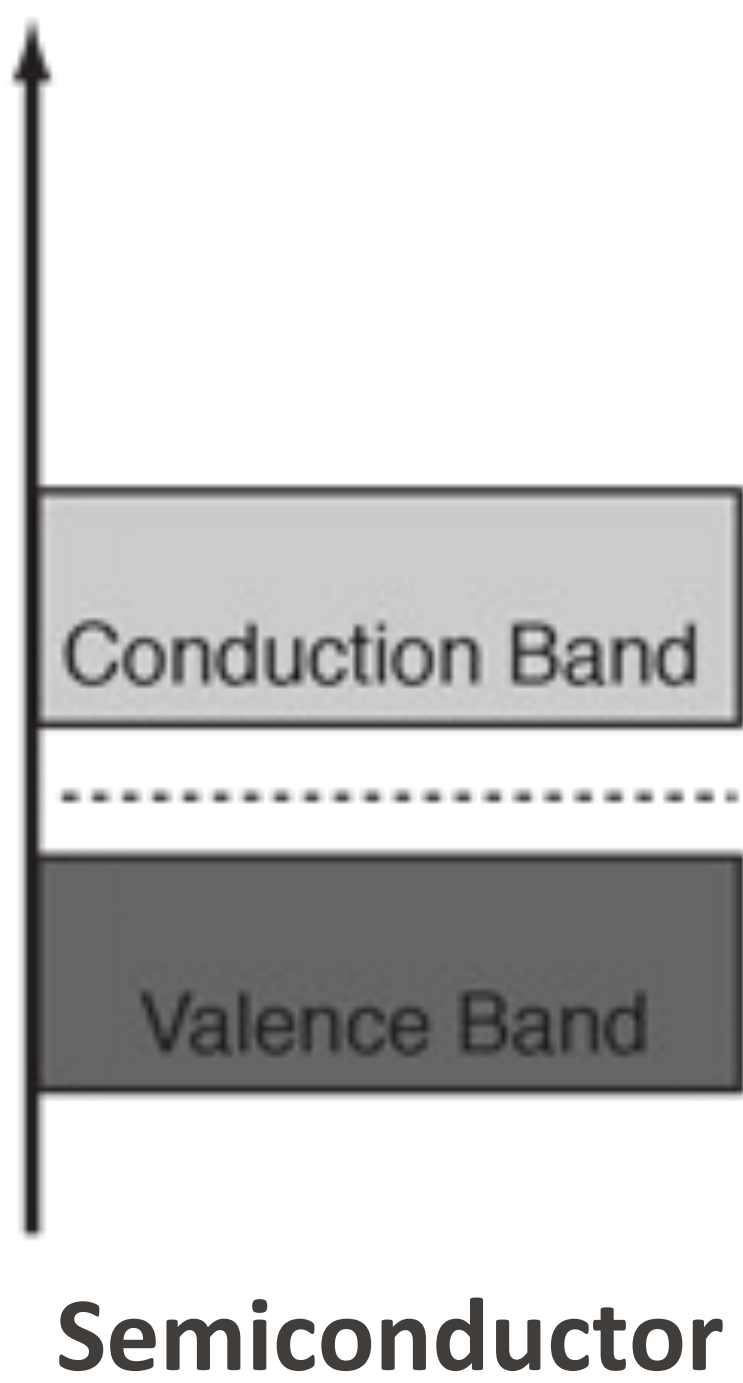
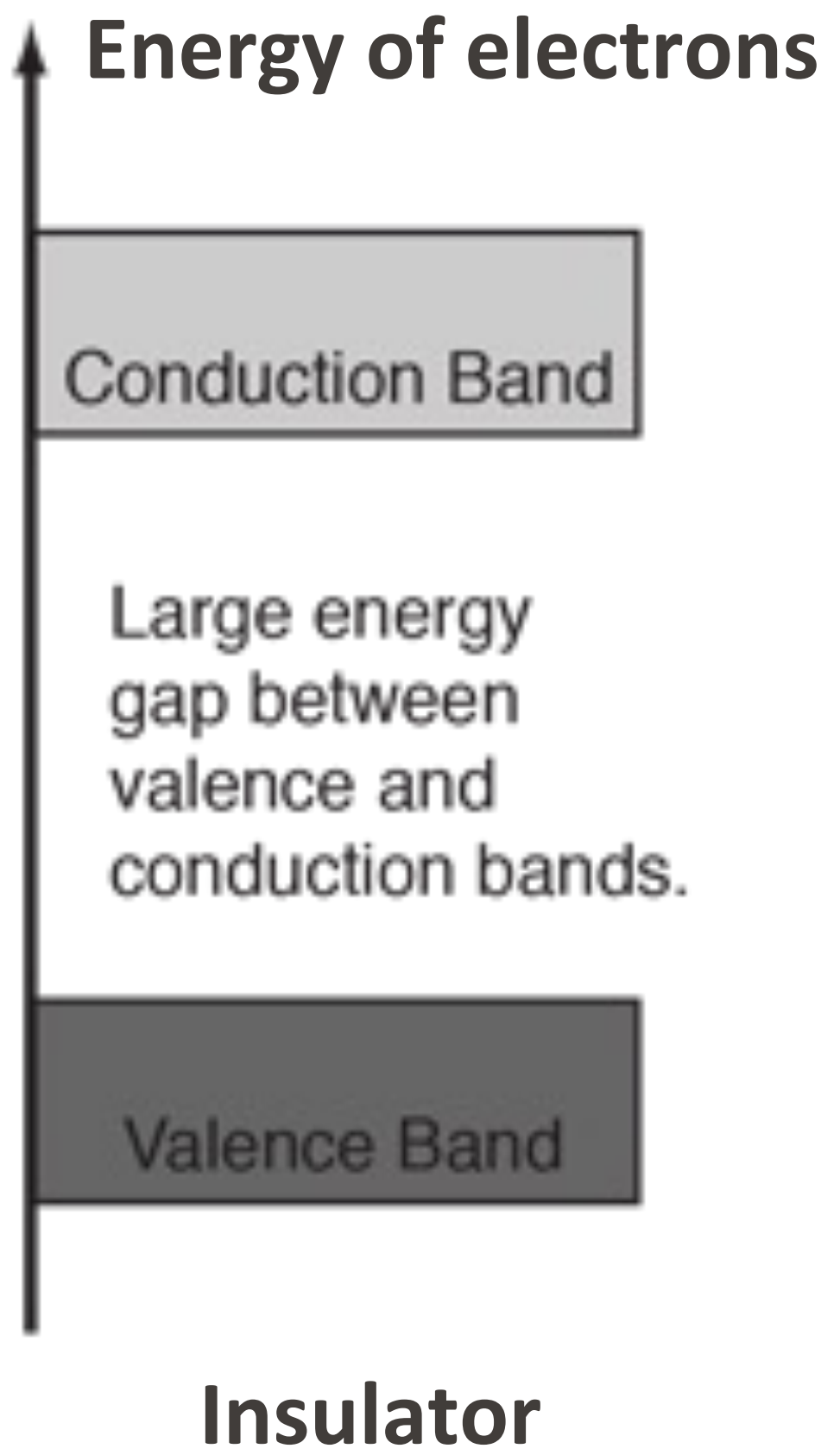
Limitations of XPS – General Challenges

- Requires UHV and clean surfaces – complex sample handling
- H and He cannot be detected (no core levels accessible)
- Slow analysis and expensive instrumentation

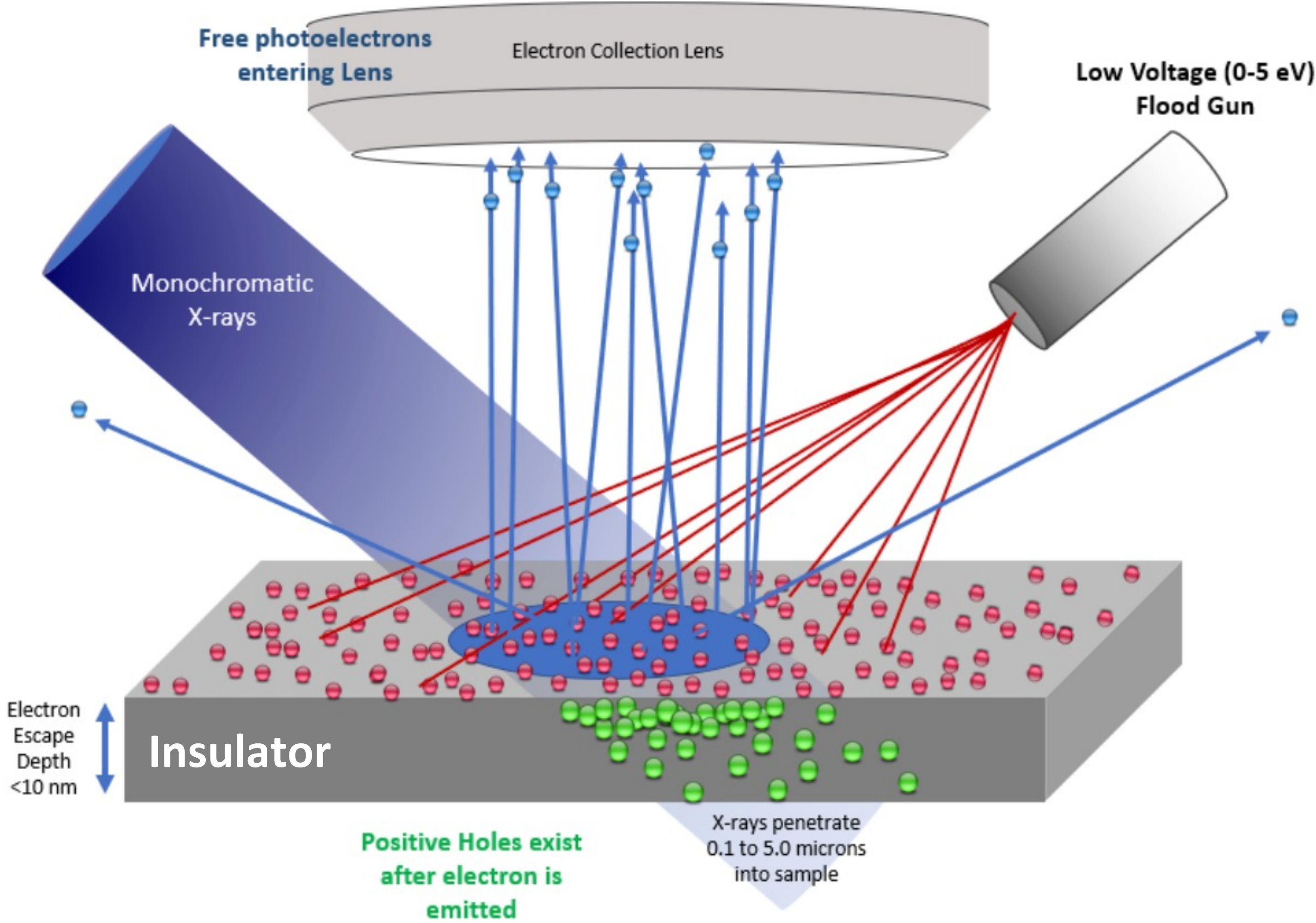


Limitations of XPS – Charging Effects on Insulators

Insulating materials charge because electrons cannot move to neutralize the positive surface left behind



Limitations of XPS – Neutralization Using Flood Gun



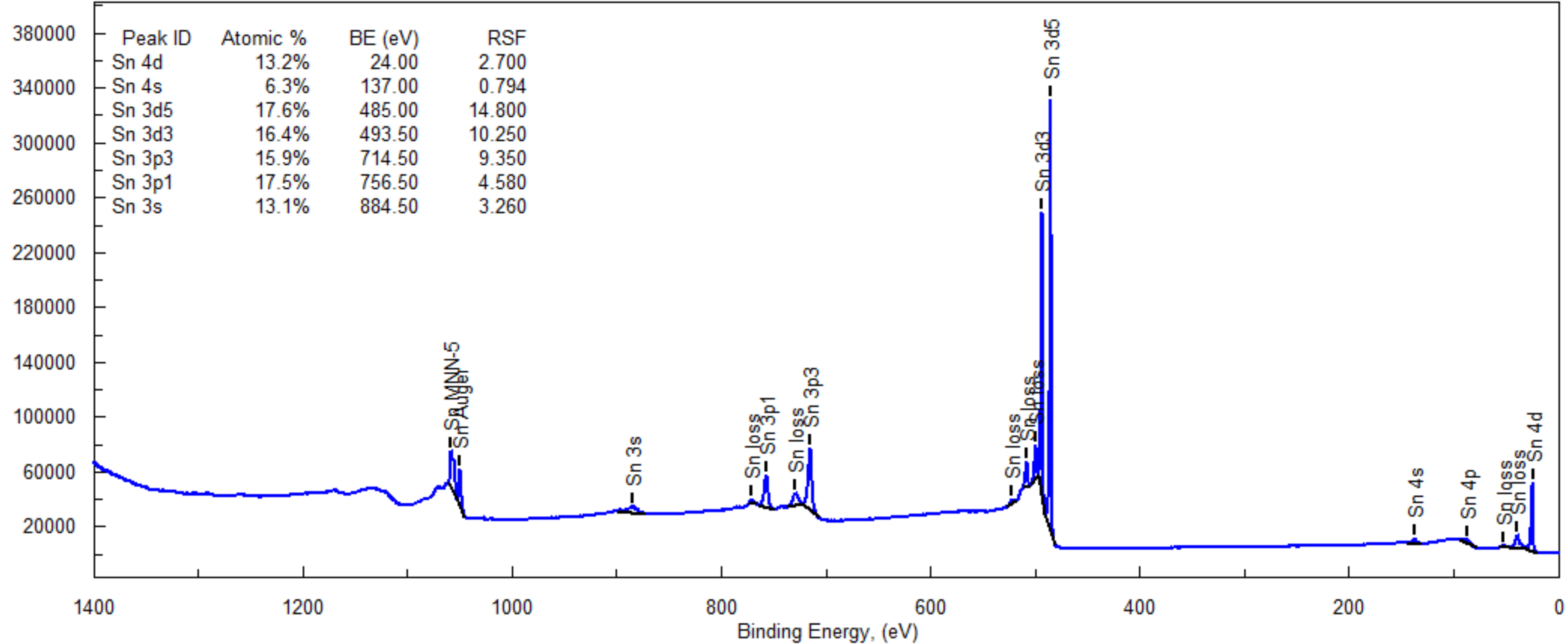
The flood gun fixes charging but reduces accuracy
XPS on insulators always requires careful peak referencing

Limitations of XPS – Peak Fitting/Referencing Challenging

This clean XPS spectra is just for a sample of tin (single material, pure and clean)

Sample Description: Sn, tin

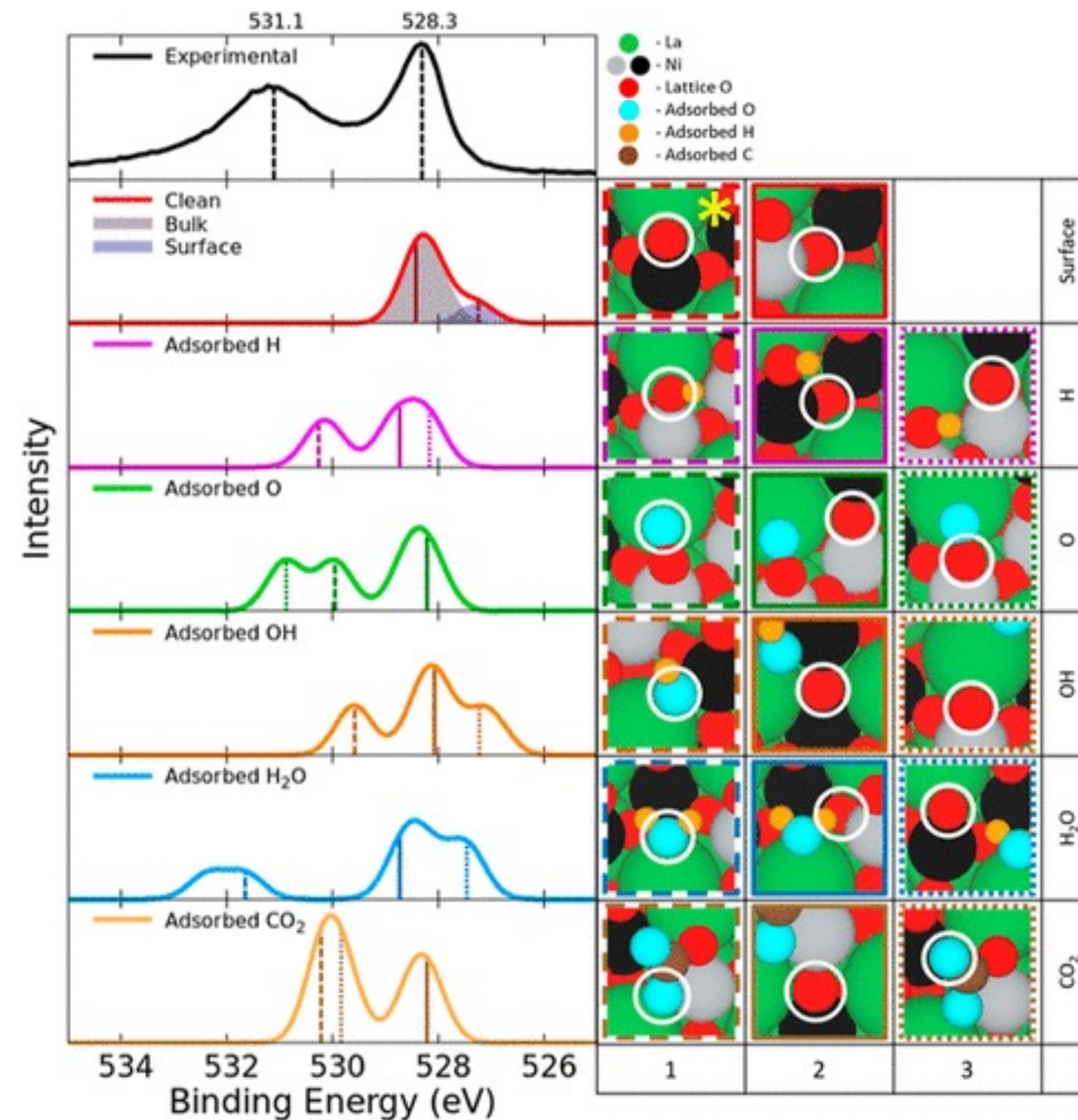
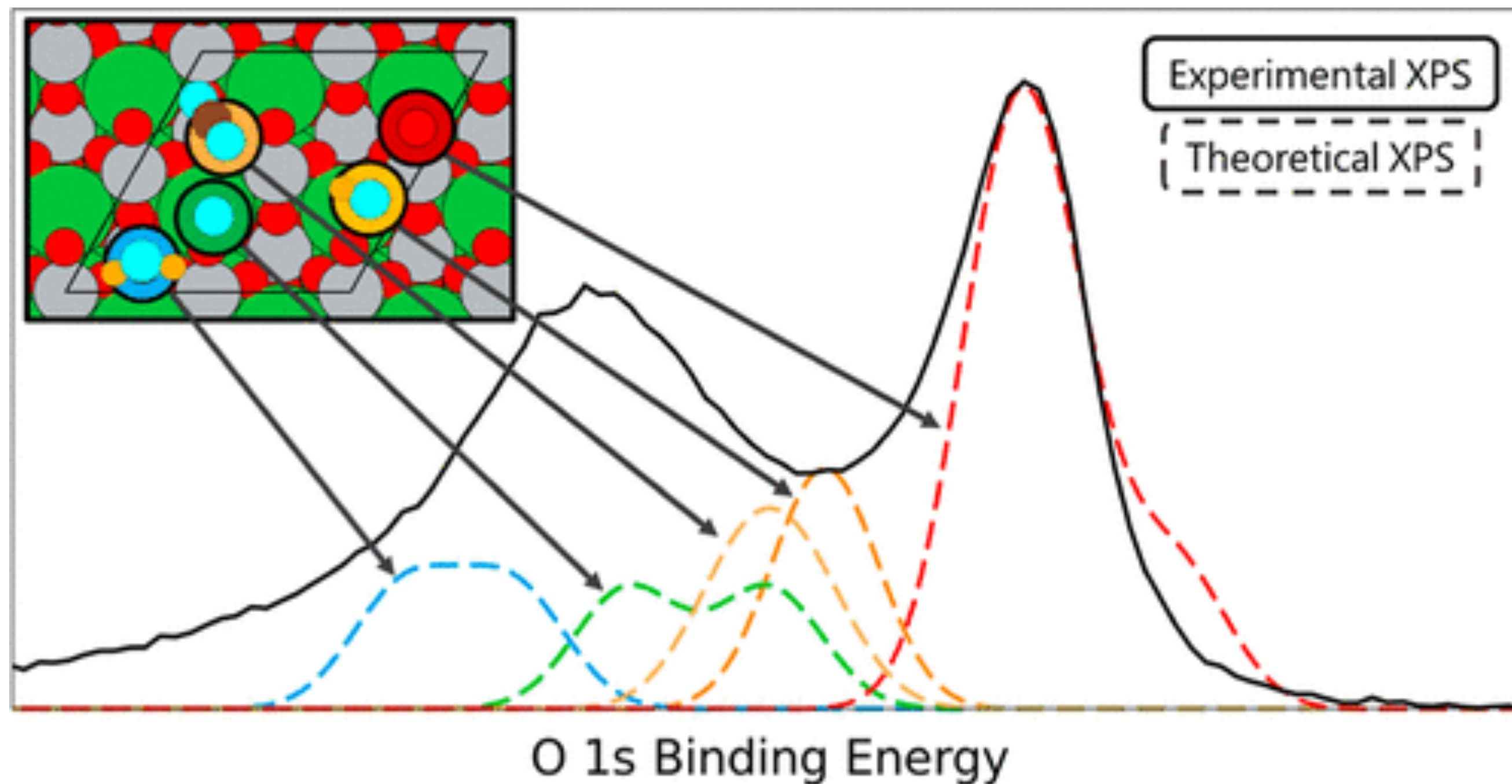
Counts



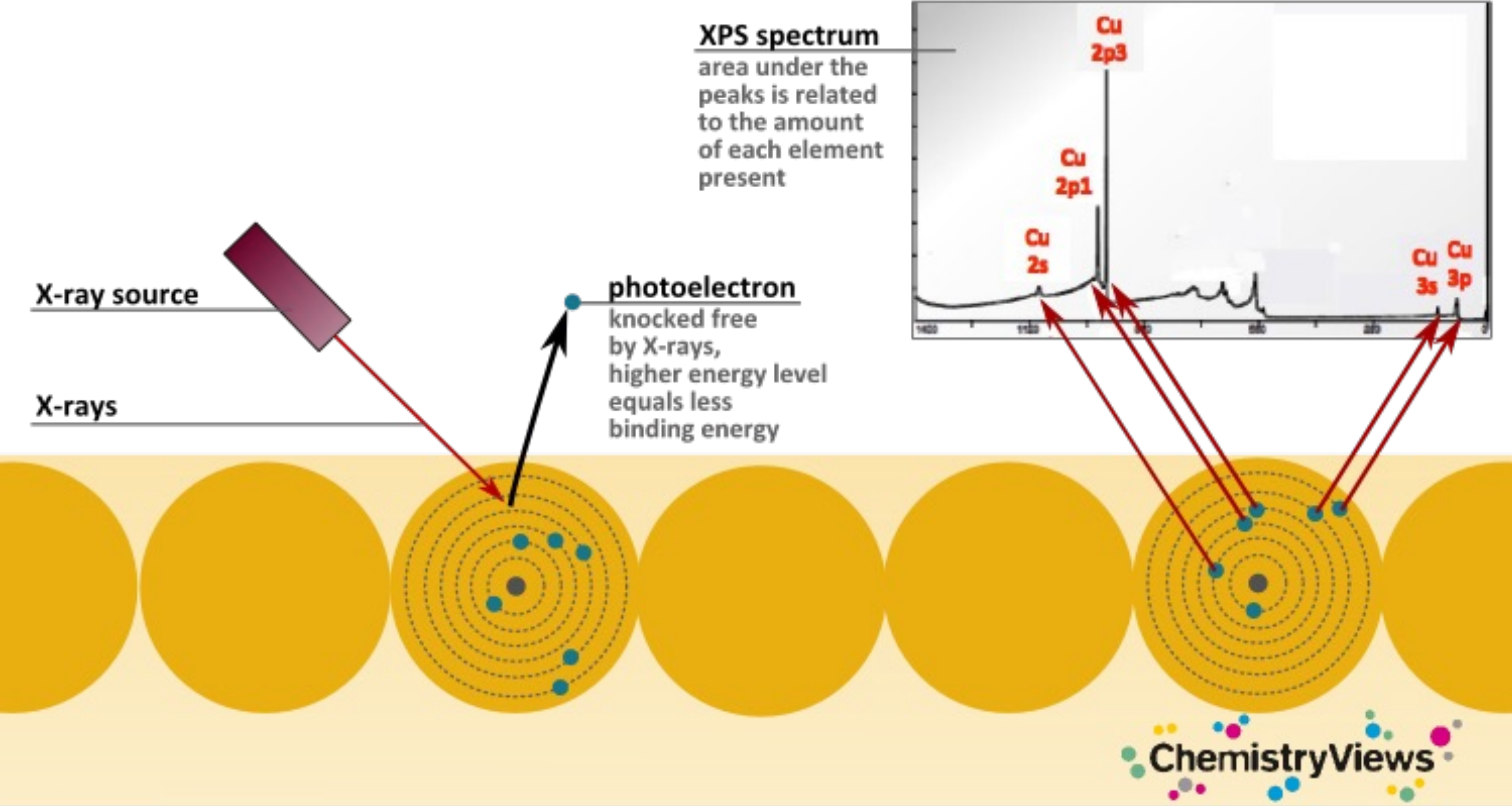
Limitations of XPS – Peak Fitting/Referencing Challenging

Peak fitting is challenging because XPS peaks can overlap, backgrounds must be subtracted, and different chemical states can look very similar so data can be misinterpreted

Perovskite-based oxides for electrochemical cells



Strength and Limitation of XPS: Sensitivity To Surface (5-10 nm)



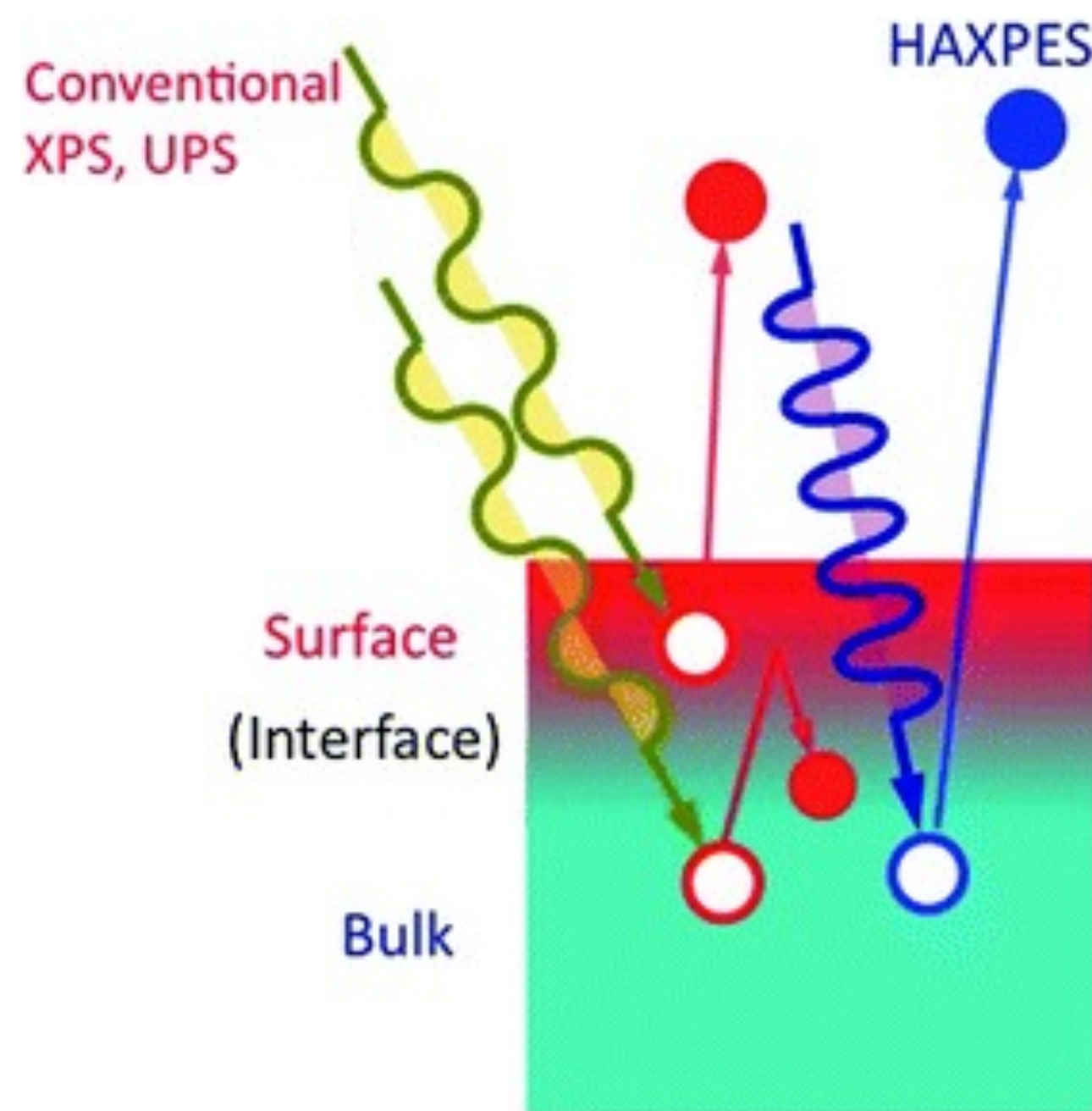
Key Takeaways

- XPS can identify elements on the surface of materials
 - XPS relies on the photoelectric effect
- Fundamental concepts: Binding energy, work function, Fermi level
 - Limitations of XPS – charging, peak fitting
- Advantage of XPS – sensitivity to 5-10 nm top of surface

What if you want to probe further?

Various Forms of Photoelectron Spectroscopy to Probe Materials

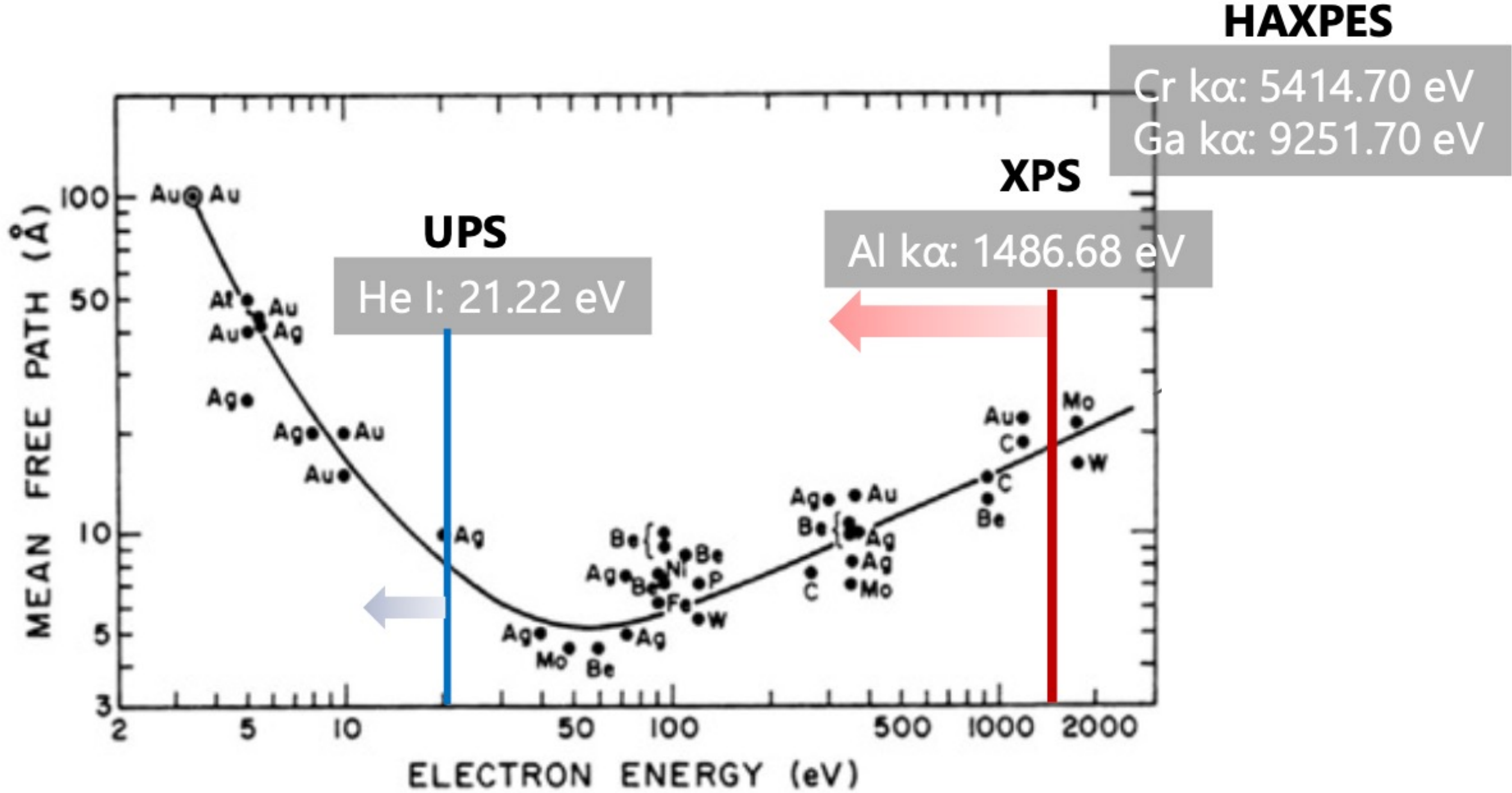
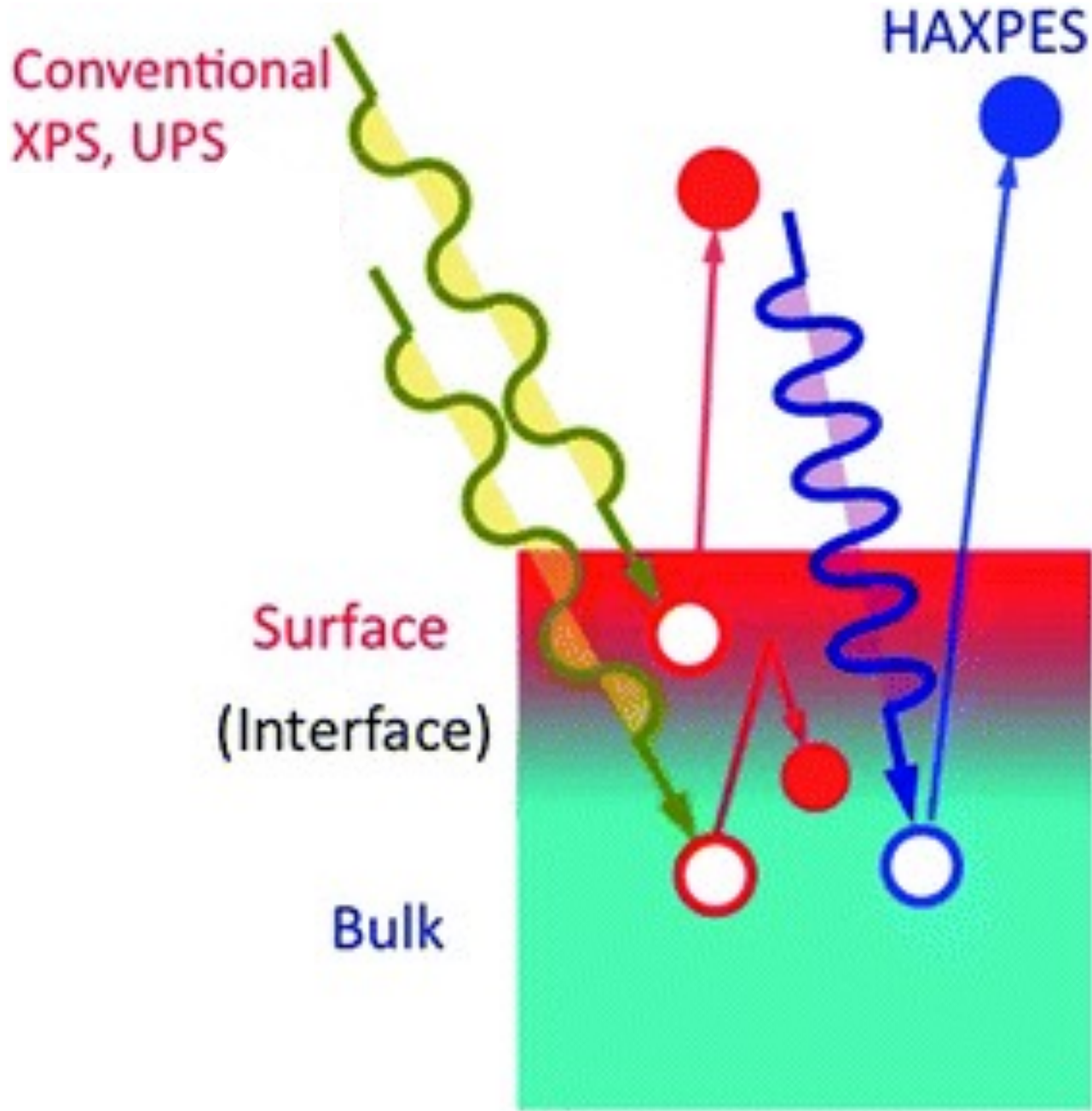
Kinetic energy of emitted electrons determines how deep into the material the technique can “see”



Technique	Photon source	Measures	Main use
UV Photoelectron Spectroscopy (UPS)	UV (20–50 eV)	Valence electrons	Electronic structure, work function, bonding at surface
X-ray Photoelectron Spectroscopy (XPS)	Soft X-rays (≈ 1.5 keV)	Core electrons	Elemental ID + chemical states at the surface
Hard X-ray Photoelectron Spectroscopy (HAXPES)	Hard X-rays (5–10 keV)	Deep core + buried layers	Probing deeper beneath surface / buried interfaces

Various Forms of Photoelectron Spectroscopy to Probe Materials

Higher photon energy → higher KE electrons → longer mean free path → deeper information



Seah & Dench. Surf. Interf. Anal. | 1979

Summary of Today's Class

- Scanning Electron Microscopy combined with electron backscatter diffraction (EBDS) and energy-dispersive x-ray spectroscopy (EDX)
- Secondary ion mass spectrometry (SIMS) and x-ray photoelectron spectroscopy (XPS)
- Challenges and opportunities of XPS
- Fundamentals: photoelectric effect, binding energy, work function

Prof. Nako Nakatsuka
nako.nakatsuka@epfl.ch

EPFL
Laboratory of Chemical Nanotechnology
Campus Biotech
Chemin des Mines 9
1202, Geneva

<https://www.epfl.ch/labs/chemina/>

