CHEMINA

Characterization of Surfaces & Interfaces
Lesson 7

MSE 304

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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

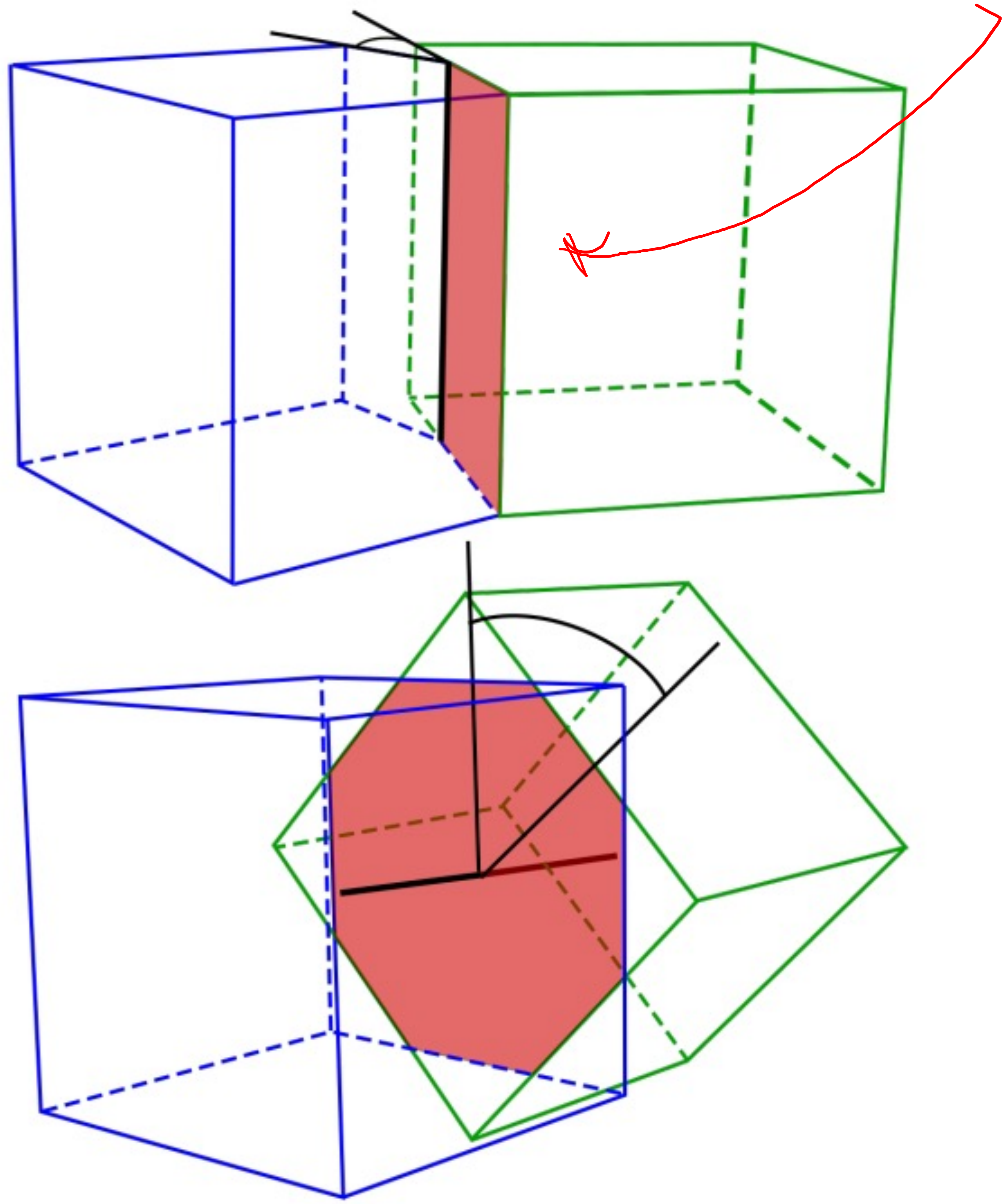
13: Biosensor Fundamentals

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



grain boundary

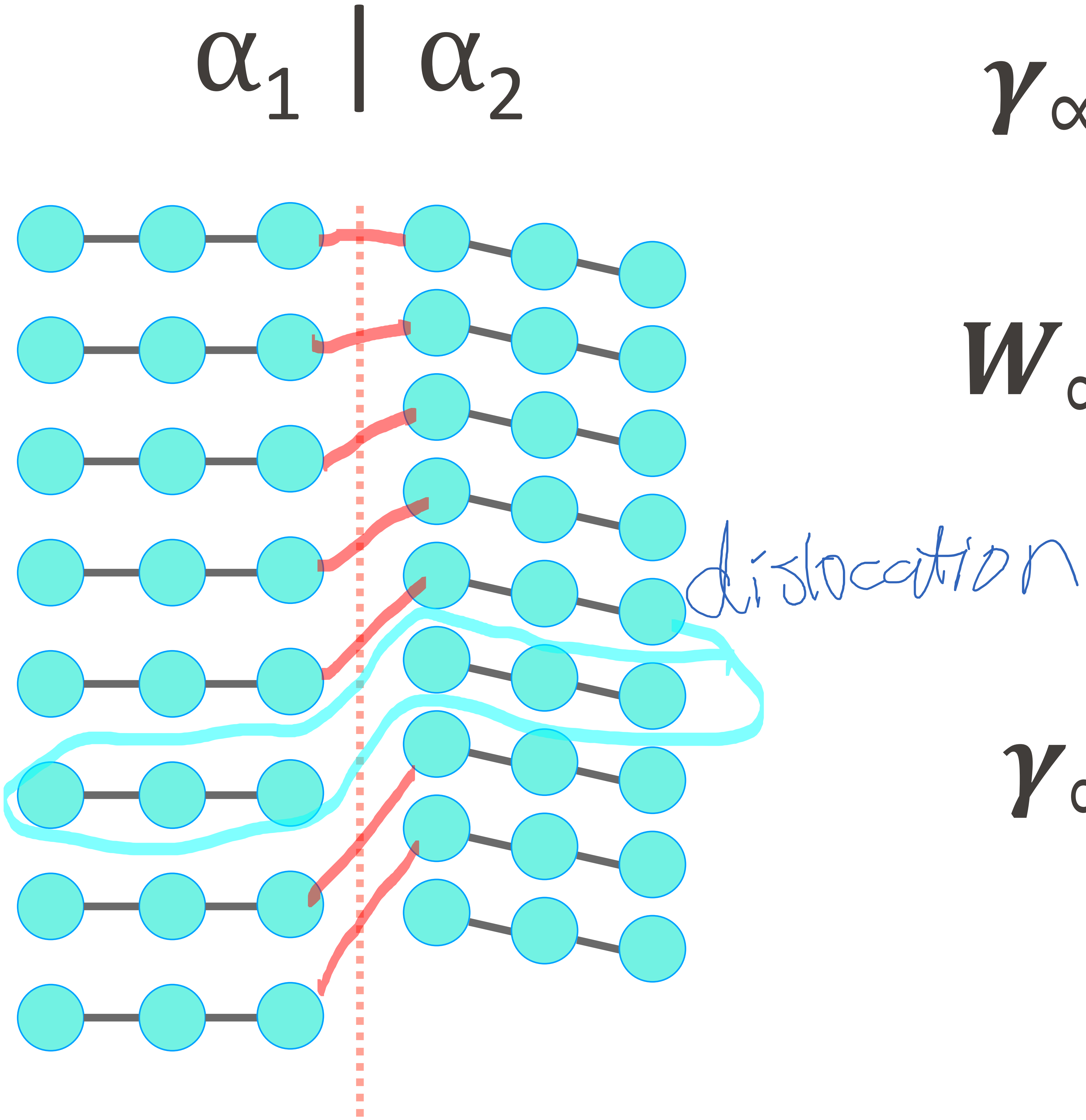
axis of rotation

Tilt grain boundary

Twist grain boundary

Recap: Thermodynamics of Homophase Solid-Solid Interfaces

Interfacial energy between two solid phases



$$\gamma_{\propto_1\propto_2} = \underline{\gamma_{\propto_1}} + \underline{\gamma_{\propto_2}} - \boxed{W_{\propto_1\propto_2}}$$

$$W_{\propto_1\propto_1} \cong \gamma_{\propto_1} + \gamma_{\propto_2}$$

$$\gamma_{\propto_1\propto_2} = \sum_i b_i + E_l$$

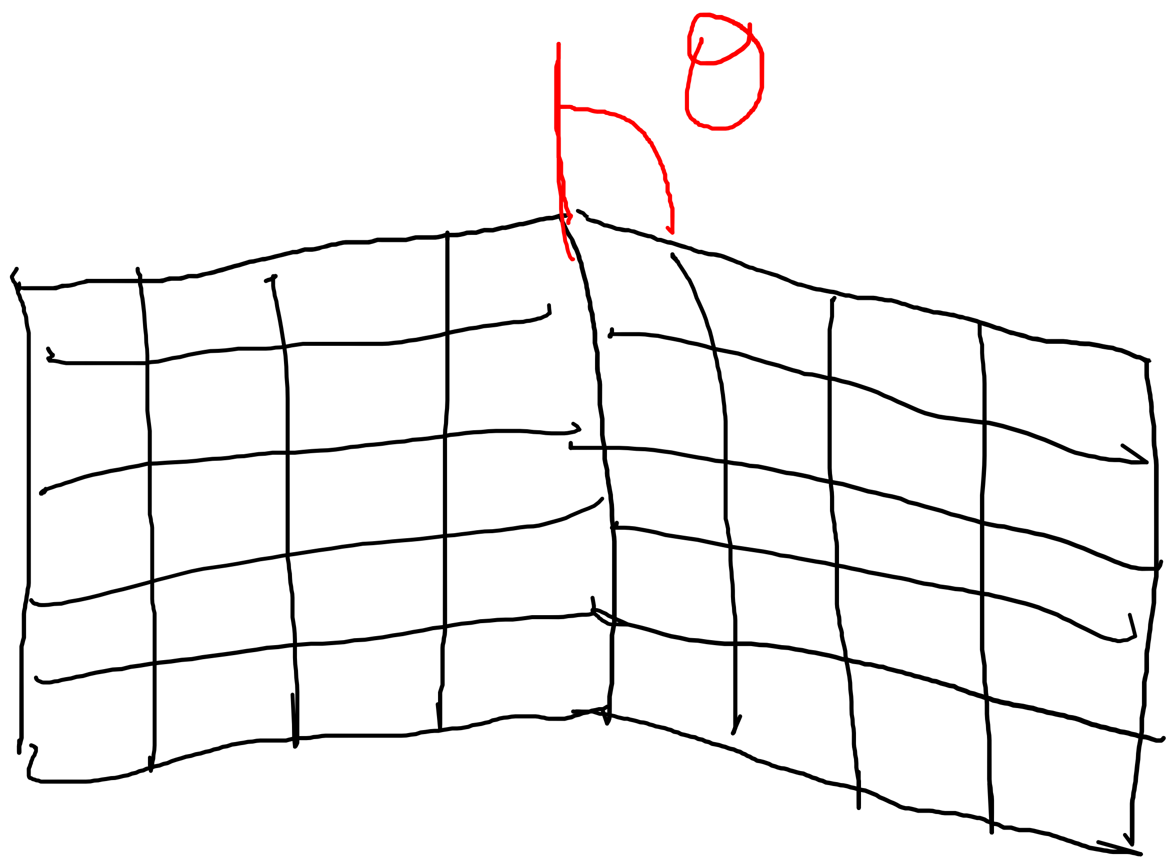
Elastic energy

Energy per broken bond

Recap: Specific Cases of Solid-Solid Interfaces

Homogeneous grain boundary with low angle

$$\alpha_1 \mid \alpha_2$$

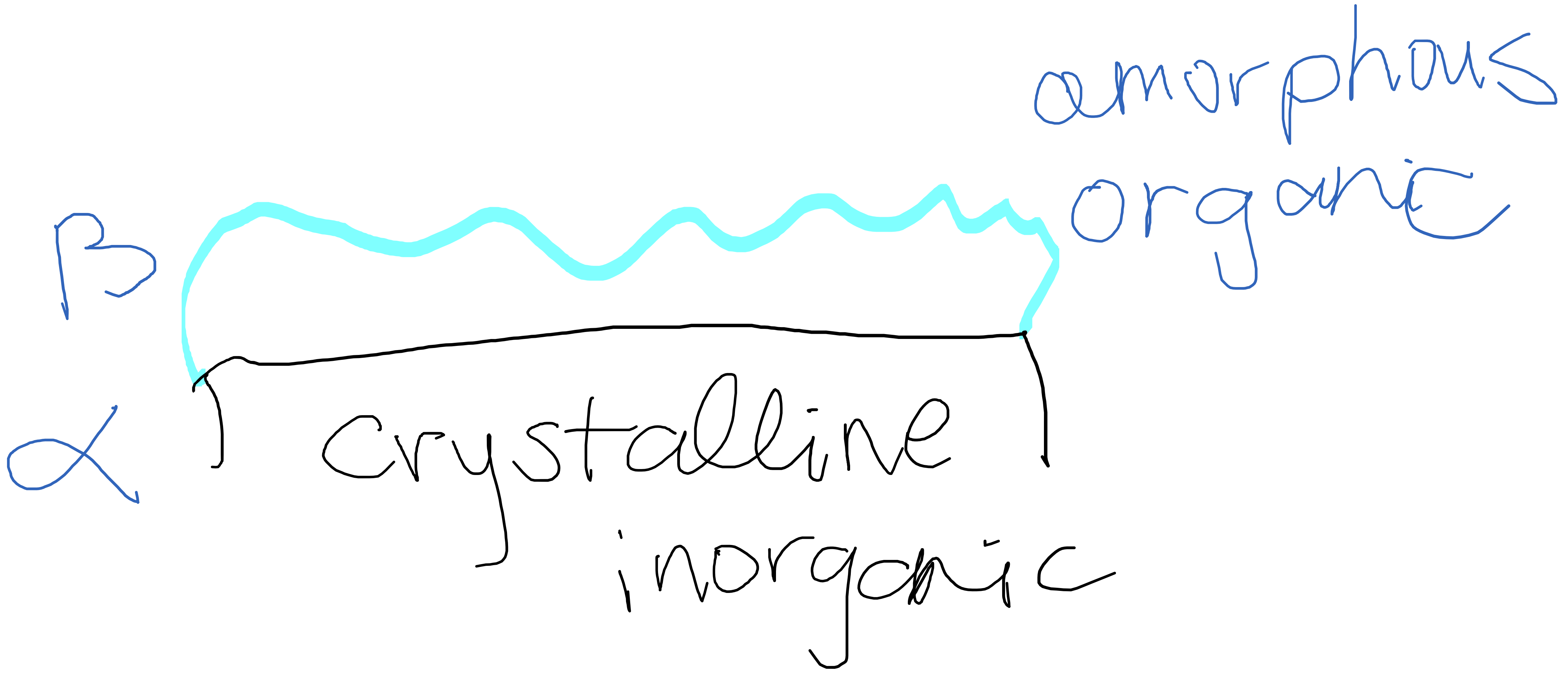


$$\gamma_{\alpha_1\alpha_2} = 2\gamma_{\alpha_1} - W_{\alpha_1\alpha_2} = \boxed{E_l}$$

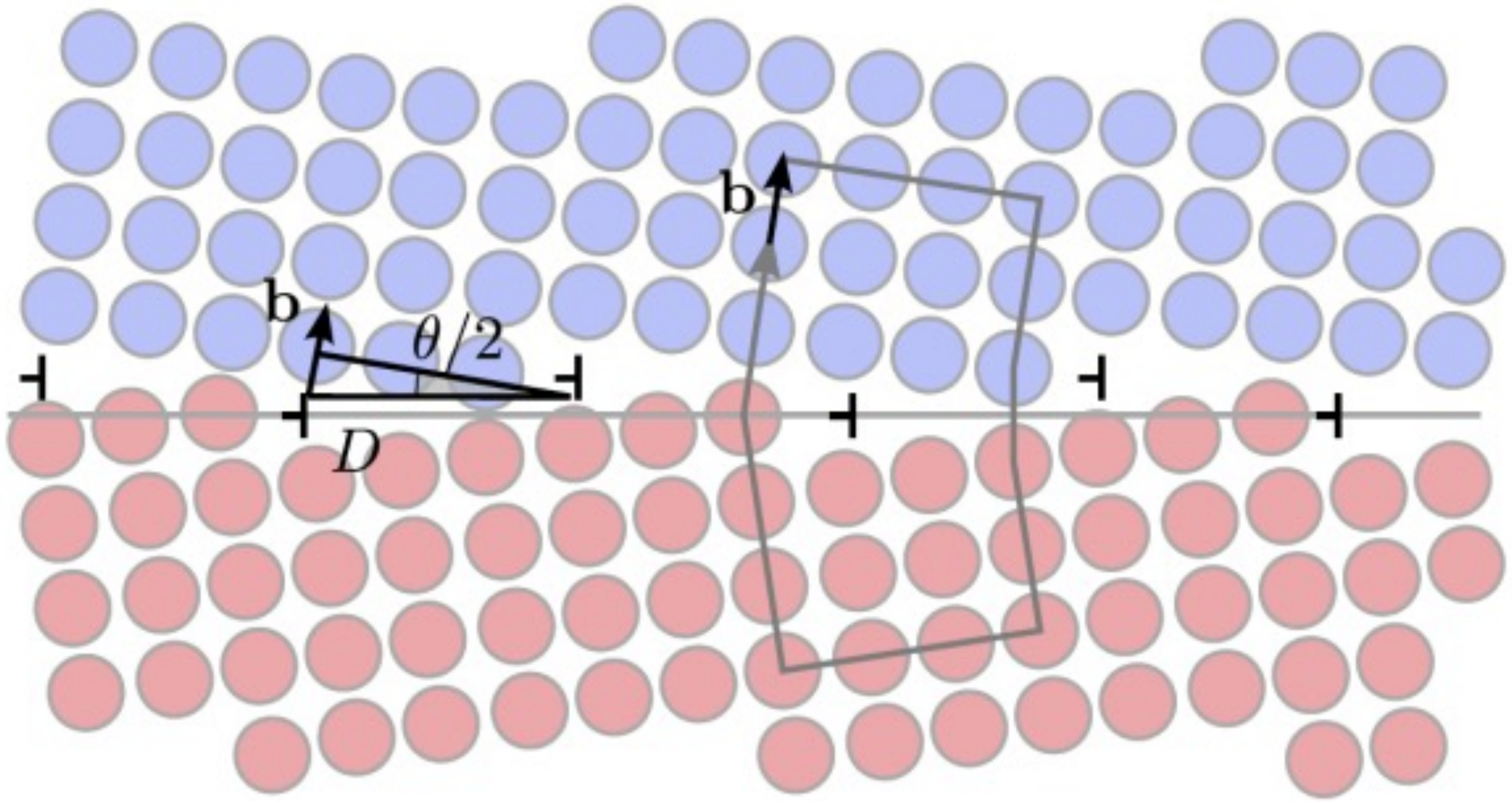
Heterogeneous solid-solid interface

$$\alpha \mid \beta$$

γ_α & γ_β dominate



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

$$\gamma_{\propto_1\propto_2} = \gamma_{\propto_1} + \gamma_{\propto_2} - W_{\propto_1\propto_2}$$

Grain boundary interfacial energy

$$\gamma_{\propto_1\propto_2} = \mathrm{E}_{\perp} \;\;\mathrm{x}\;\; (1/D)$$

Energy associated per dislocation

Density of dislocation

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

Larger θ ➔ more dislocations per unit length

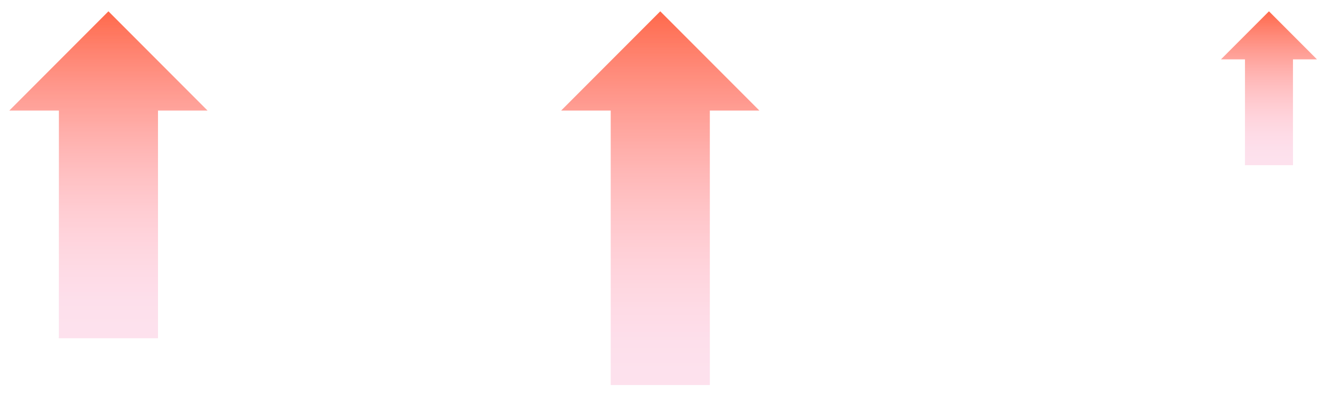
Smaller θ ➔ dislocations farther apart

Entropy vs. Enthalpy in Grain Boundaries

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

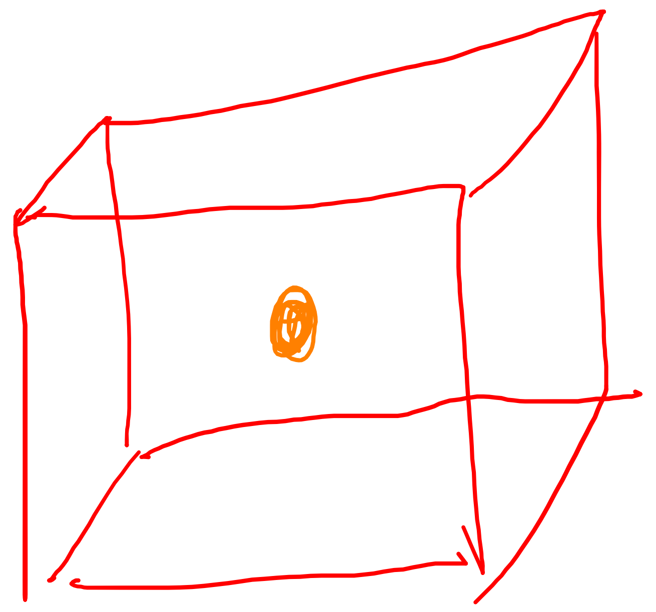
BUT this entropy gain is small *vs.* enthalpy cost due to bond distortion and grain boundary energy

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



More atomic disorder ➔ more microstates
Dislocation density measures disorder

Broken bonds + elastic strain
γ_{GB} = high



Different defects have different stabilizing factors:

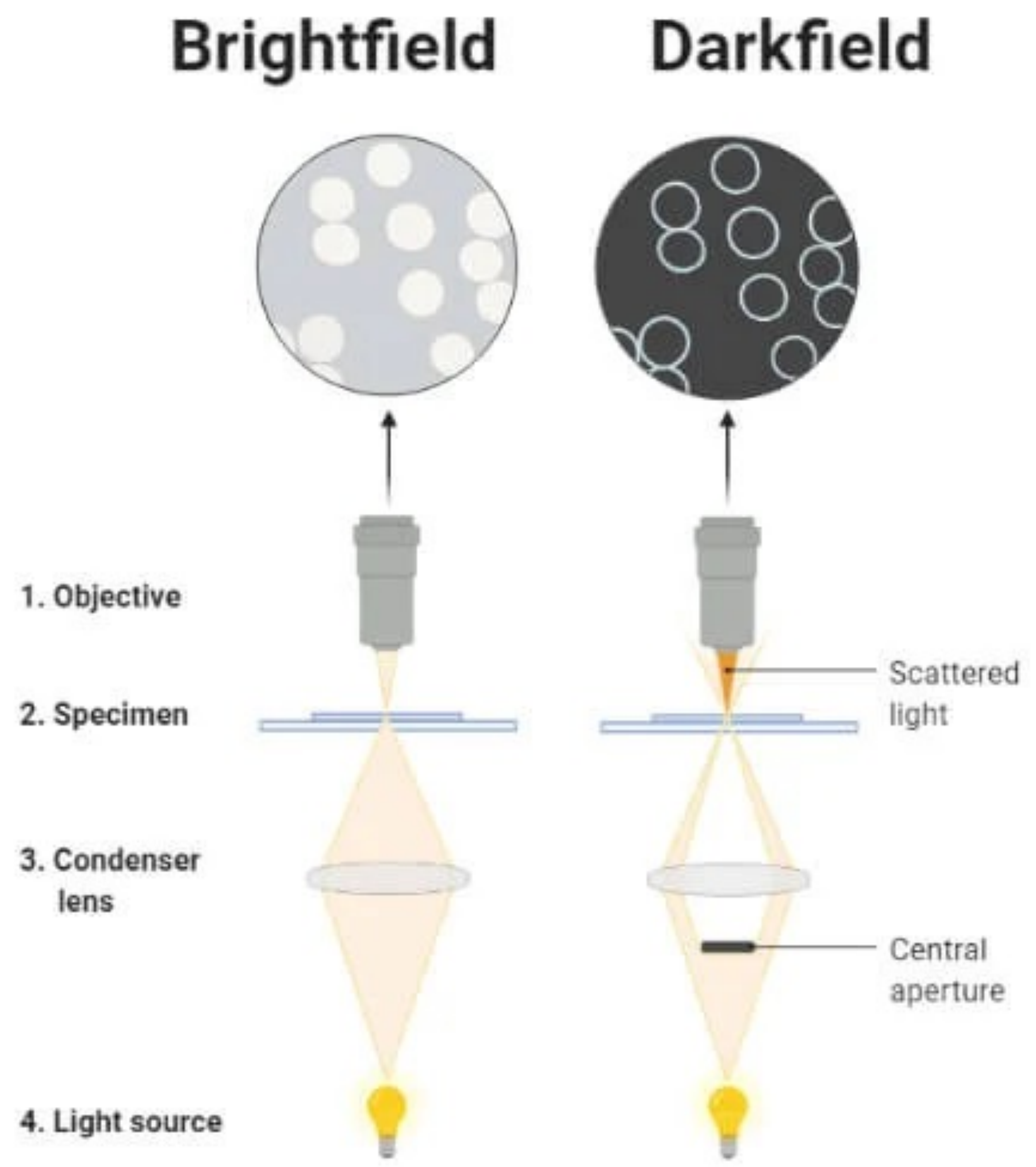
- Point defects stabilized by **entropy** ➔ always exist at equilibrium
- Grain boundaries dominated by **enthalpy** ➔ system tries to remove them

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

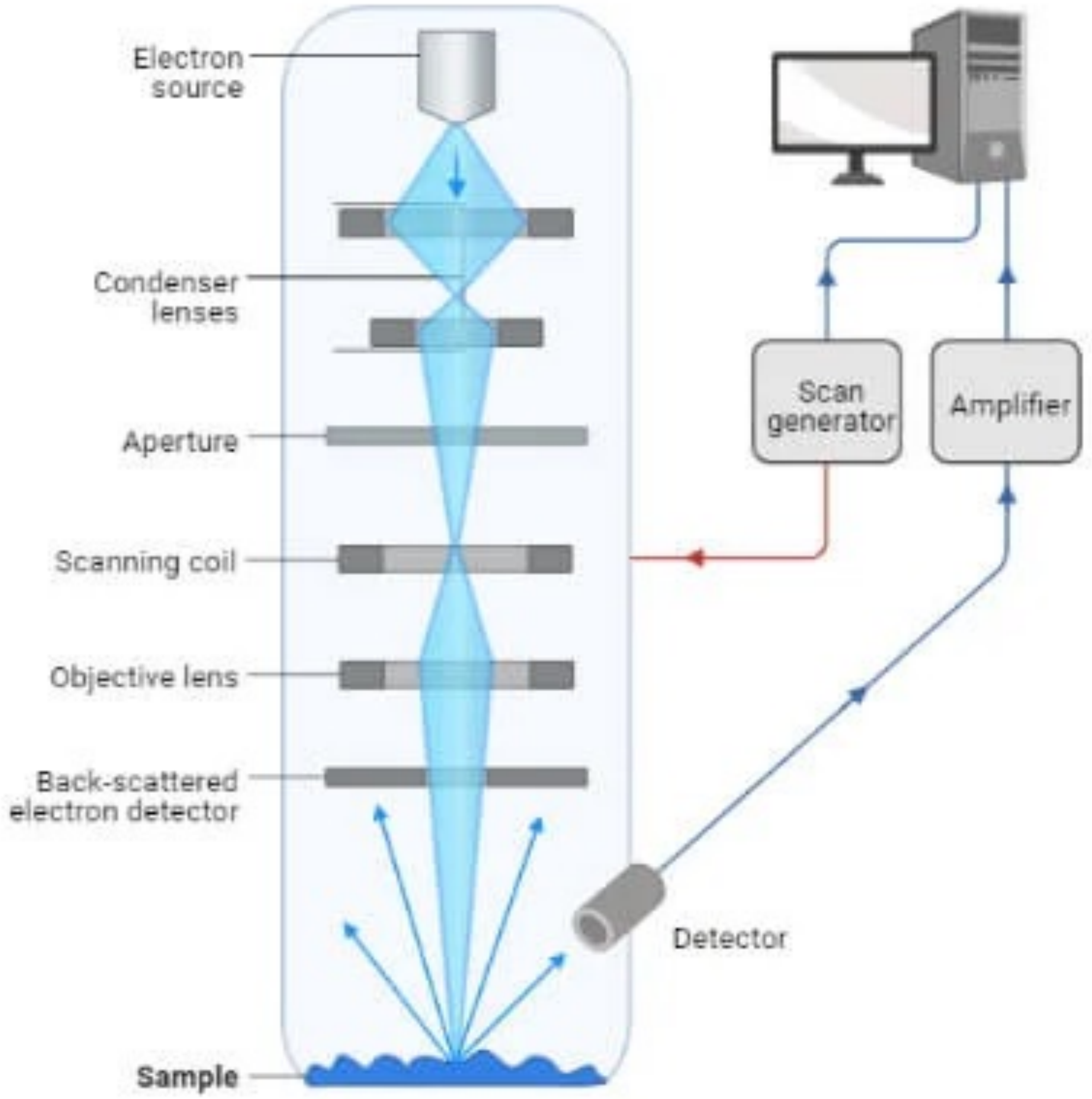
Electron Microscopy to Visualize Real Surfaces and Materials

Light Microscopy

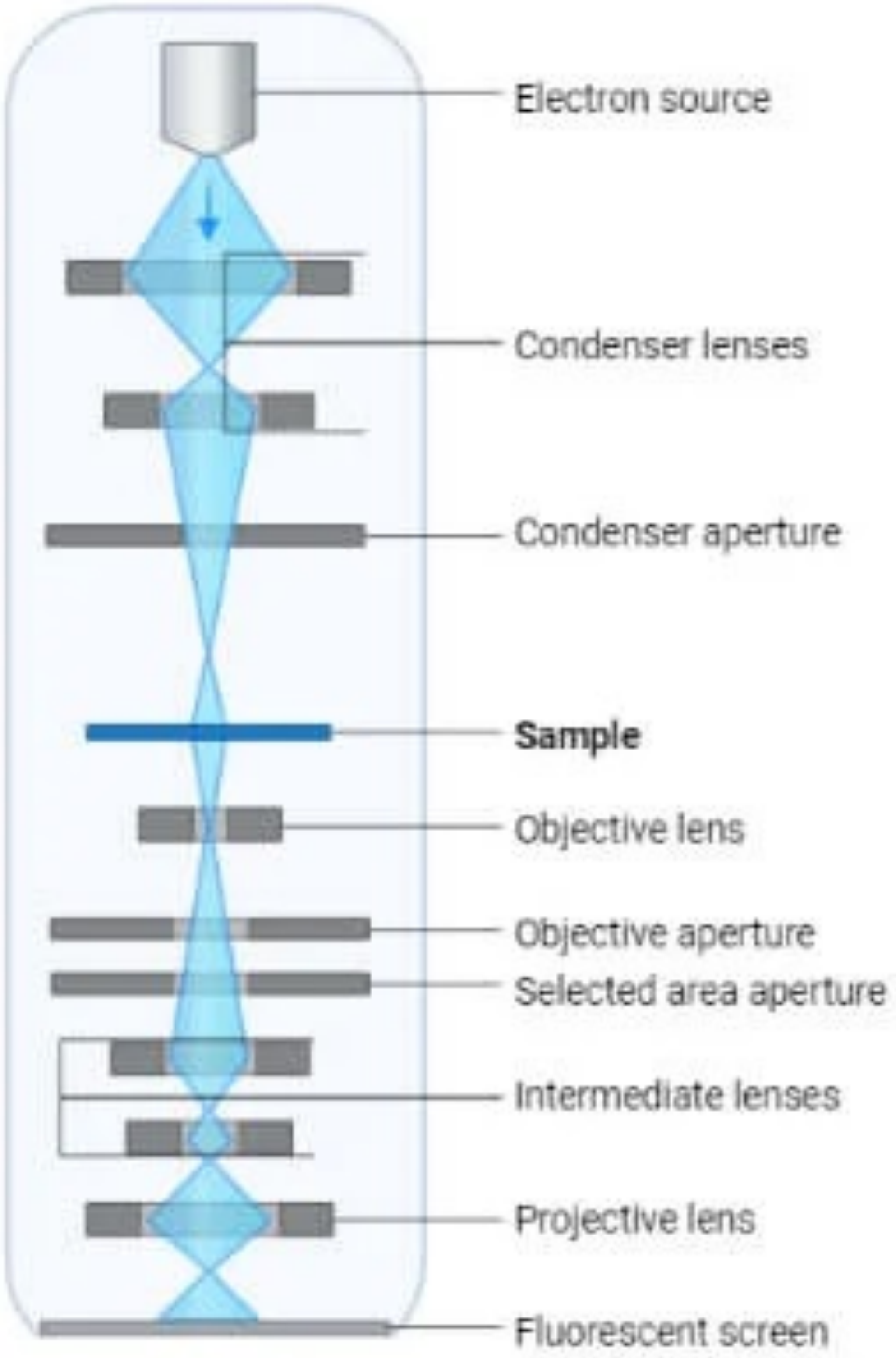


Electron Microscopy

Scanning Electron Microscopy (SEM)



Transmission Electron Microscopy (TEM)



Microbe Notes

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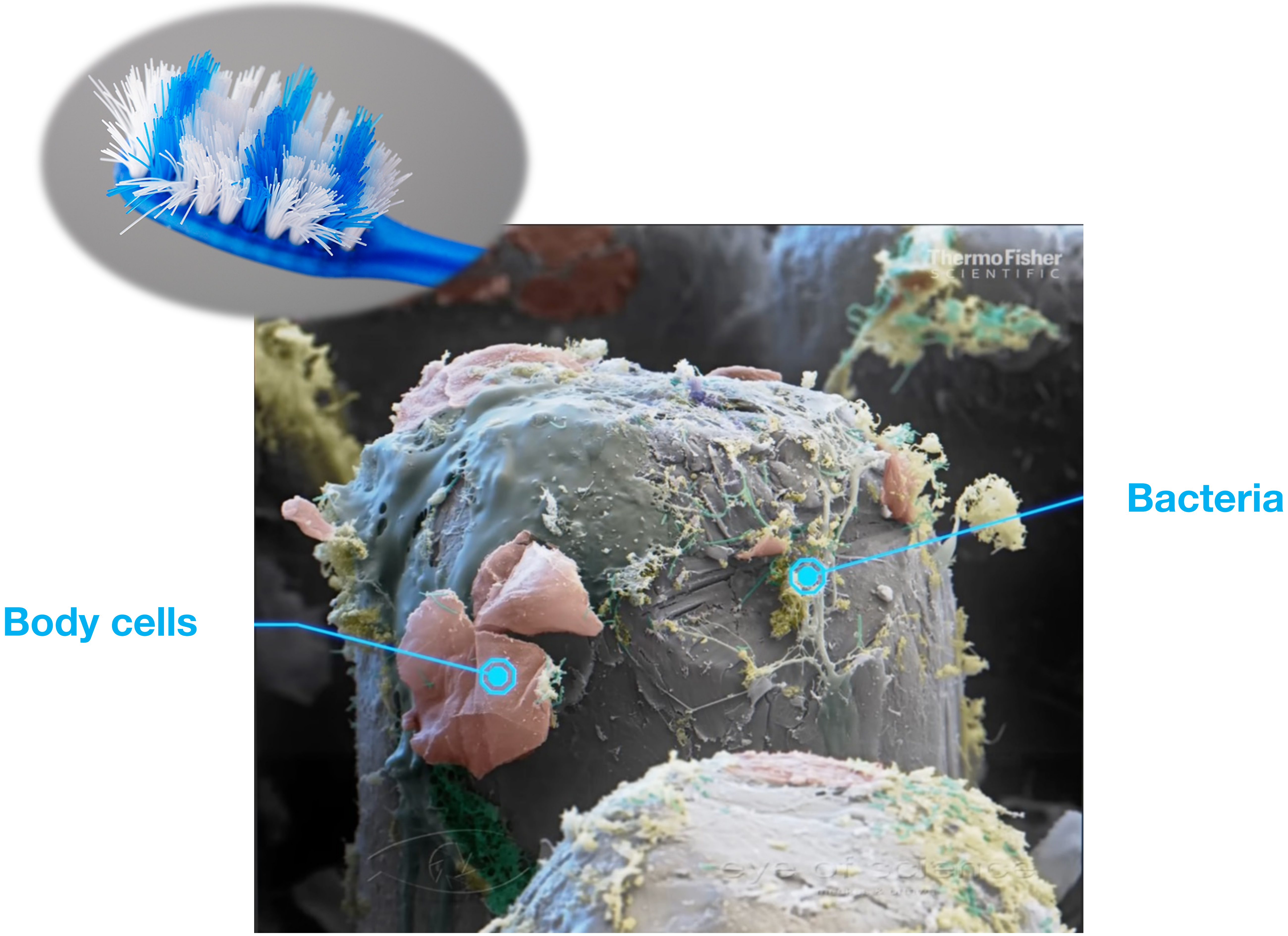
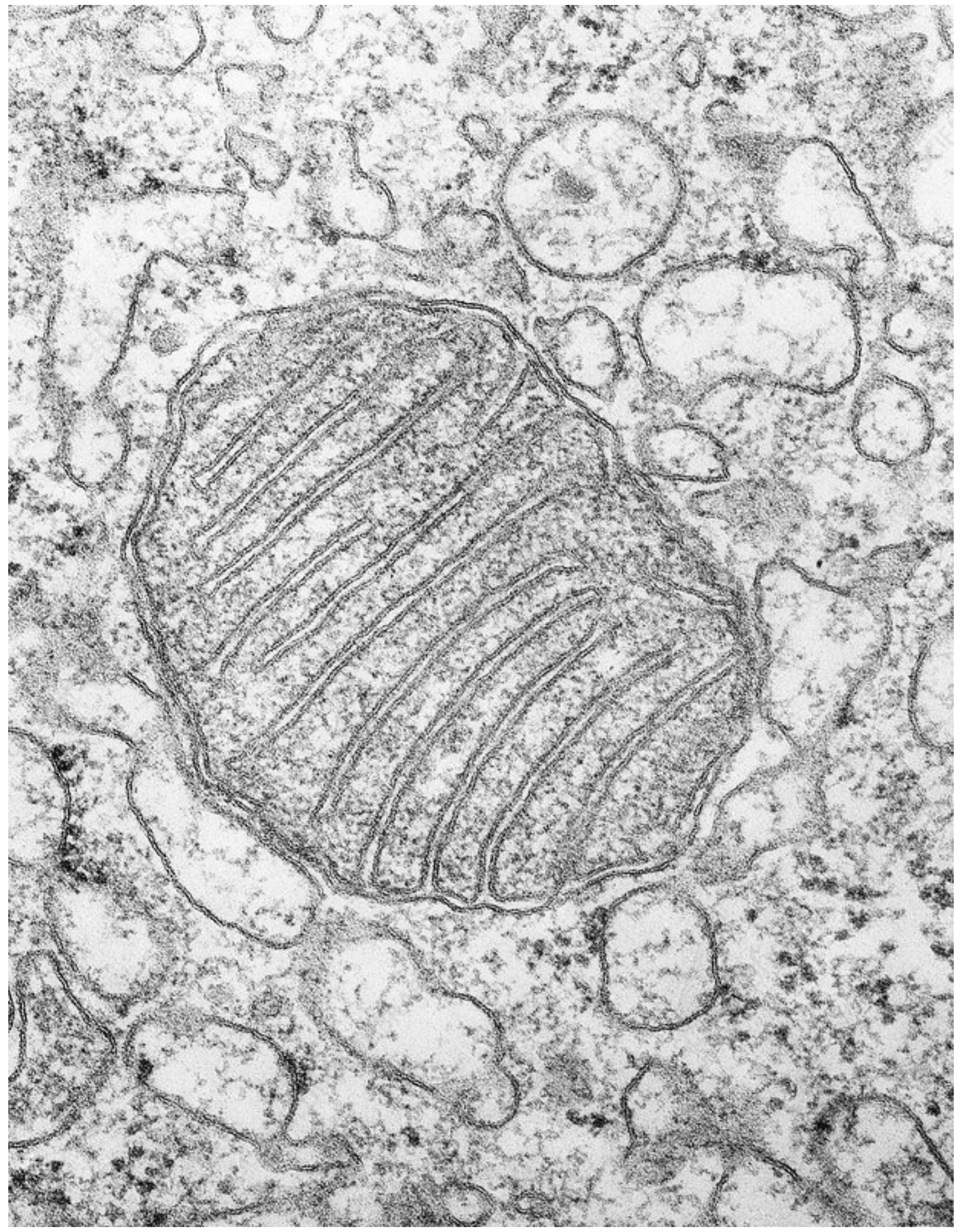
Electron Microscopy Techniques

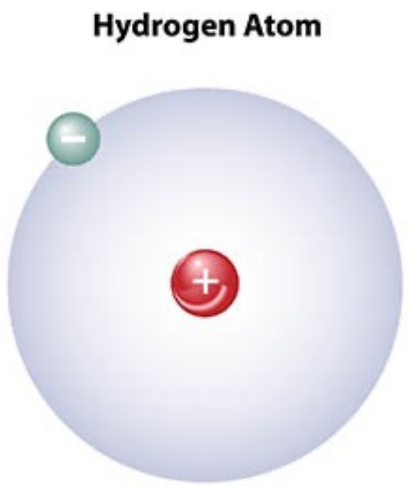
Scanning Electron Microscopy (SEM)



Max resolution: 1 nm

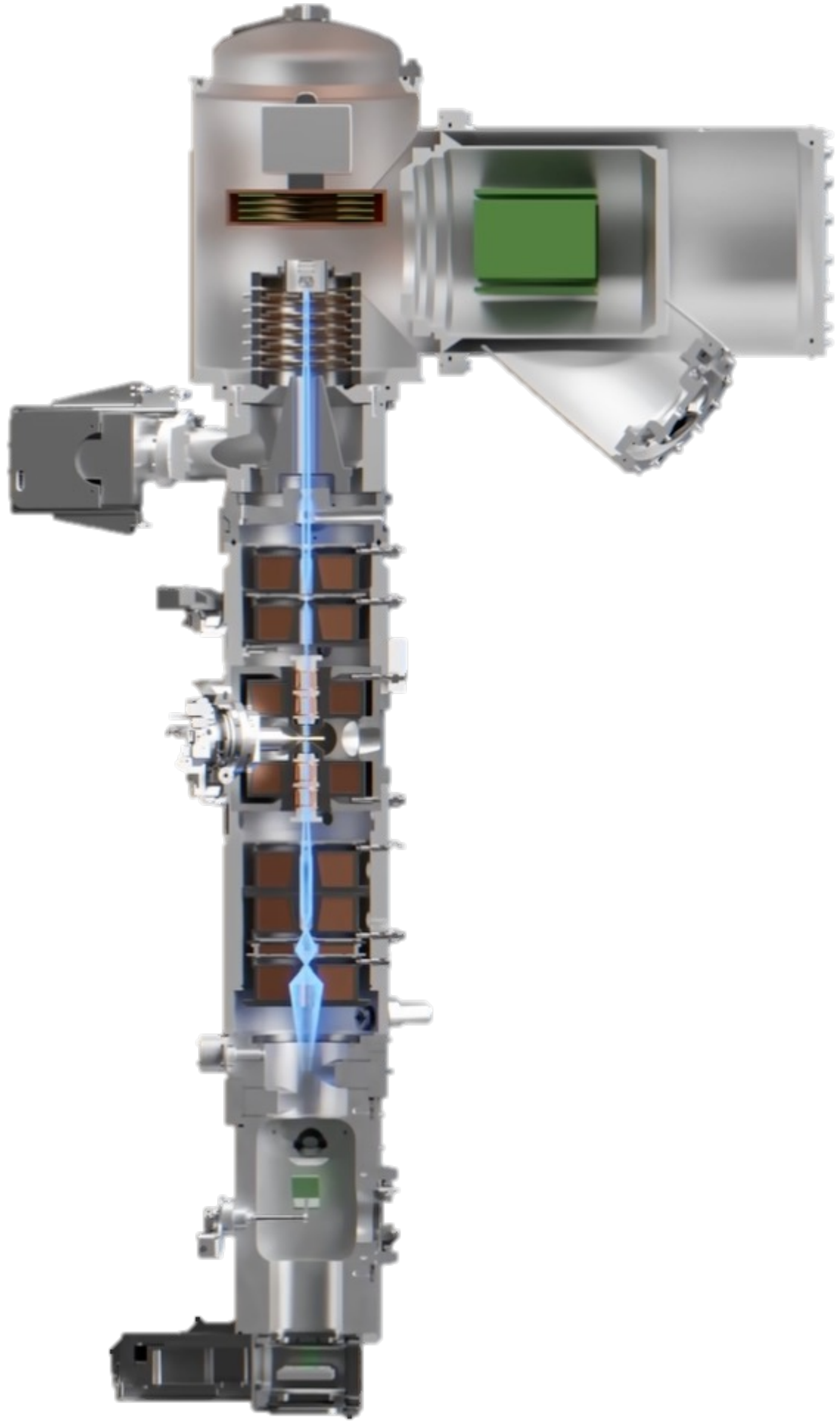
Transmission Electron Microscopy (TEM)



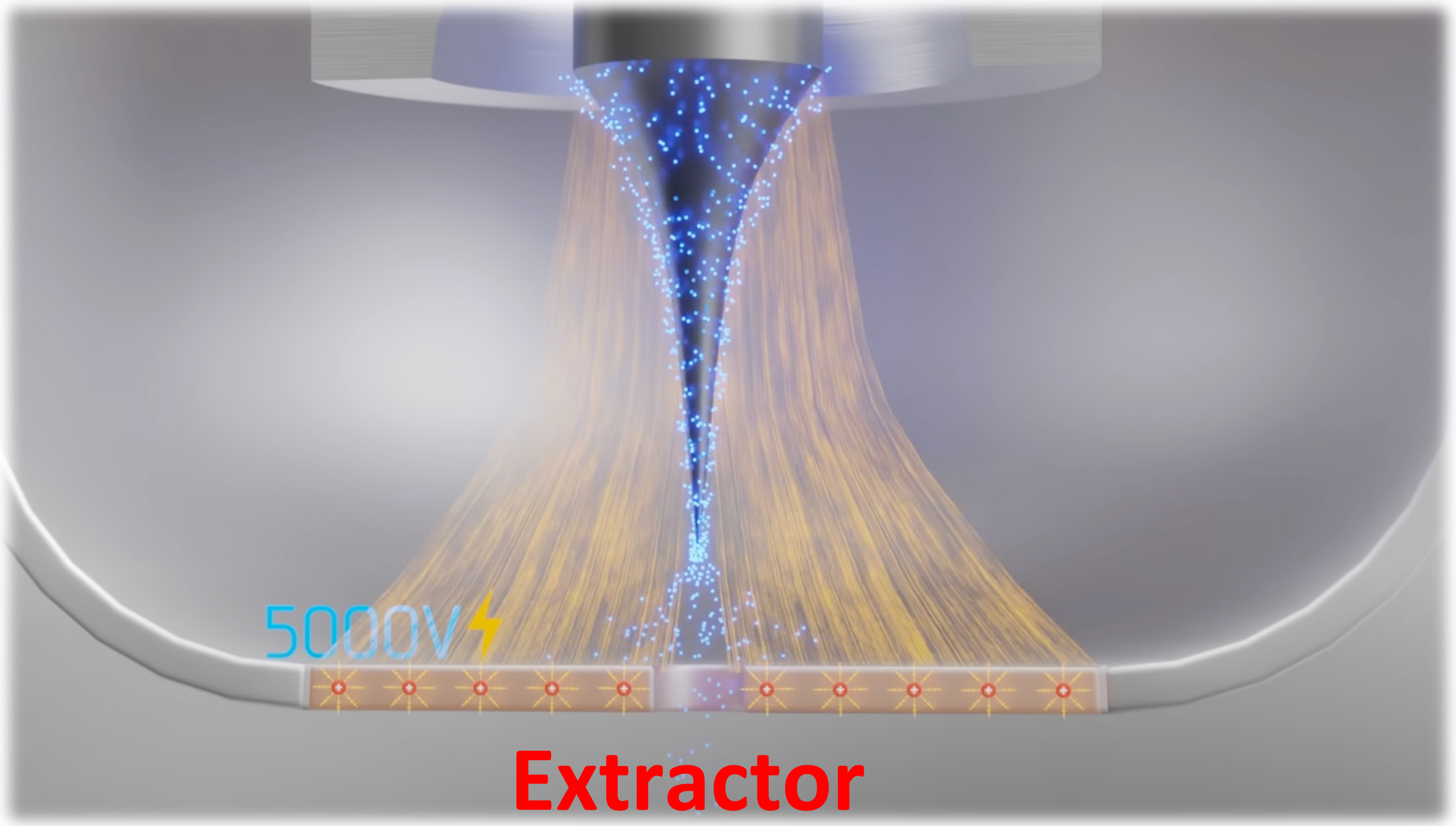


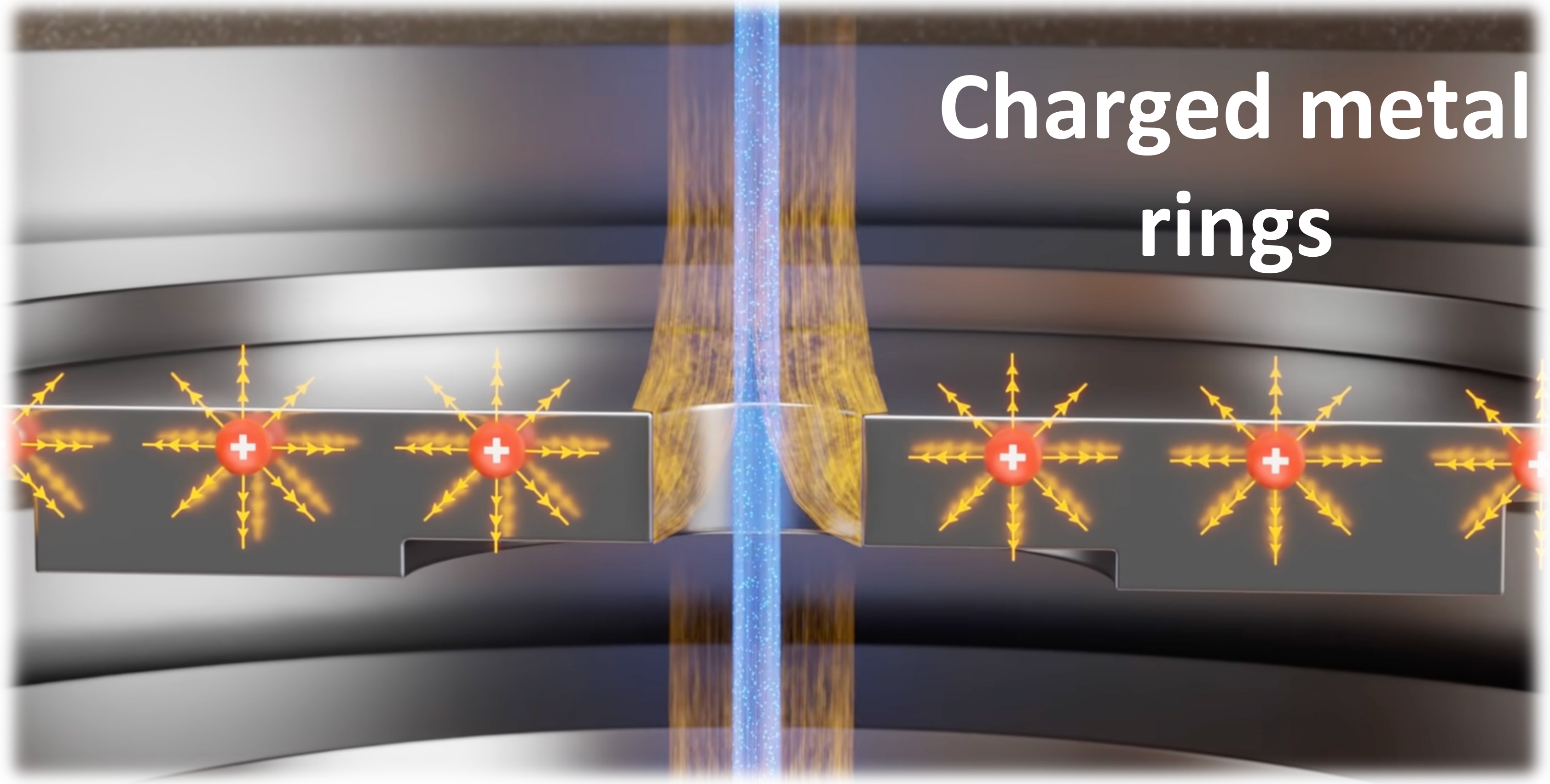
Max resolution: 50 pm

Transmission Electron Microscopy Recap

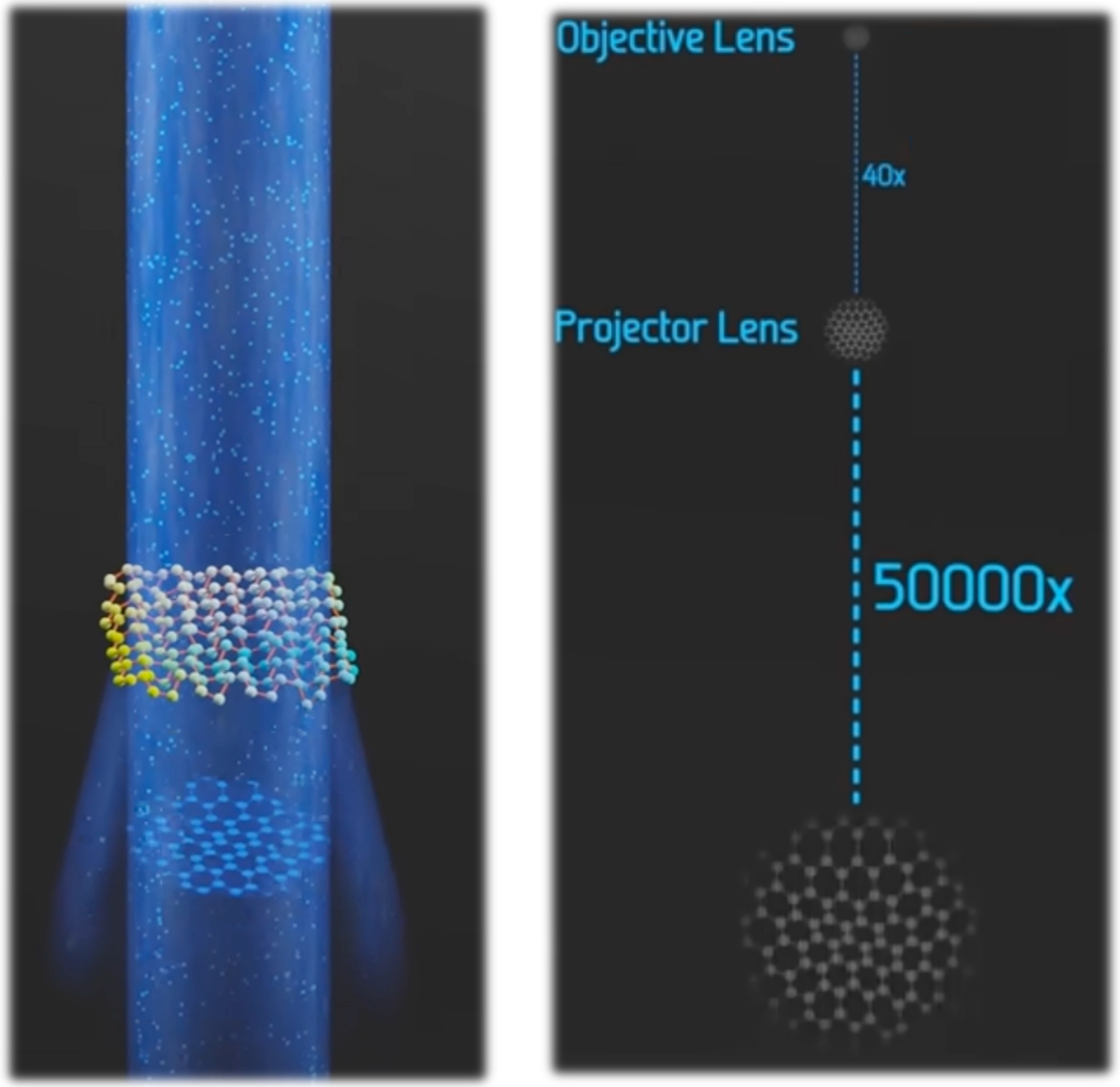


Tungsten crystal needle



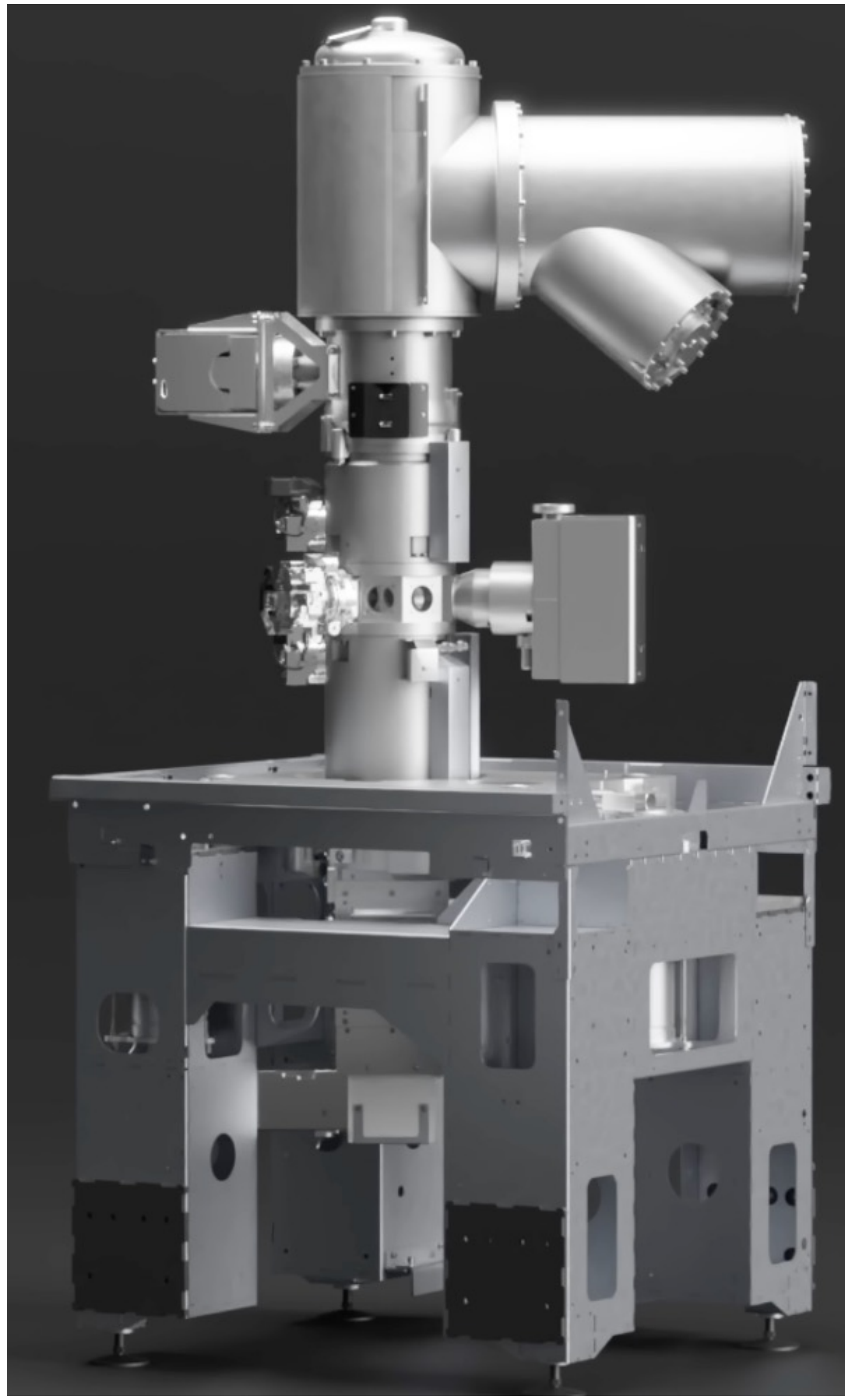


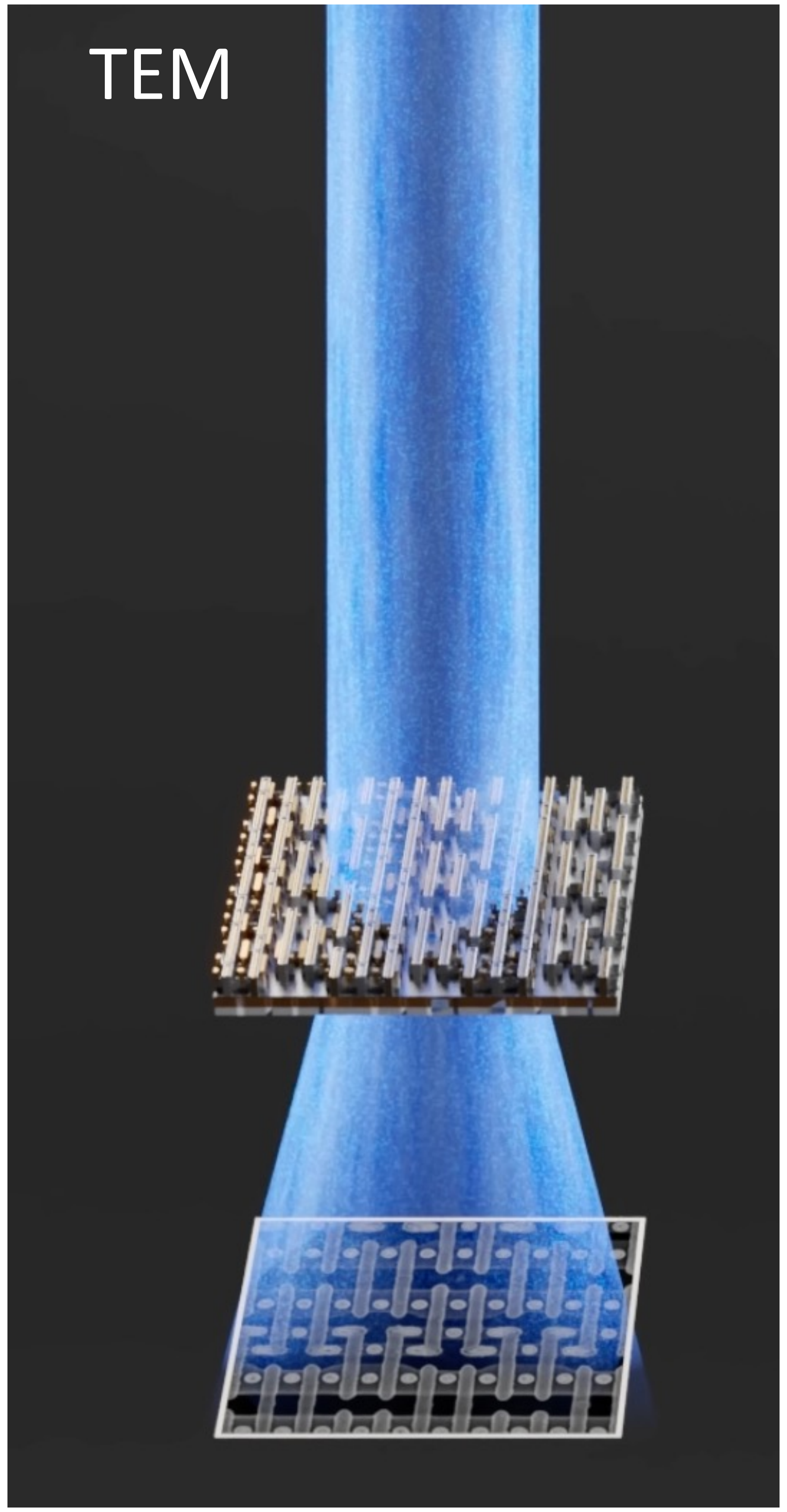
Accelerate electrons



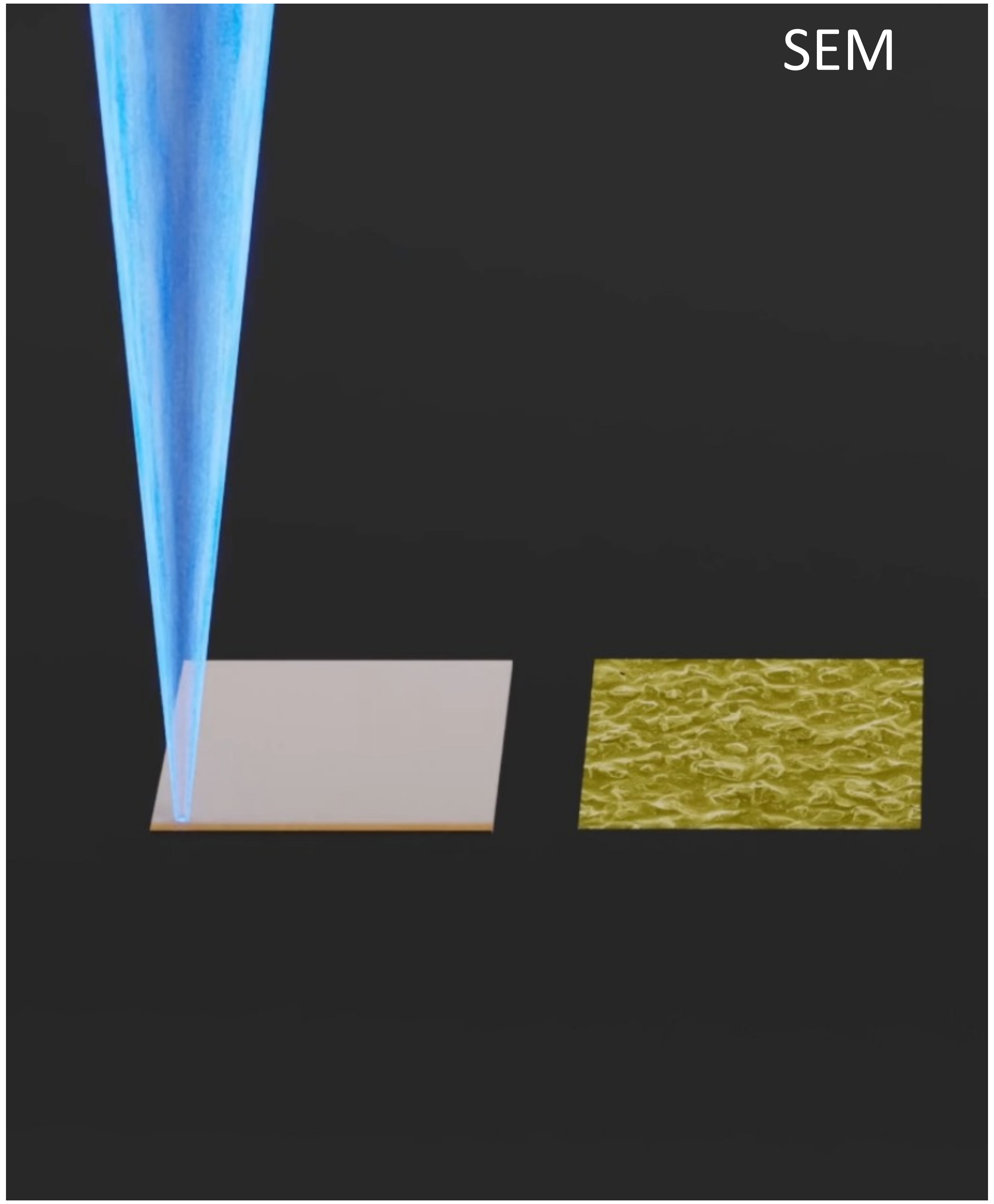
Imprint image of specimen on transmitted beam and amplify

Scanning Electron Microscopy





Illuminate specimen and imprint image



Create a focus spot and scan across the specimen

Branch Education

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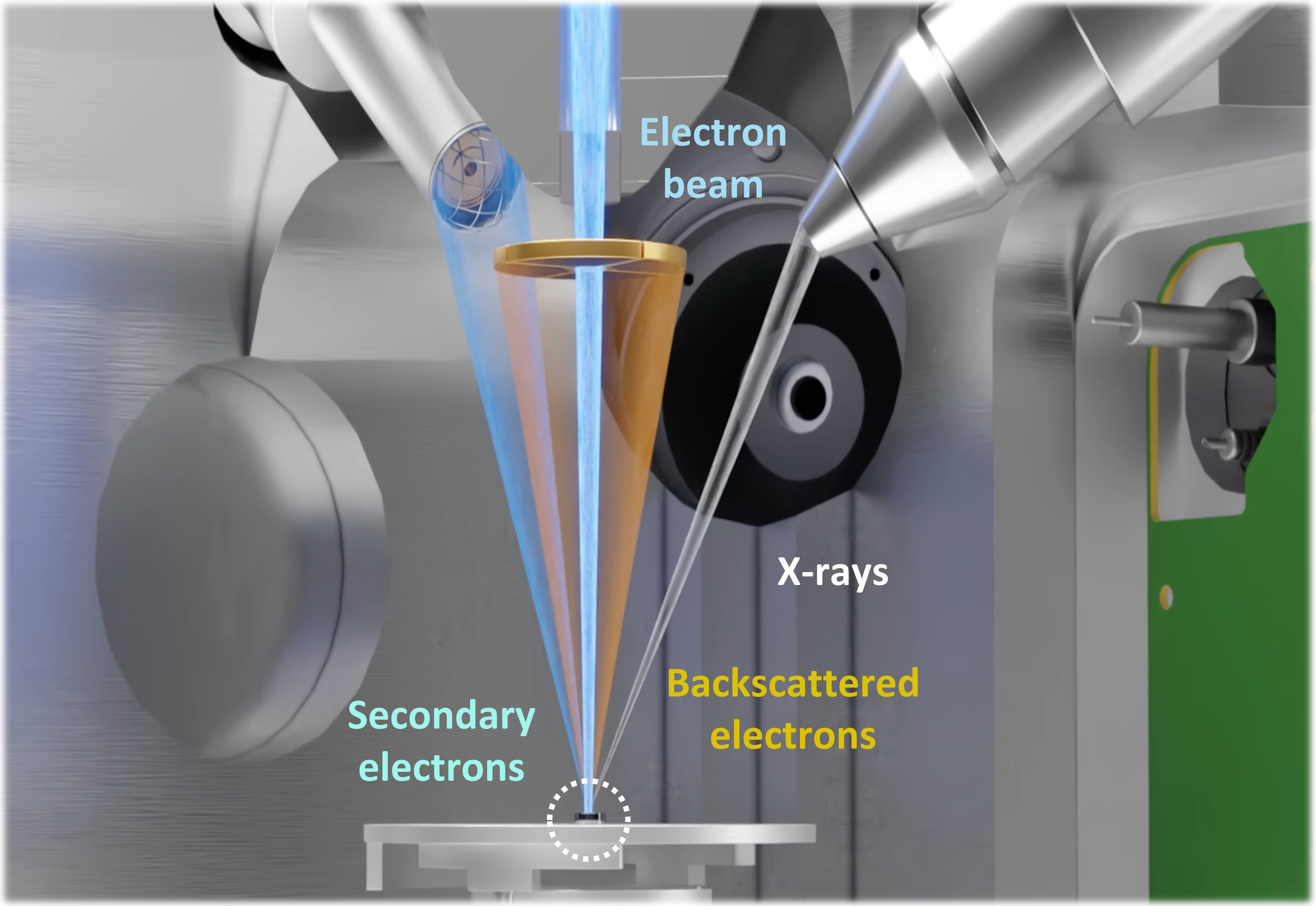
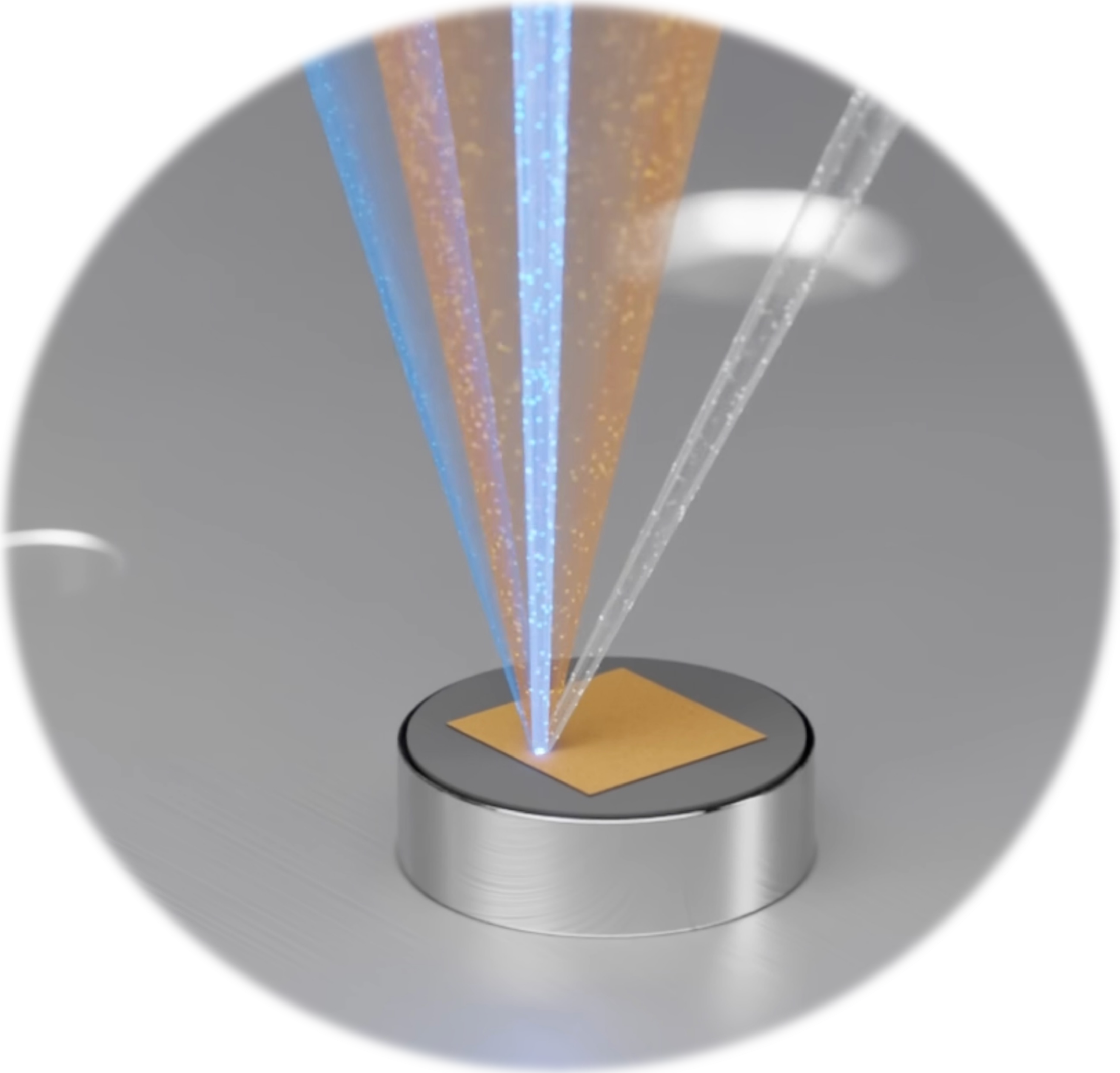
Scanning Electron Microscopy

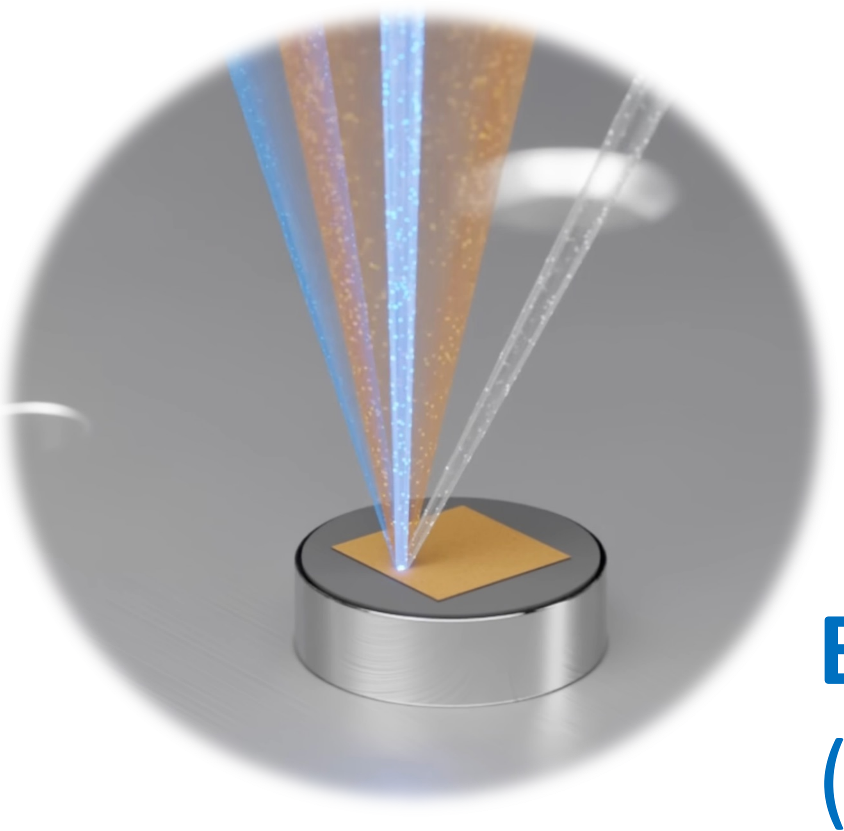


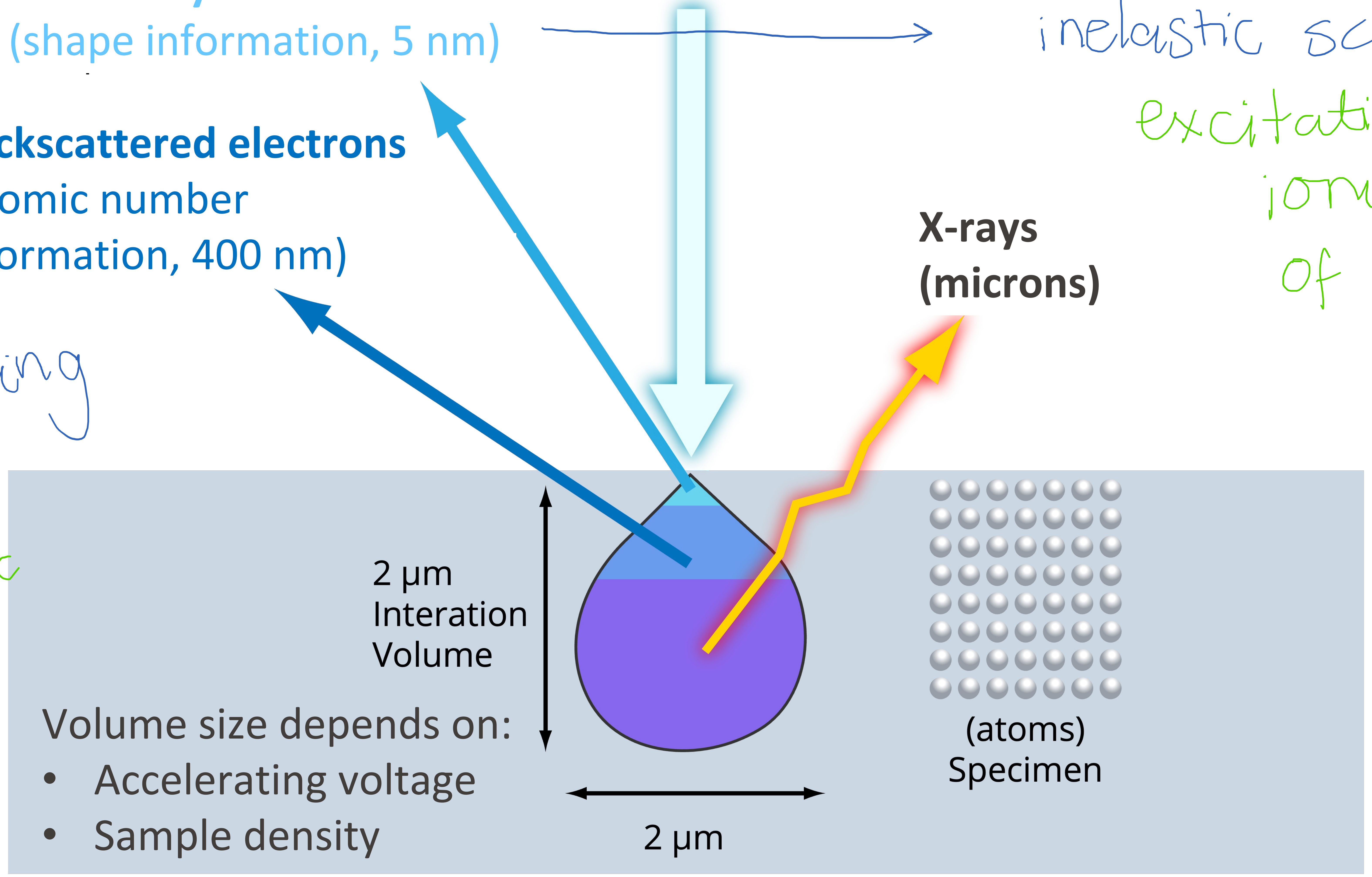
Electrons accelerated at specified accelerating voltage (1-30 keV)



Branch Education CHEMINA

Scanning Electron Microscopy Spatial Resolution





Primary electron beam (2-200 nm diameter)

Secondary electrons
(shape information, 5 nm)

inelastic scattering

excitation/
ionization
of inner shell/
valence e⊖s

Backscattered electrons
(atomic number information, 400 nm)

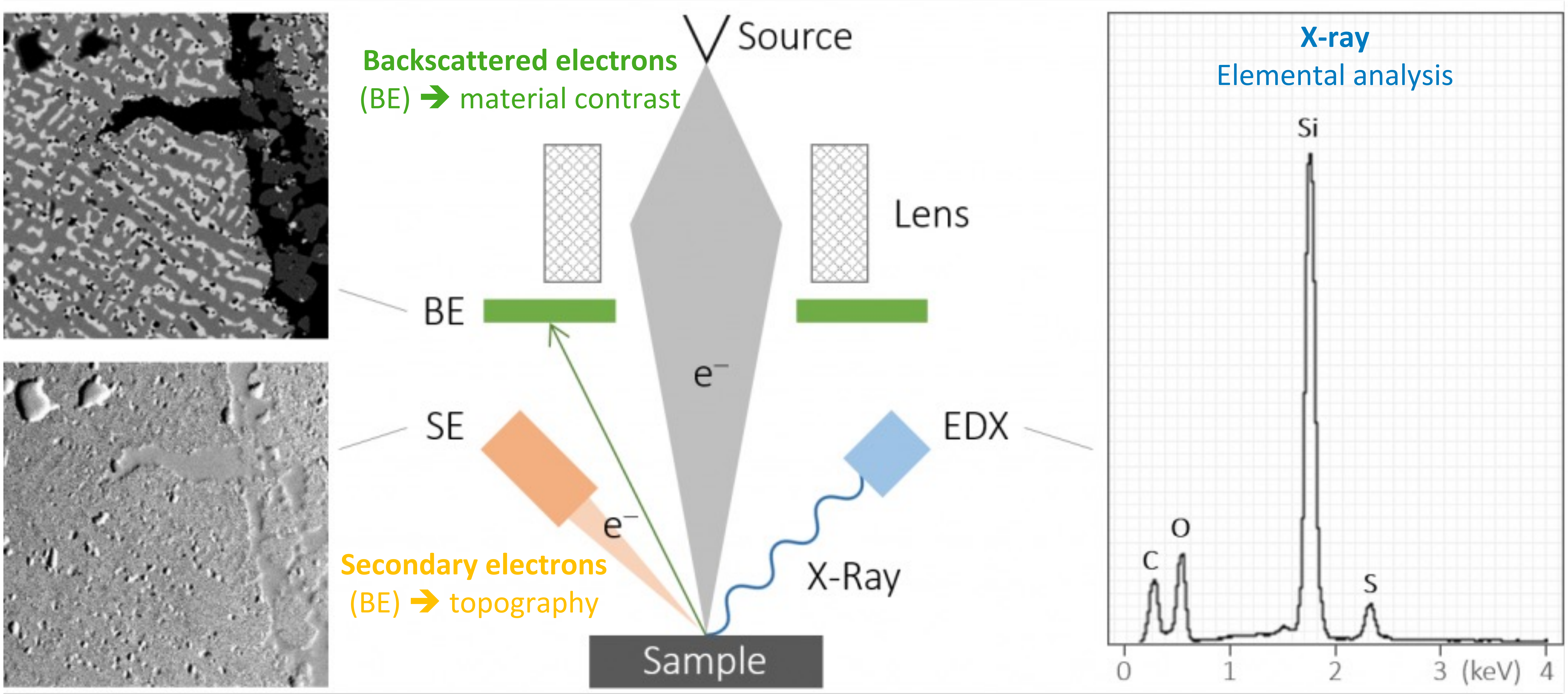
elastic scattering

e^- deflected
by electrostatic
field of
nucleus

X-rays (microns)

Volume size depends on:
- Accelerating voltage
- Sample density

Scanning Electron Microscopy Spatial Resolution



Backscattered electrons
(BE) ➔ material contrast

Secondary electrons
(BE) ➔ topography

X-ray
Elemental analysis

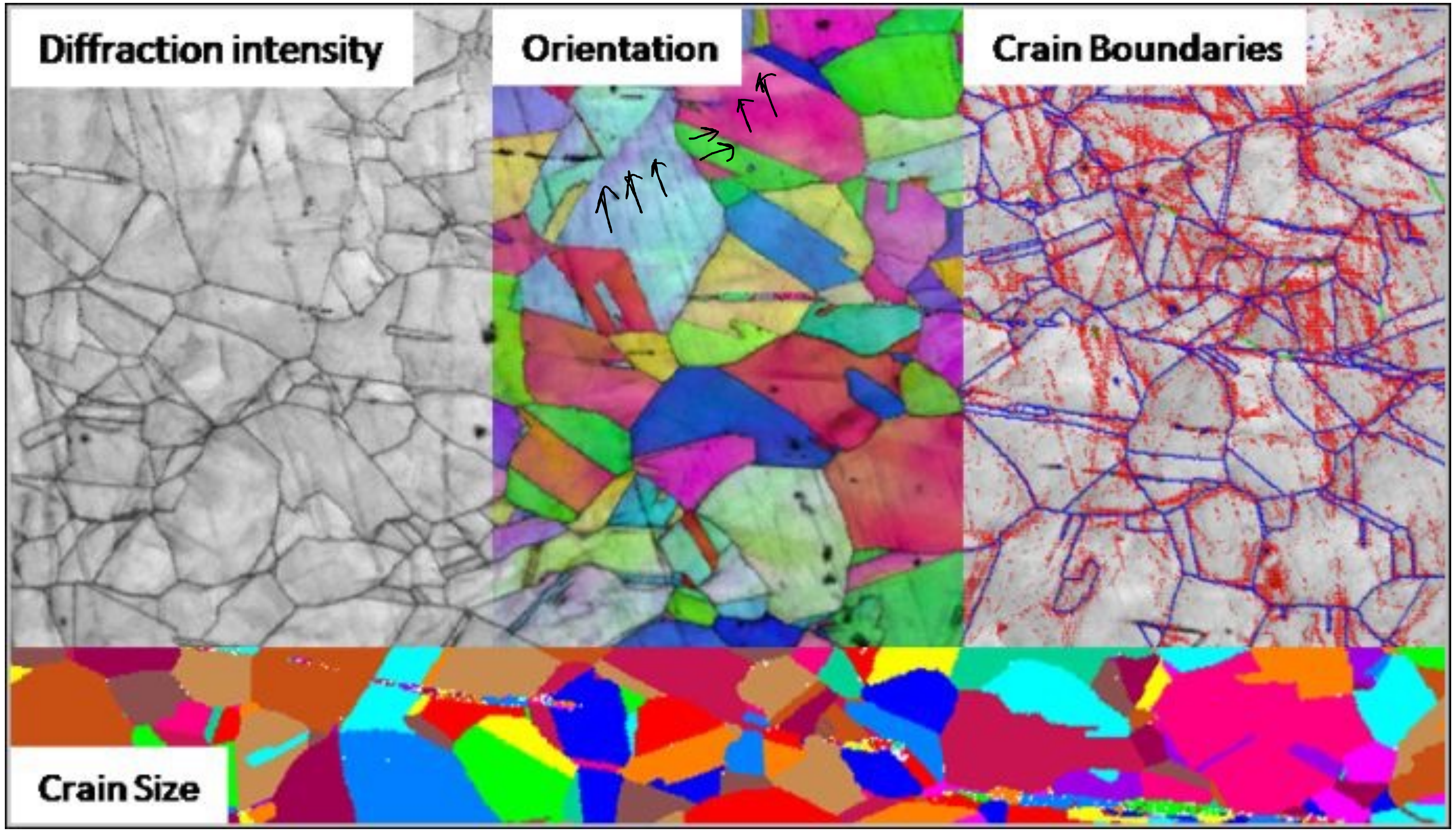
Scanning Electron Microscopy Spatial Resolution

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

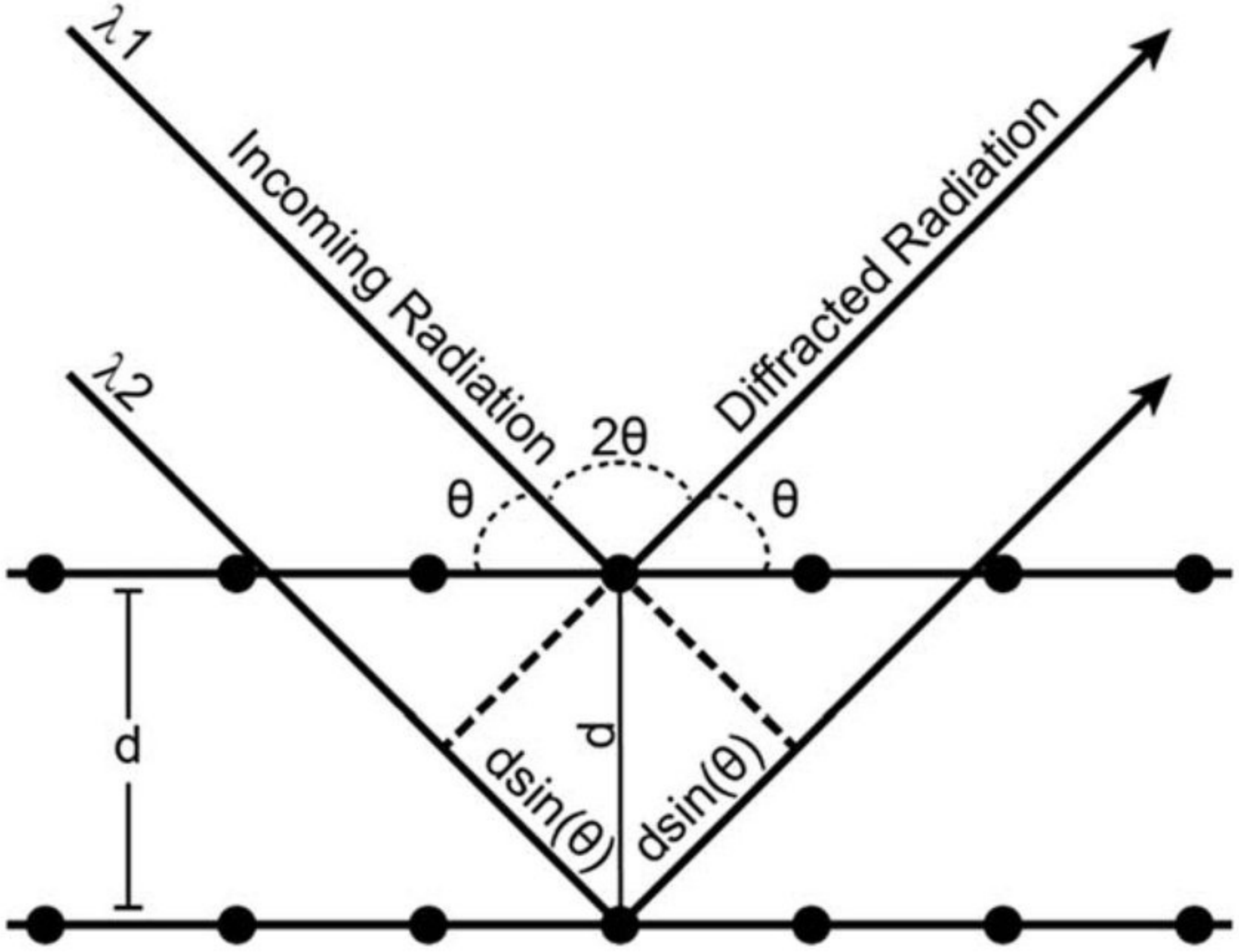


The EBSD Pattern is Due to Bragg Diffraction

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

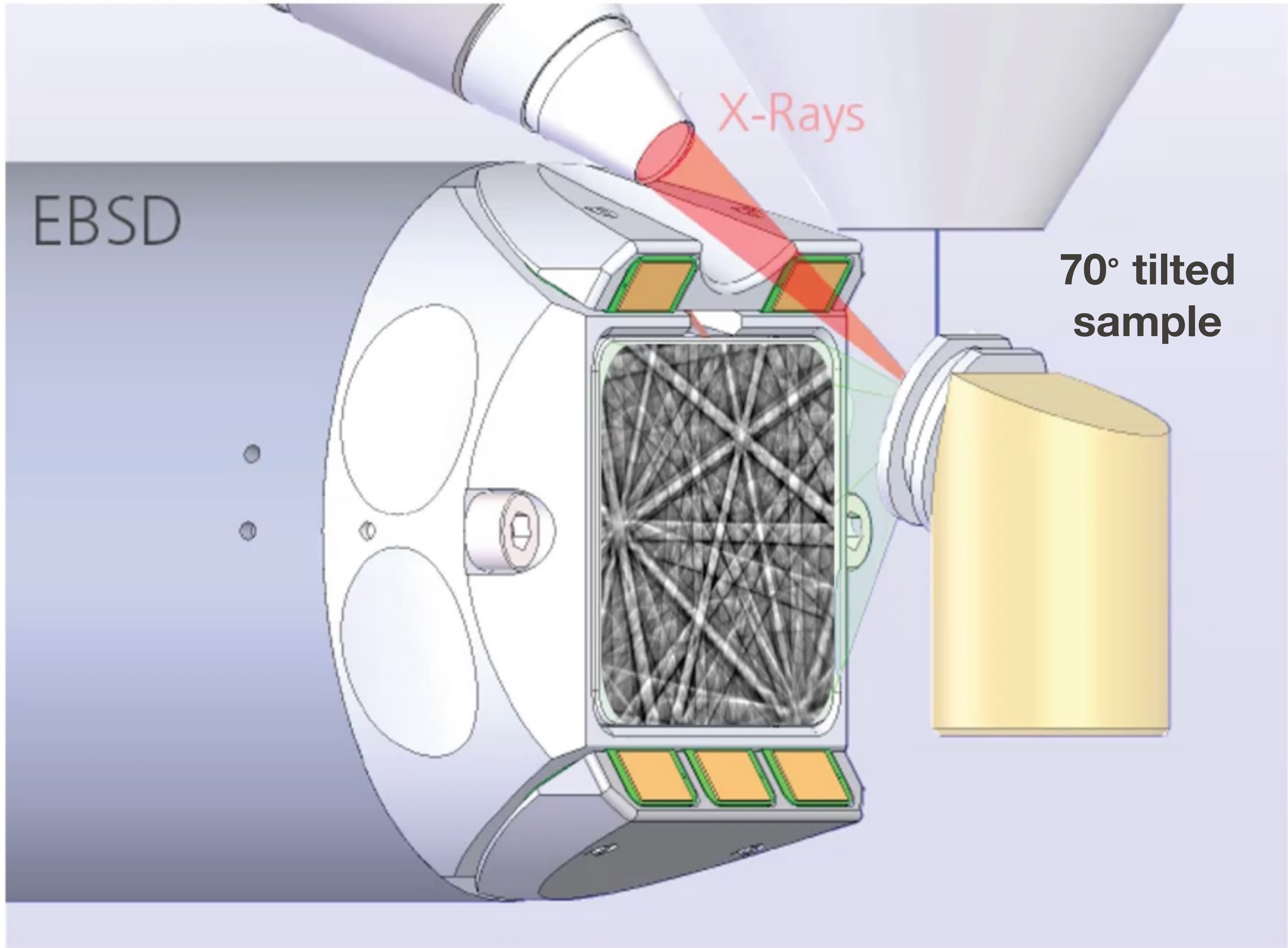
Bragg's Law

λ: the wavelength of the electron
d: lattice spacing
θ: angle between incident ray and the scatter plane

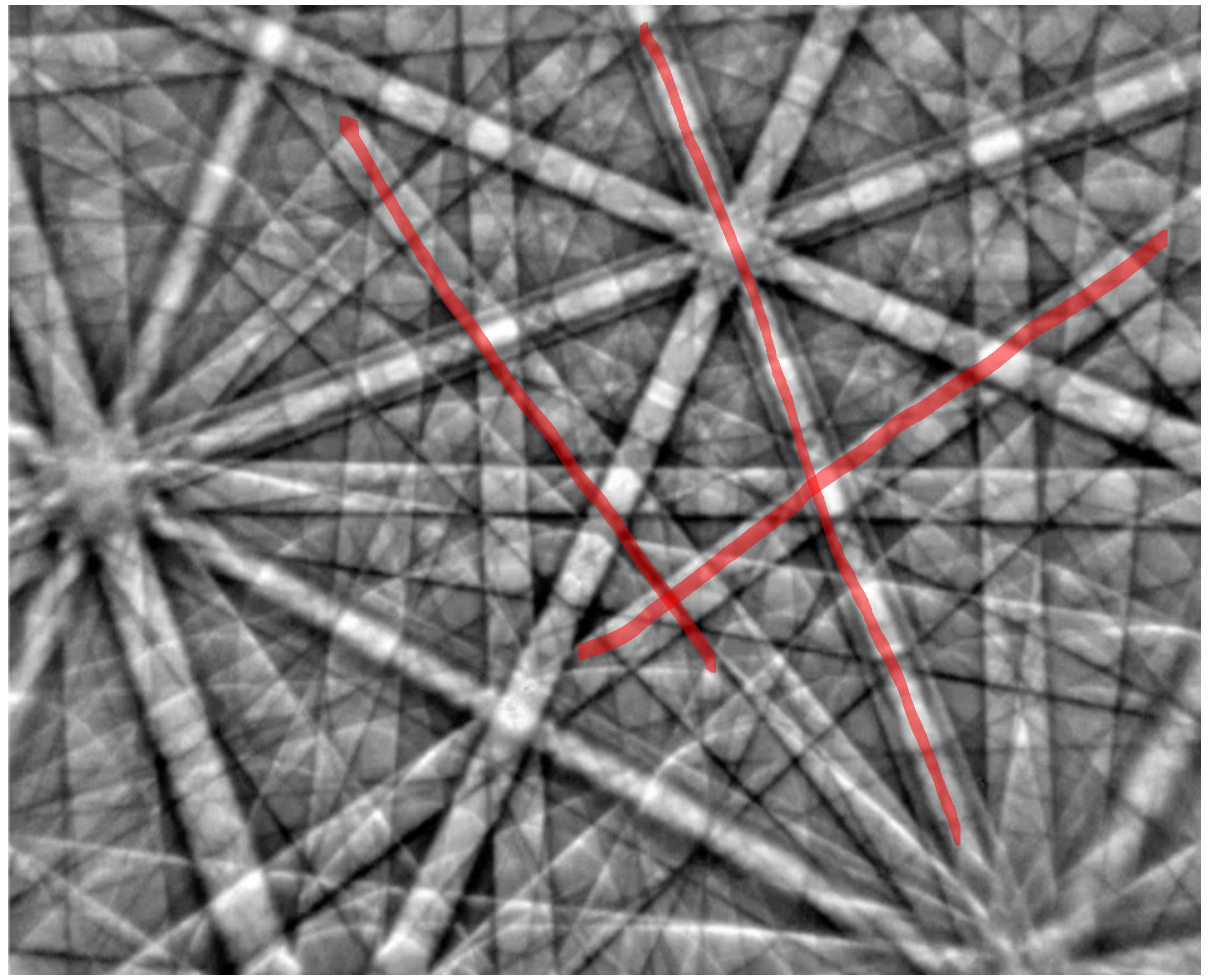


Electron Backscatter Diffraction (EBSD)

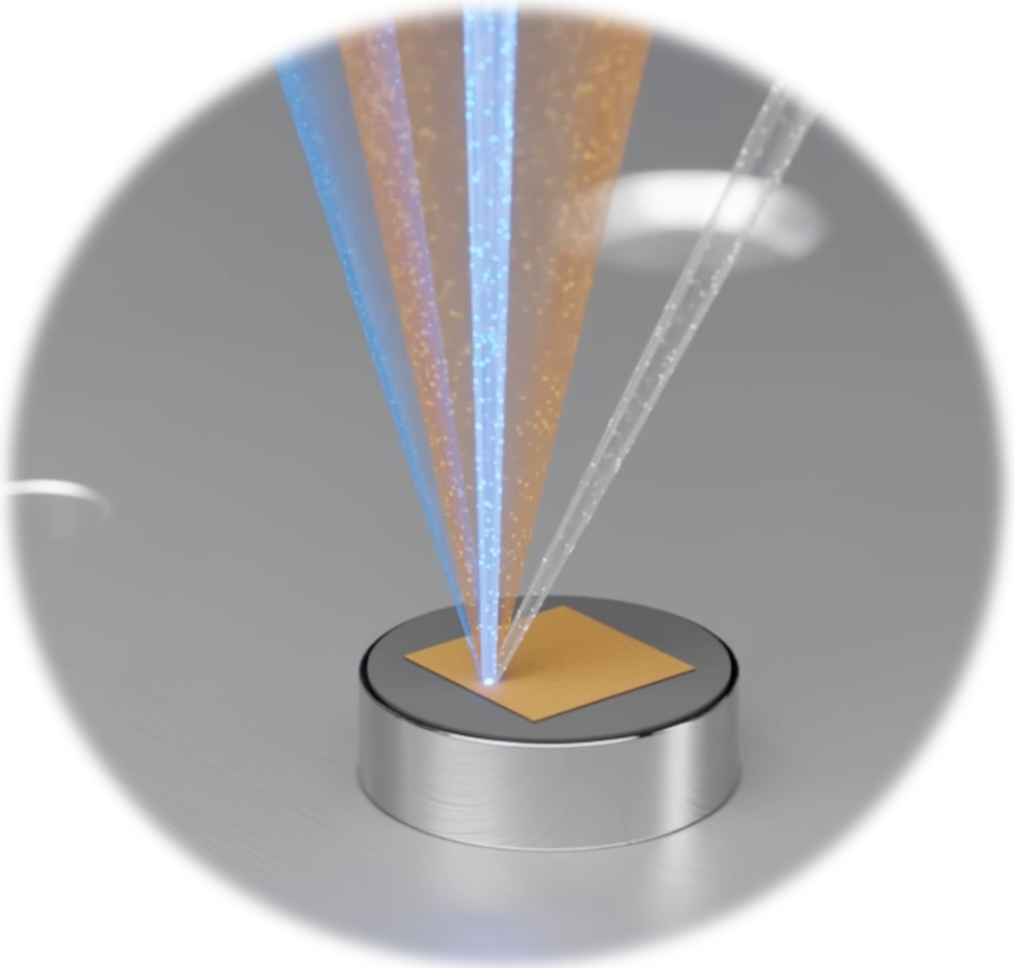
An SEM-based diffraction technique to measure crystalline materials



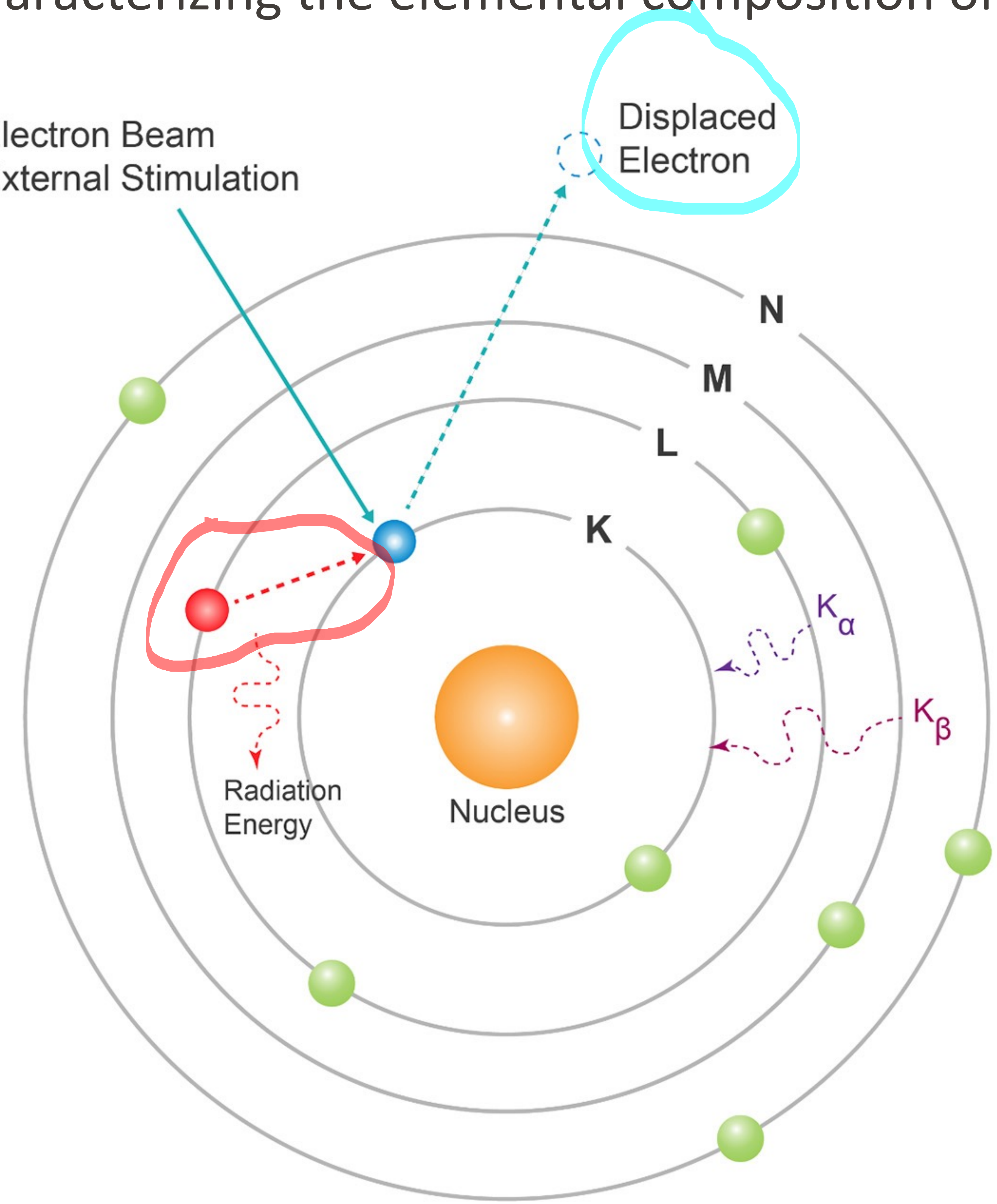
Kikuchi Line



Energy Dispersive X-Ray Spectroscopy (EDS/EDX)



Characterizing the elemental composition on the microscale

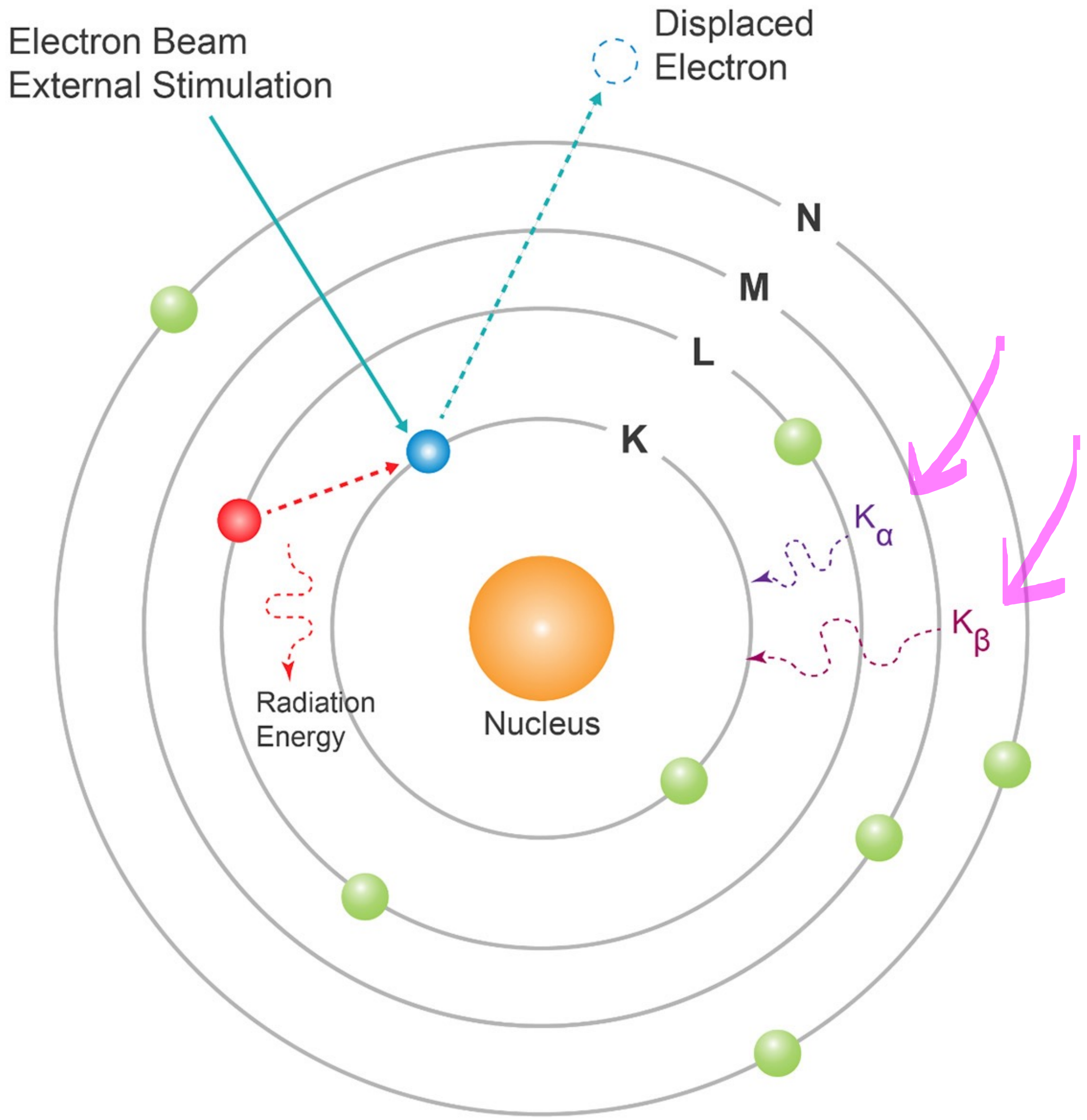


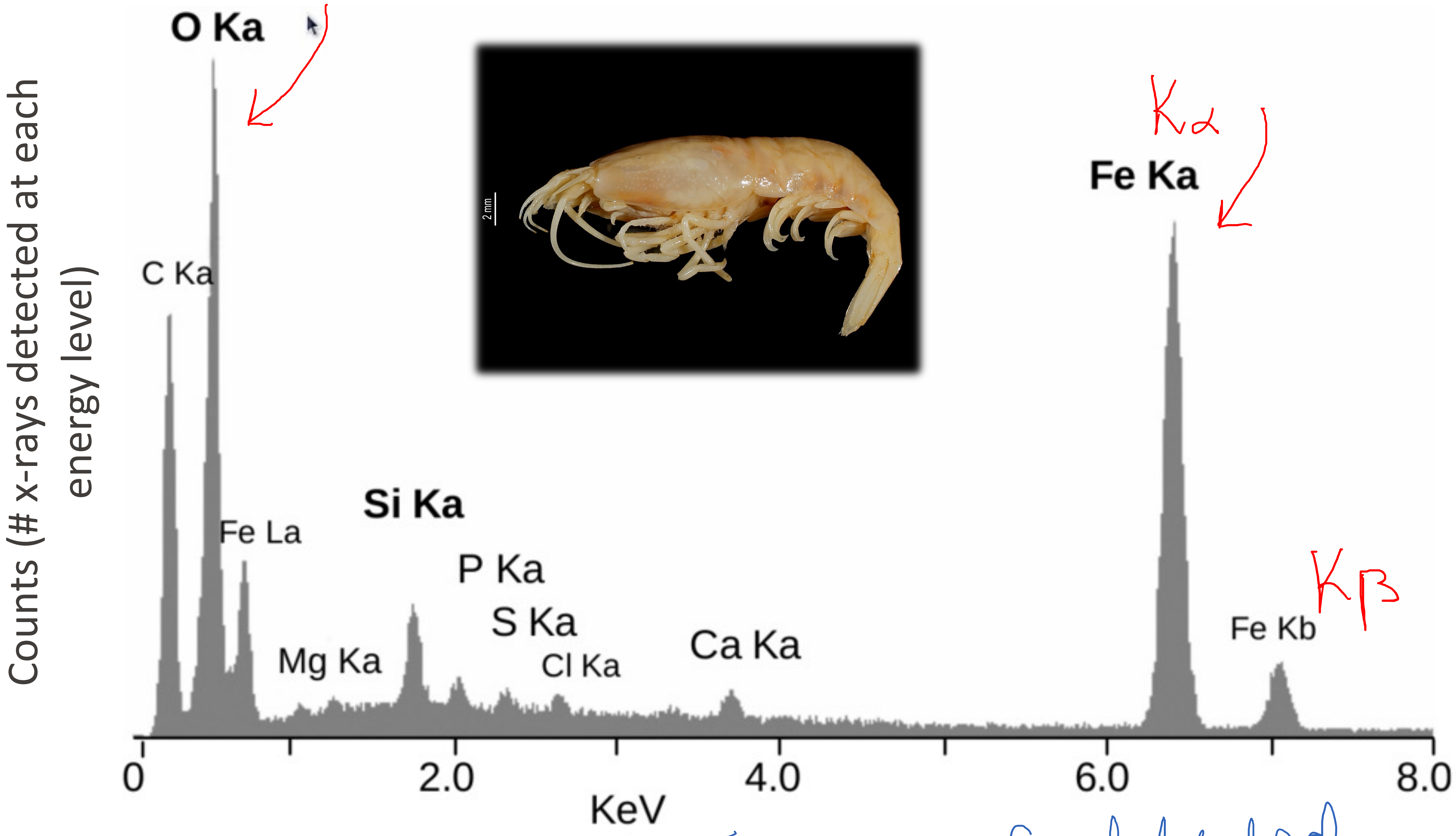
1. Beam interacts with the atom, displaces electron out of its shell
2. Void filled by another electron from higher energy level
3. Energy released correlates to individual elements while proportional counts relate to the quantity of element

Each element has unique K_α and K_β energies (X-ray peaks produced when electron falls into lower energy shell)

Energy Dispersive X-Ray Spectroscopy (EDS/EDX)

Characterizing the elemental composition on the microscale

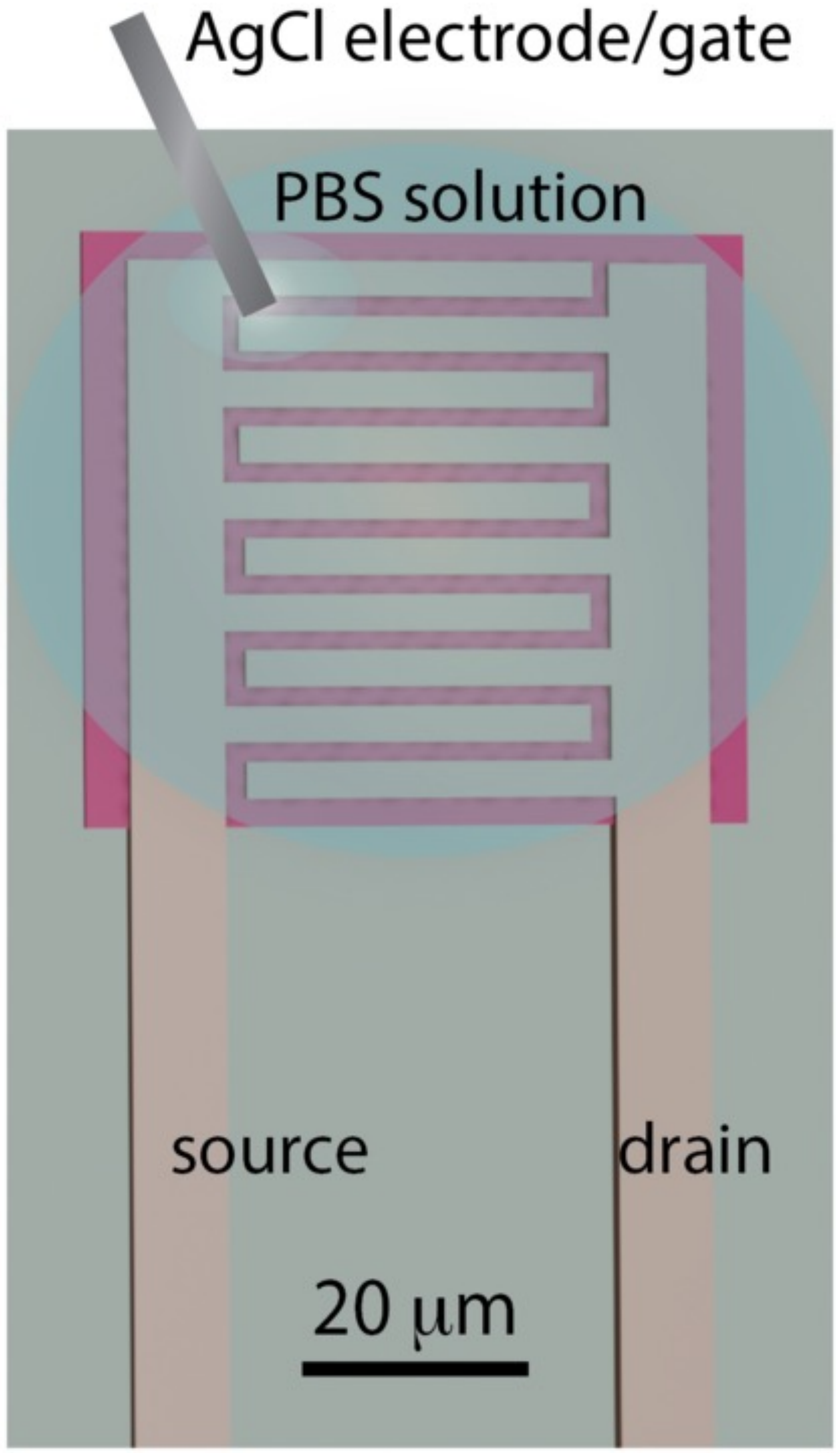


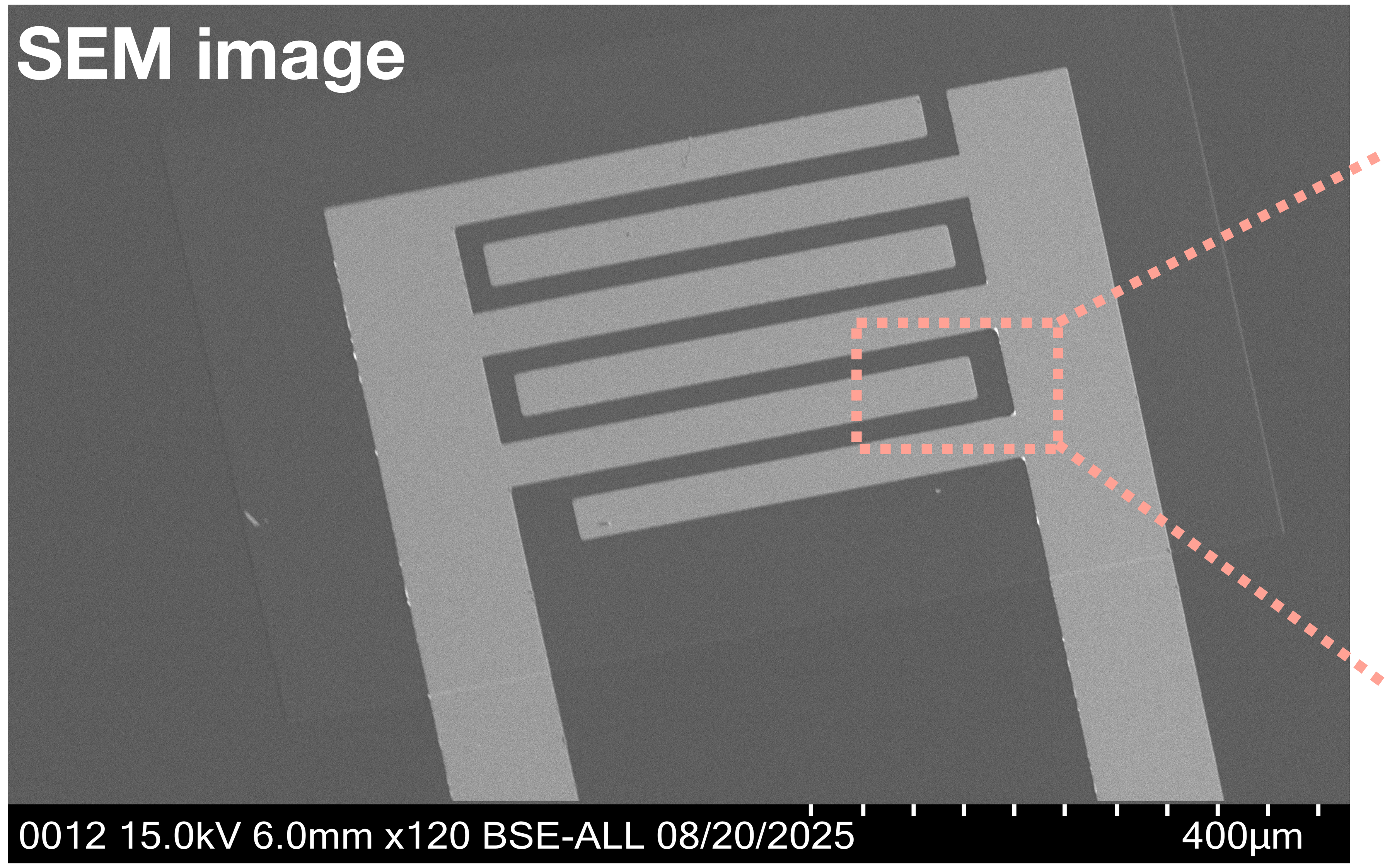


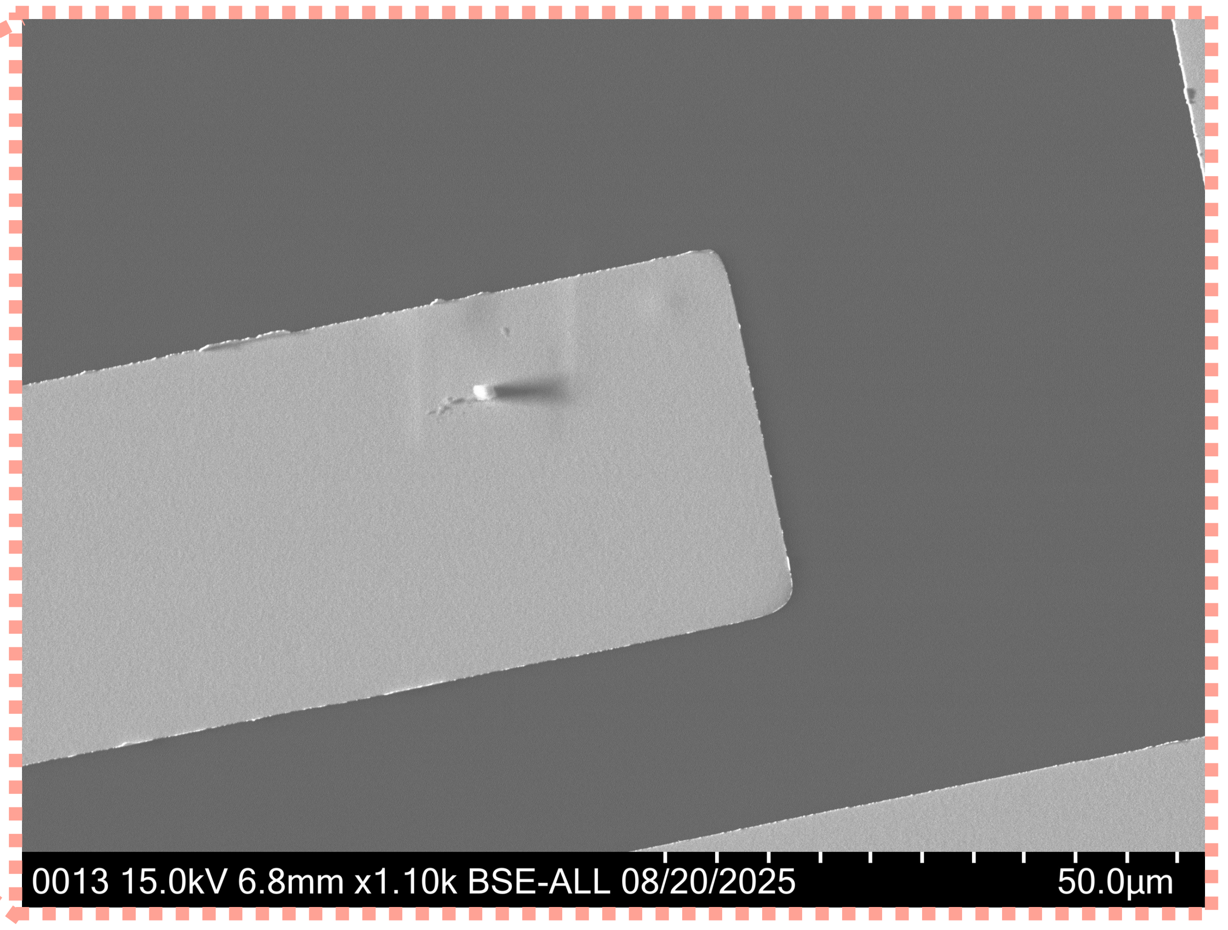
Energy of detected x-rays

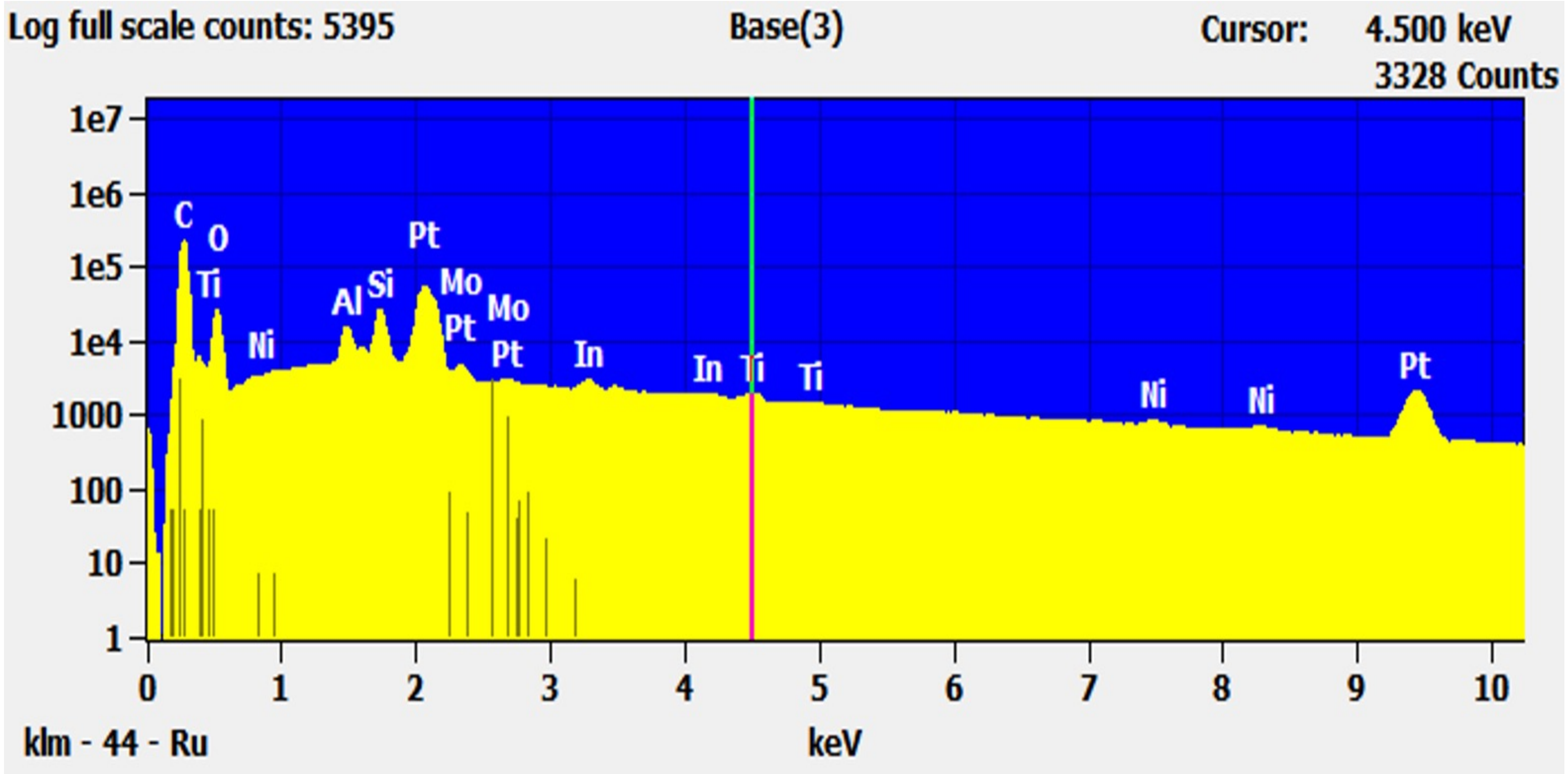
Transistor Imaging using SEM + EDX in Our Research

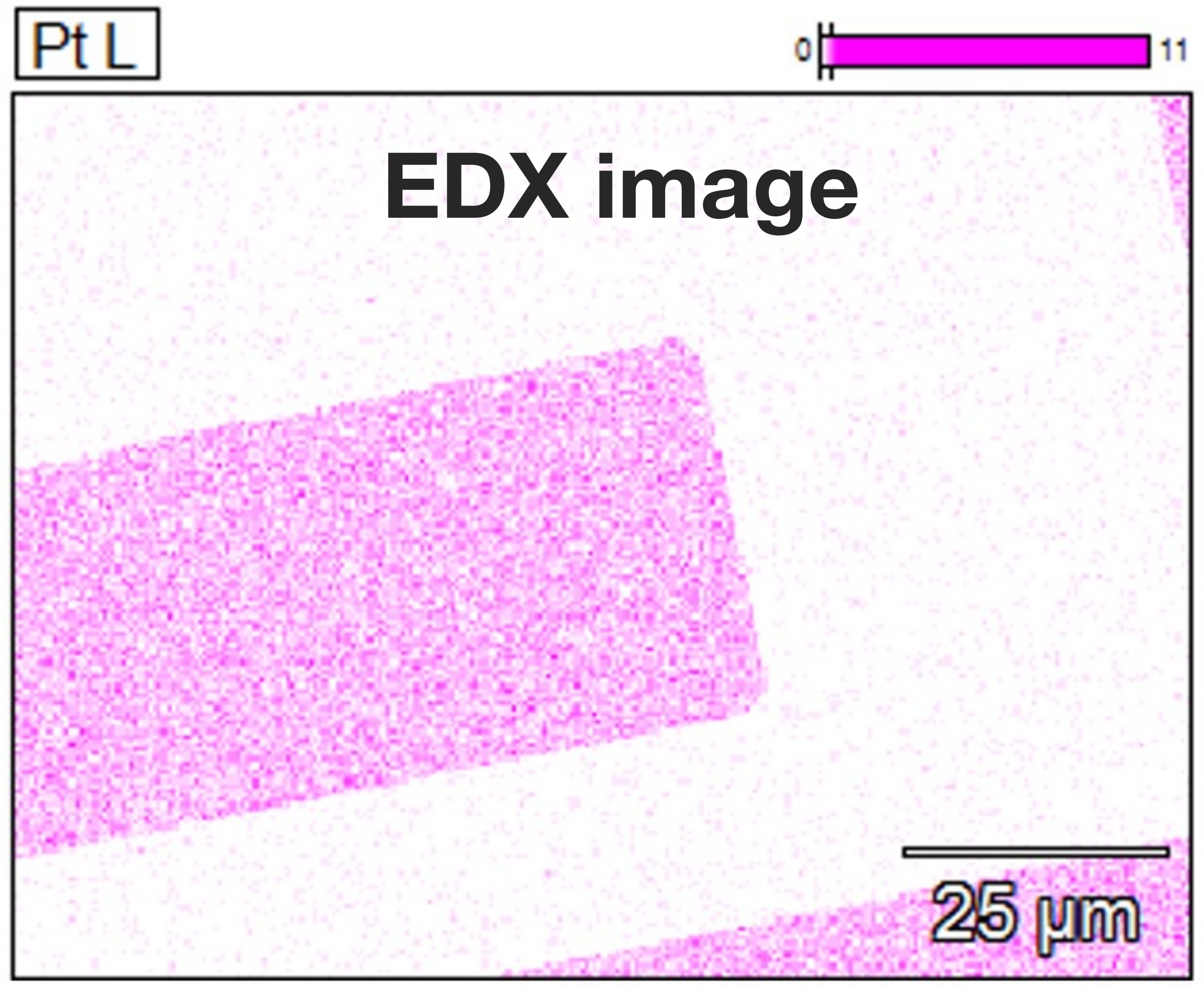
Sandra
Hernandez
Escobar



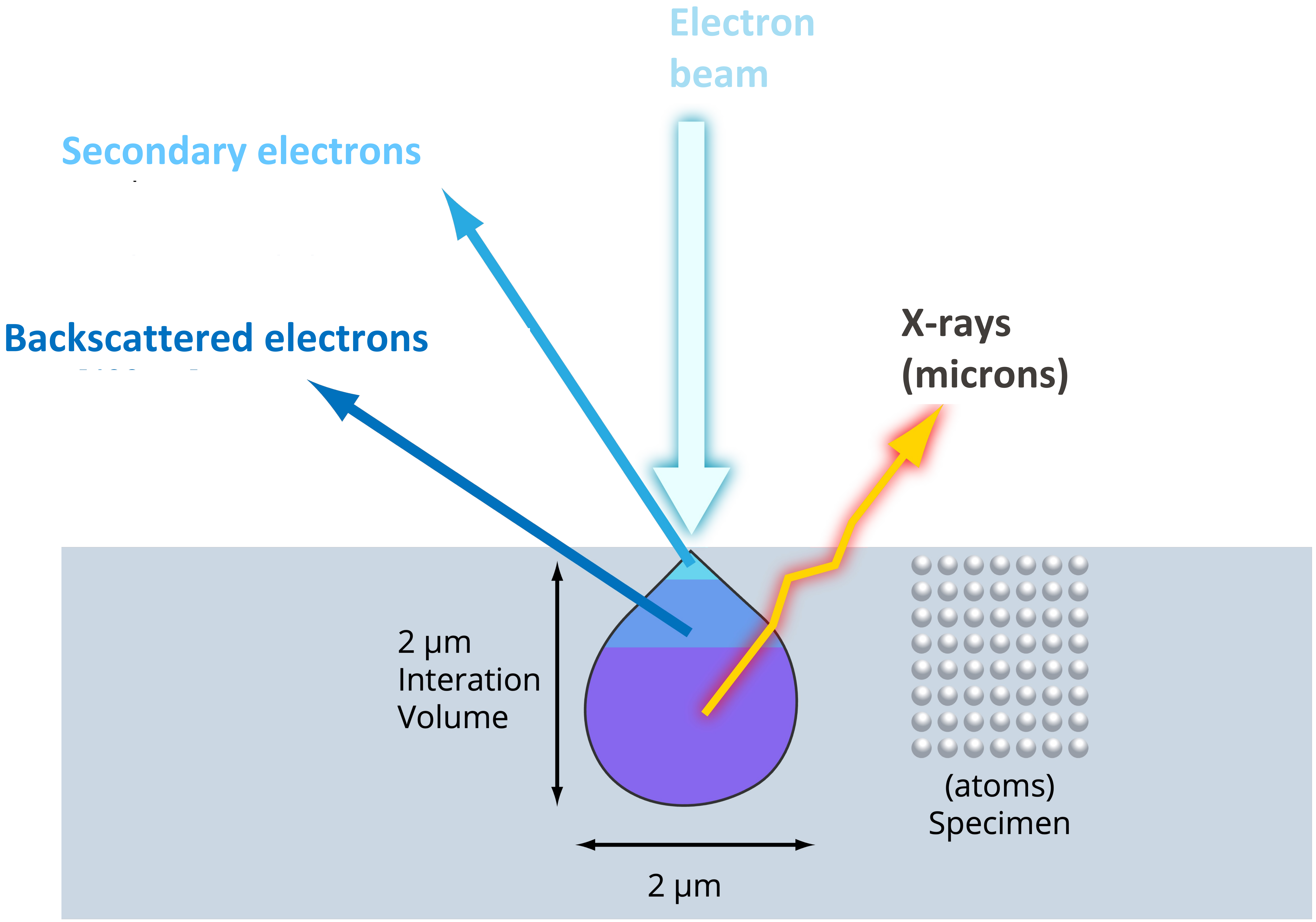








EDS/EDX is a Bulk Measurement, NOT Surface Measurement



Teardrop-shaped interaction volume much larger than the surface

1-2 μm penetration in metals/oxides

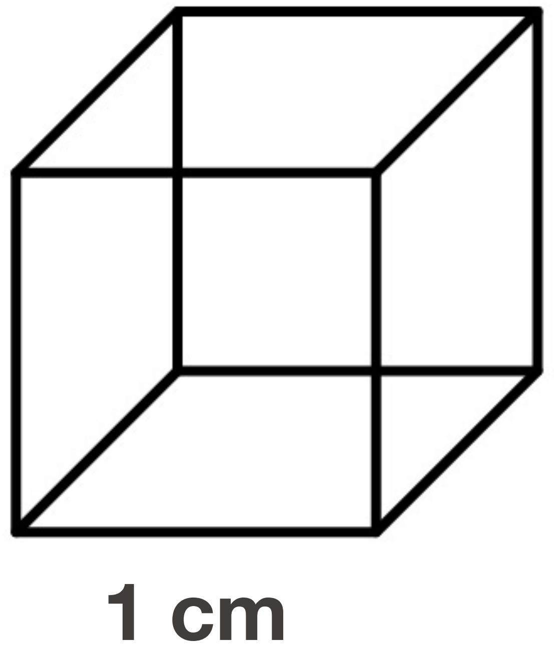
Several μm in light-element materials

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 ovwerhelmed with bulk signal



Number of atoms in a 1 cm^3 cube

Bulk atoms = 10^{23}

Surface atoms = 10^{15}

Tricks to overcome this challenge

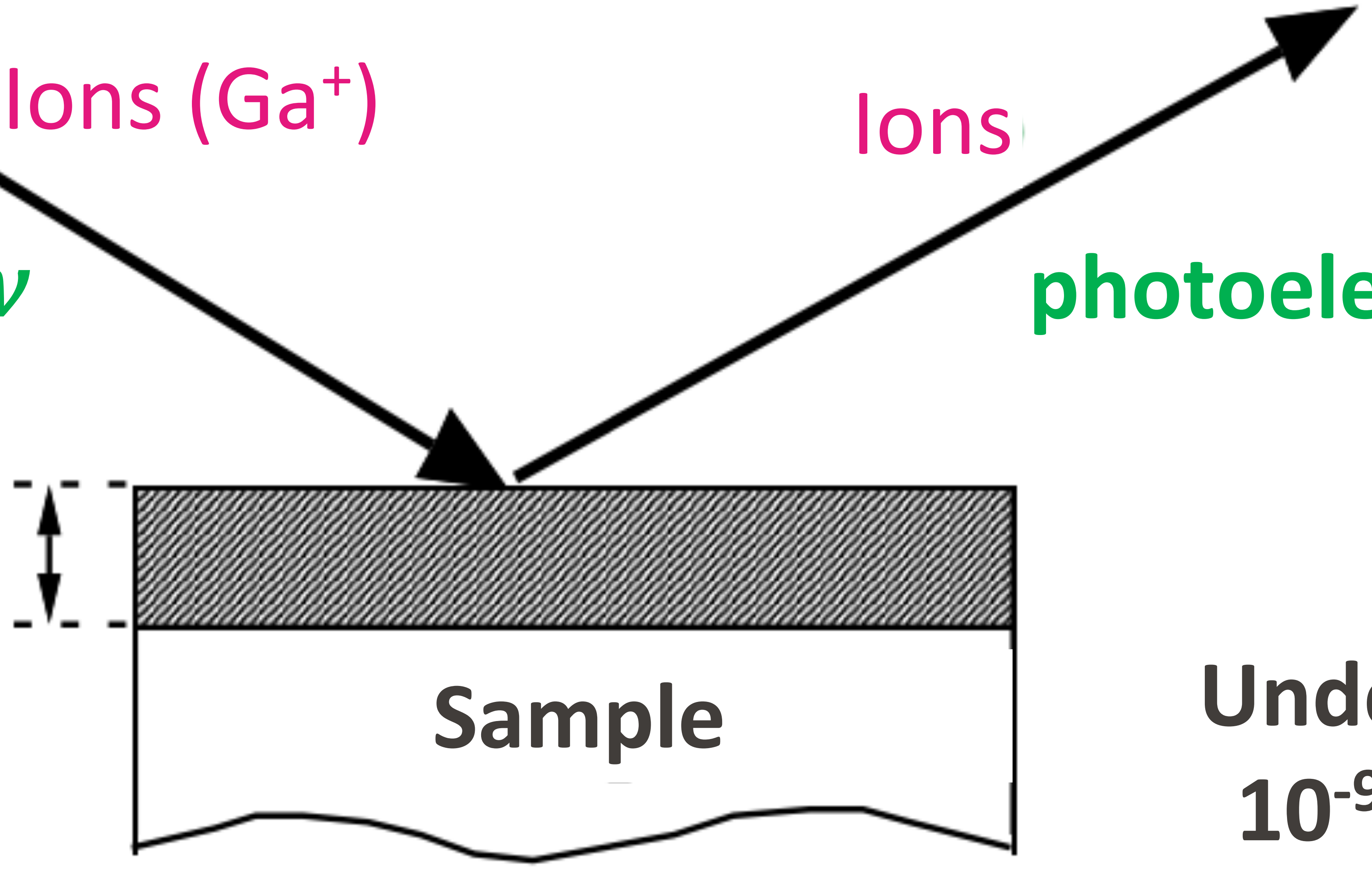
Ions: do not penetrate too much into the surface

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

Secondary ion mass spectrometry (SIMS)

X-ray photoelectron spectroscopy (XPS)



Primary beam

Ions (Ga^+)

$h\nu$

Ions

photoelectron

Secondary particles to detector

Depth analyzed

Sample

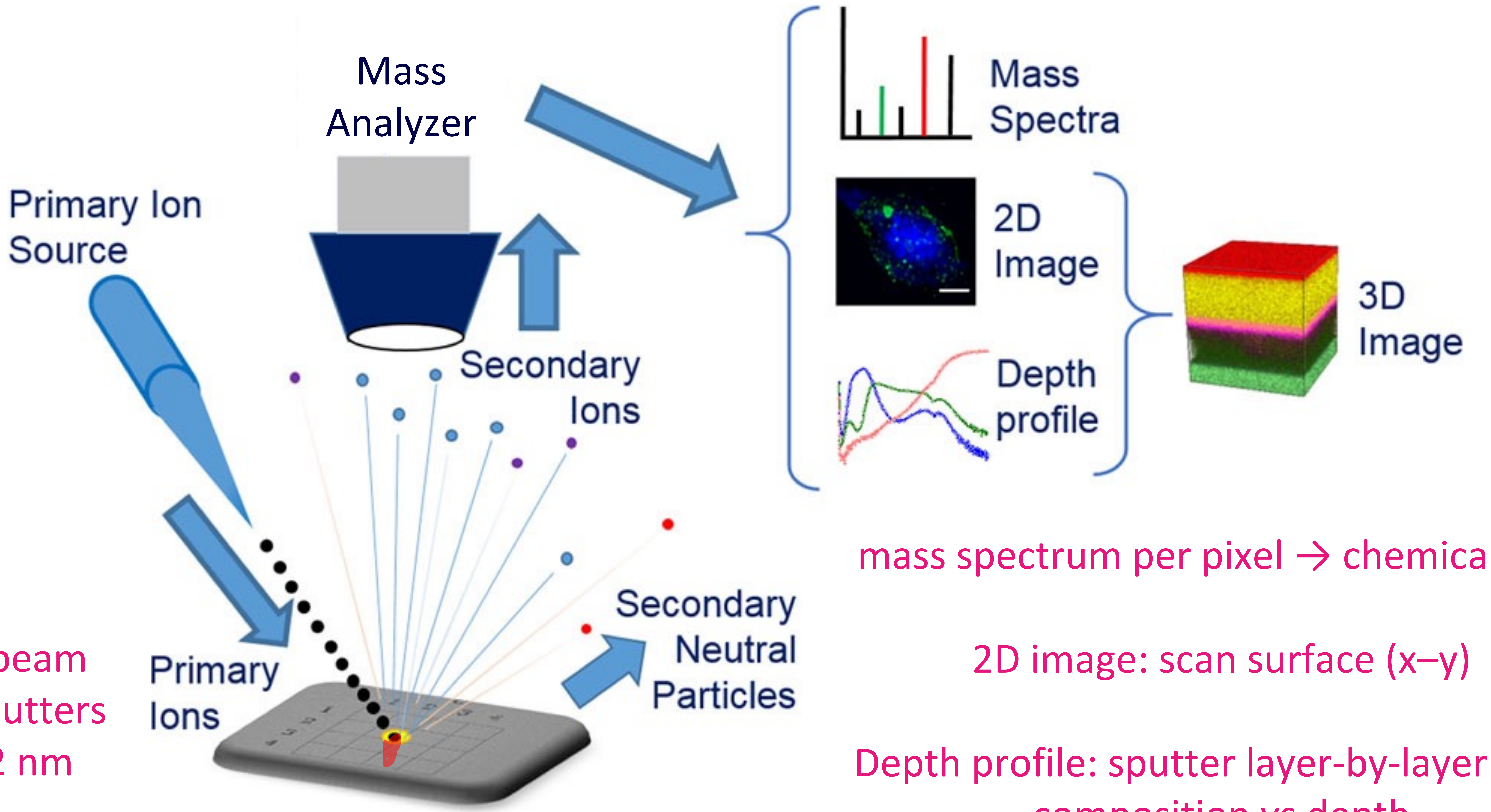
1-2 nm (monolayer)

5-10 nm

Under UHV
10^{-9} mbar

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

Secondary Ion Mass Spectrometry (SIMS)



Pulsed ion beam (*e.g.*, Ga^+) sputters the top 1-2 nm

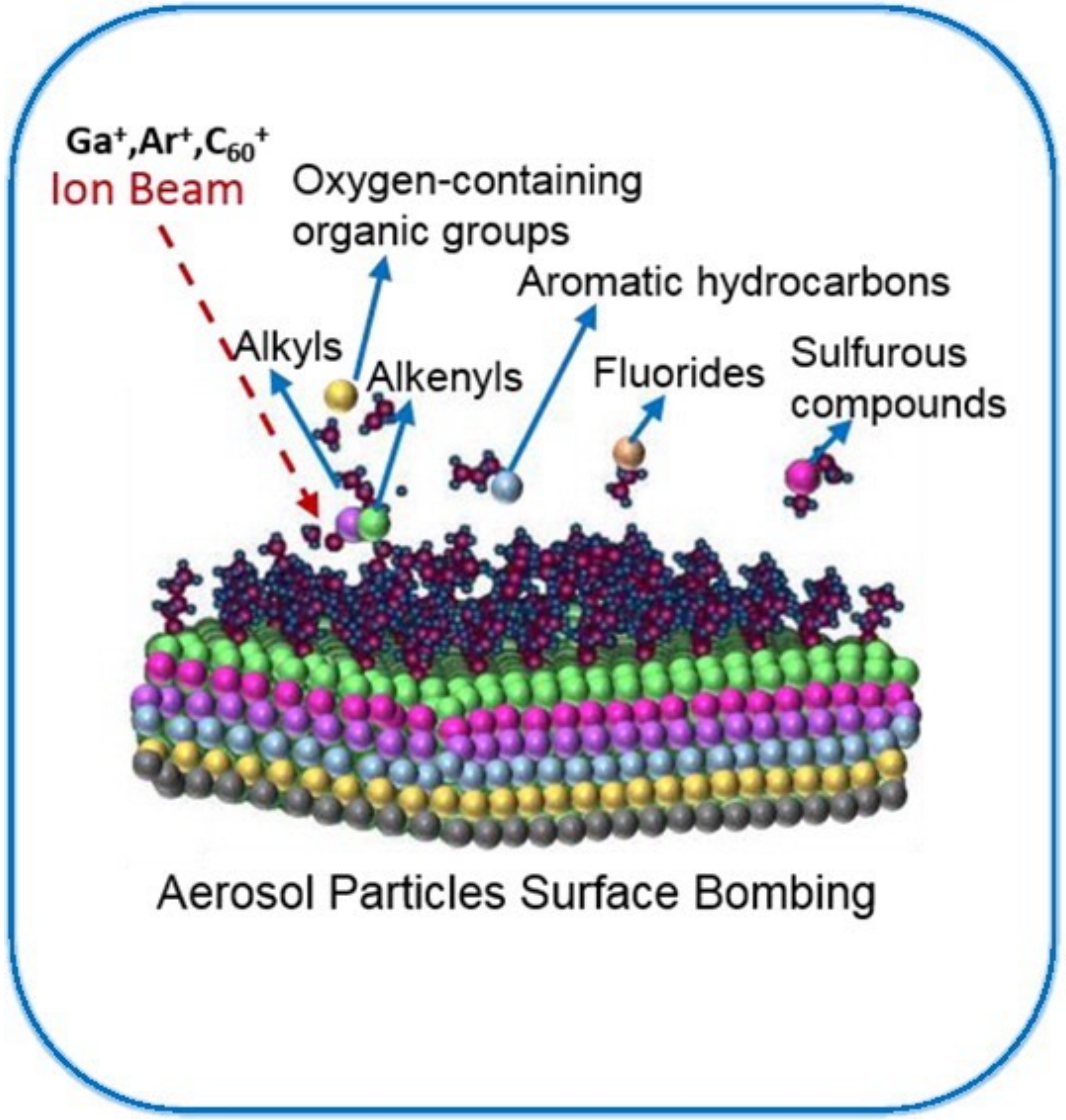
mass spectrum per pixel → chemical map

2D image: scan surface (x–y)

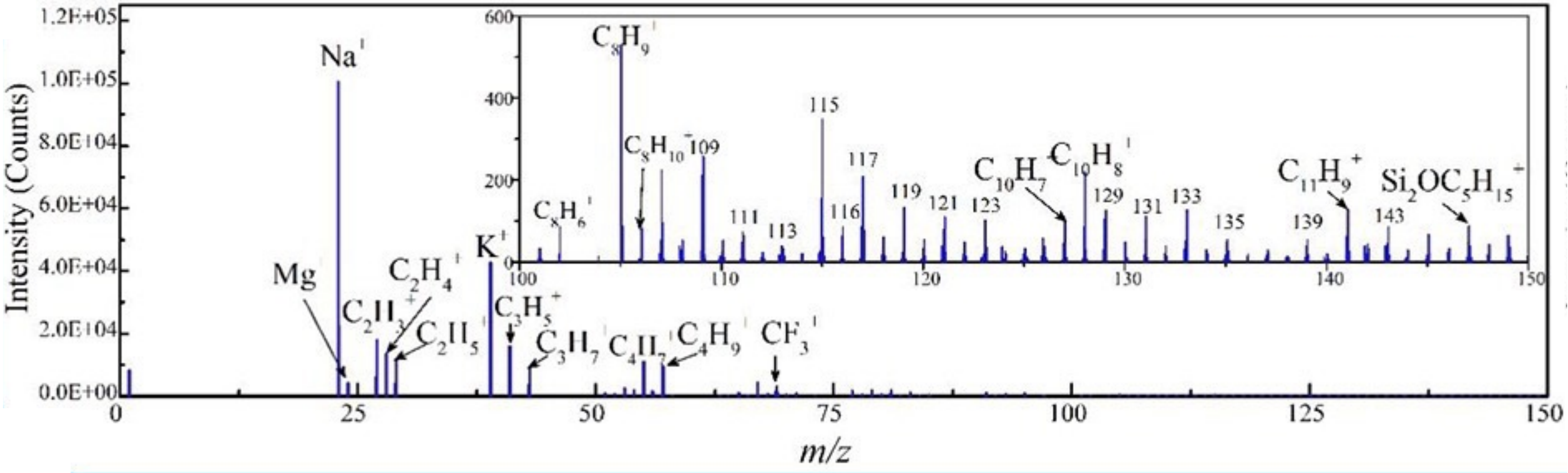
Depth profile: sputter layer-by-layer (z) → composition vs depth

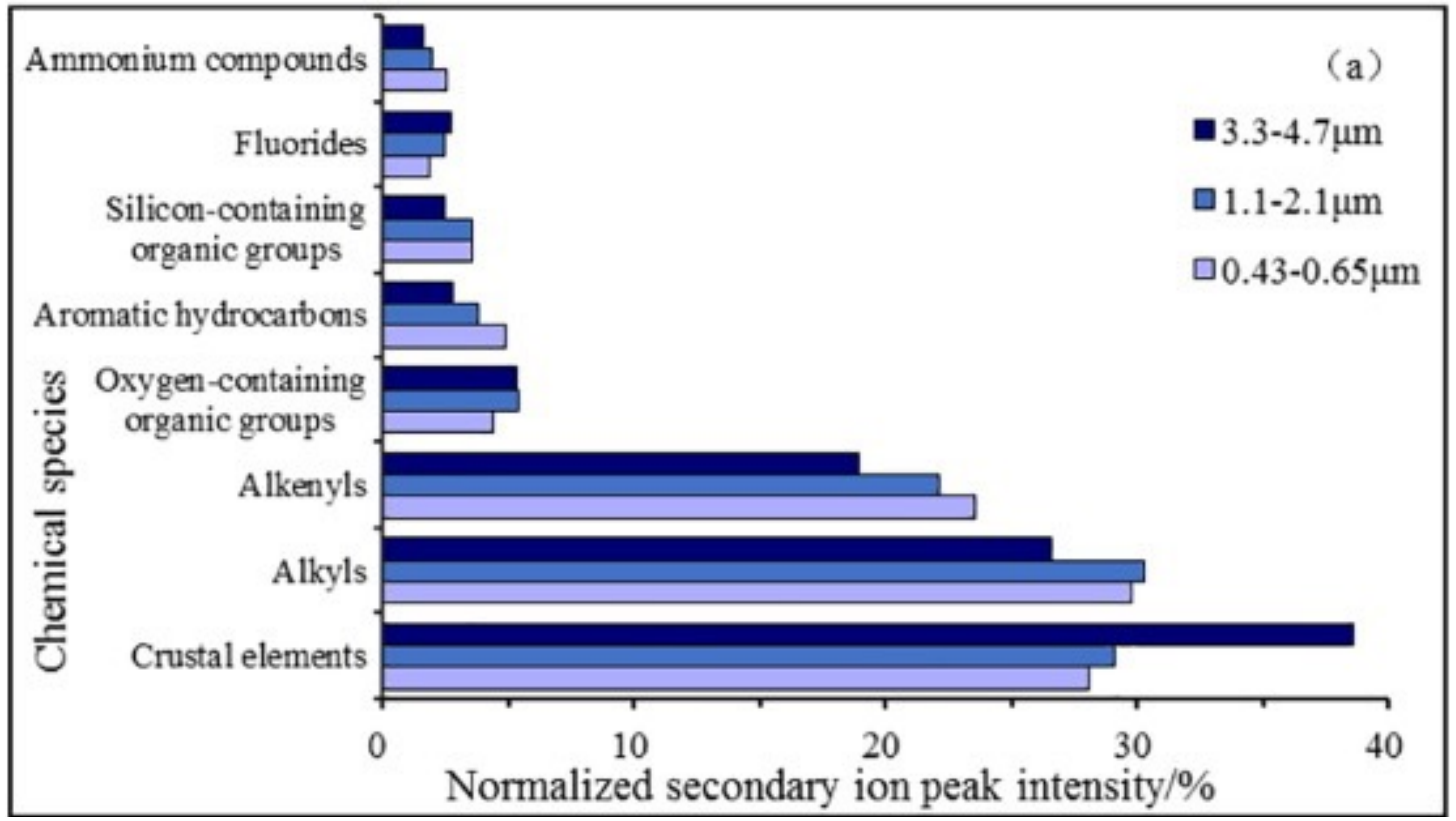
Secondary Ion Mass Spectrometry (SIMS) Used in Reality

Quantifying atmospheric aerosol particles during heavy air pollution event in Beijing



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

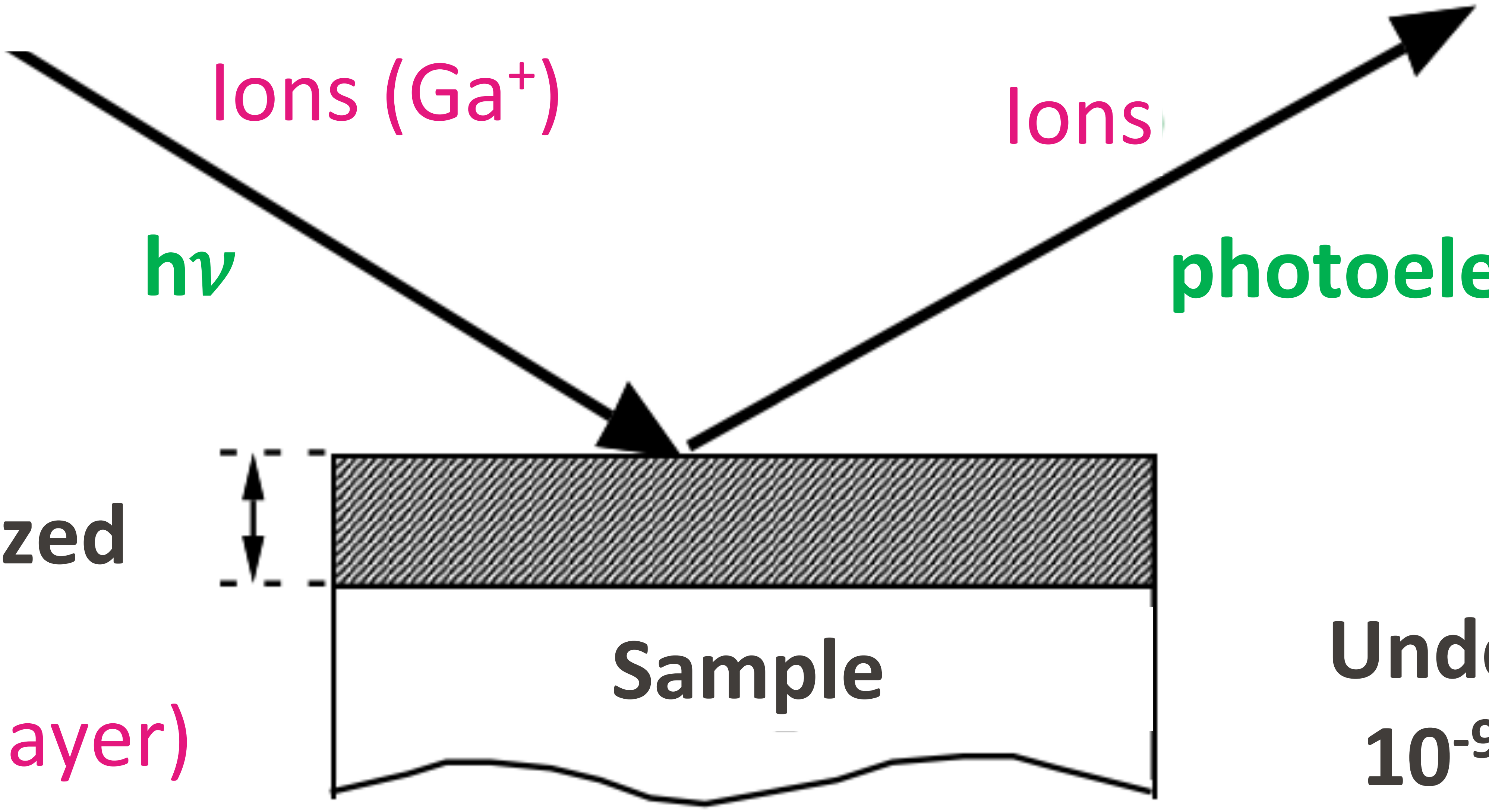




Technologies to Monitor Surface Science: XPS and SIMS

Secondary ion mass spectrometry (SIMS)

X-ray photoelectron spectroscopy (XPS)



Primary beam

Ions (Ga^+)

$h\nu$

Secondary particles to detector

Ions

photoelectron

Depth analyzed

1-2 nm (monolayer)

5-10 nm

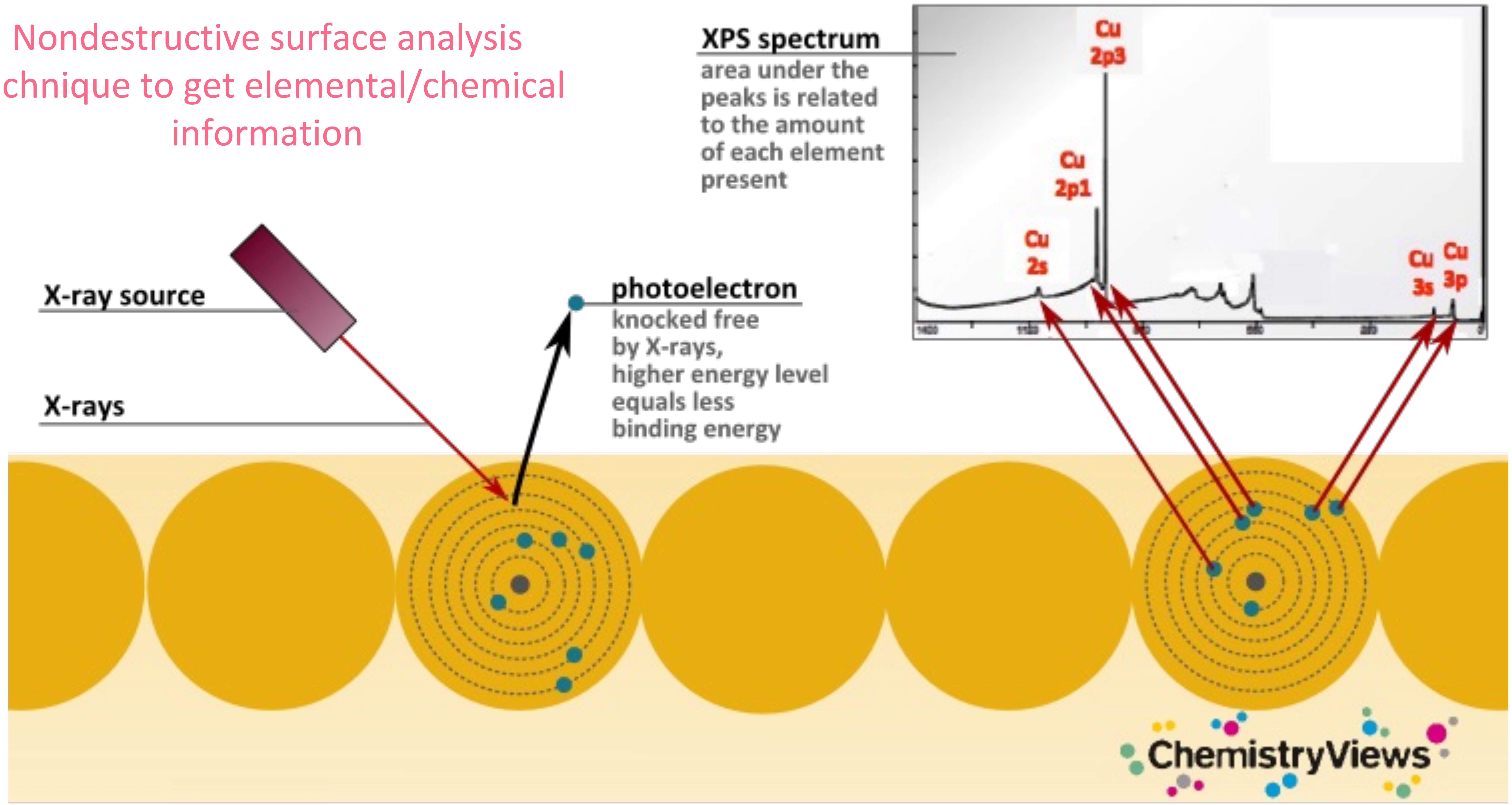
Sample

Under UHV
10^{-9} mbar

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



XPS spectrum
area under the peaks is related to the amount of each element present

X-ray source

X-rays

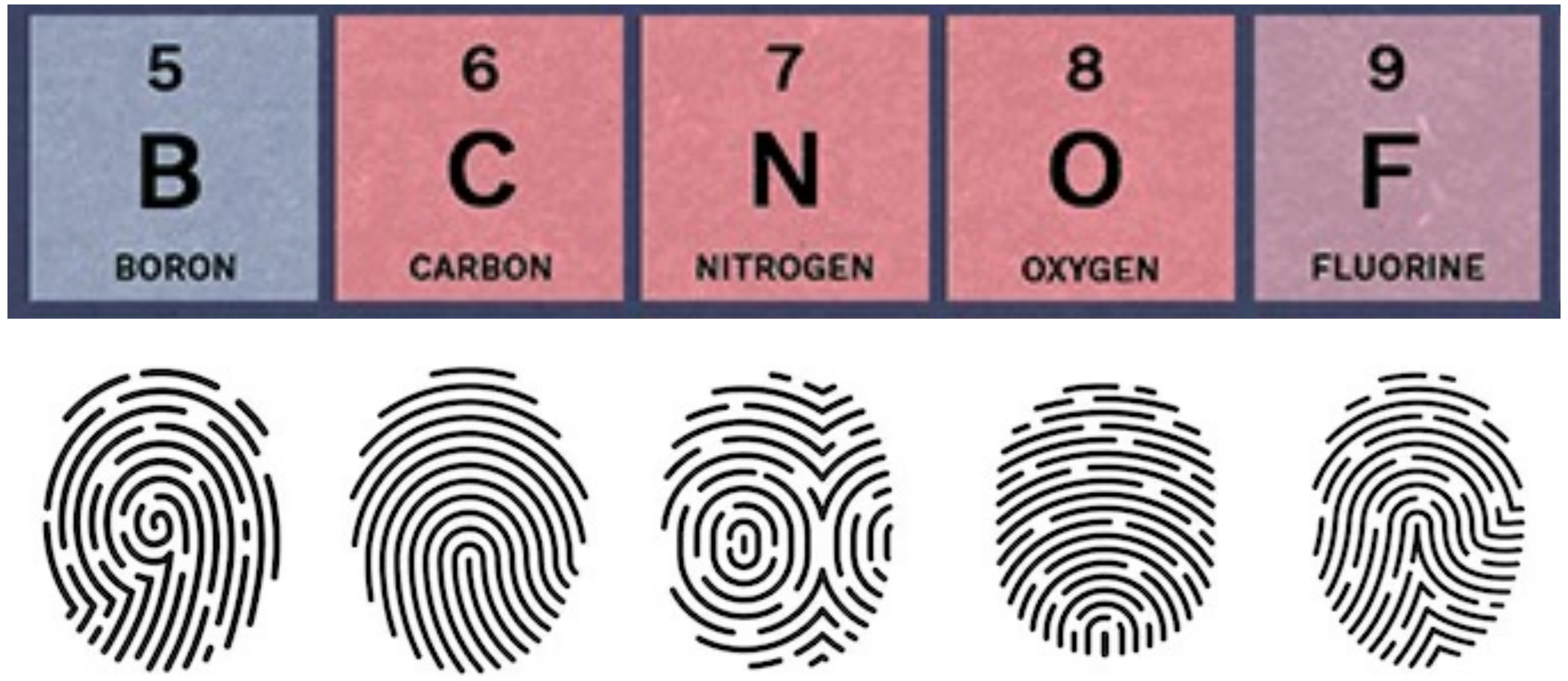
photoelectron
knocked free by X-rays, higher energy level equals less binding energy

ChemistryViews

What Information Can XPS Provide?

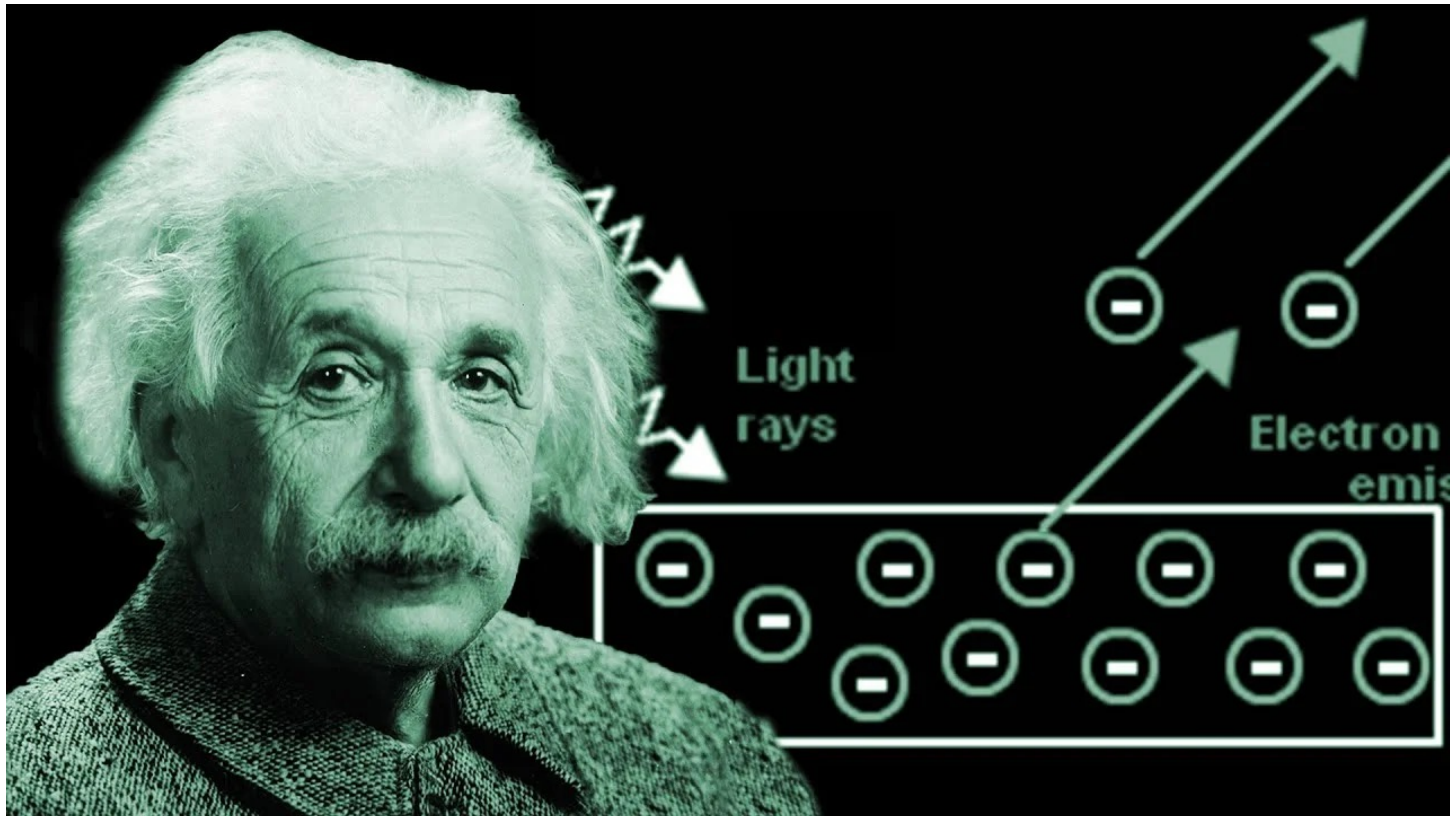
Analytical capabilities of XPS:

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



XPS Relies on the Photoelectric Effect

Photoelectric Effect

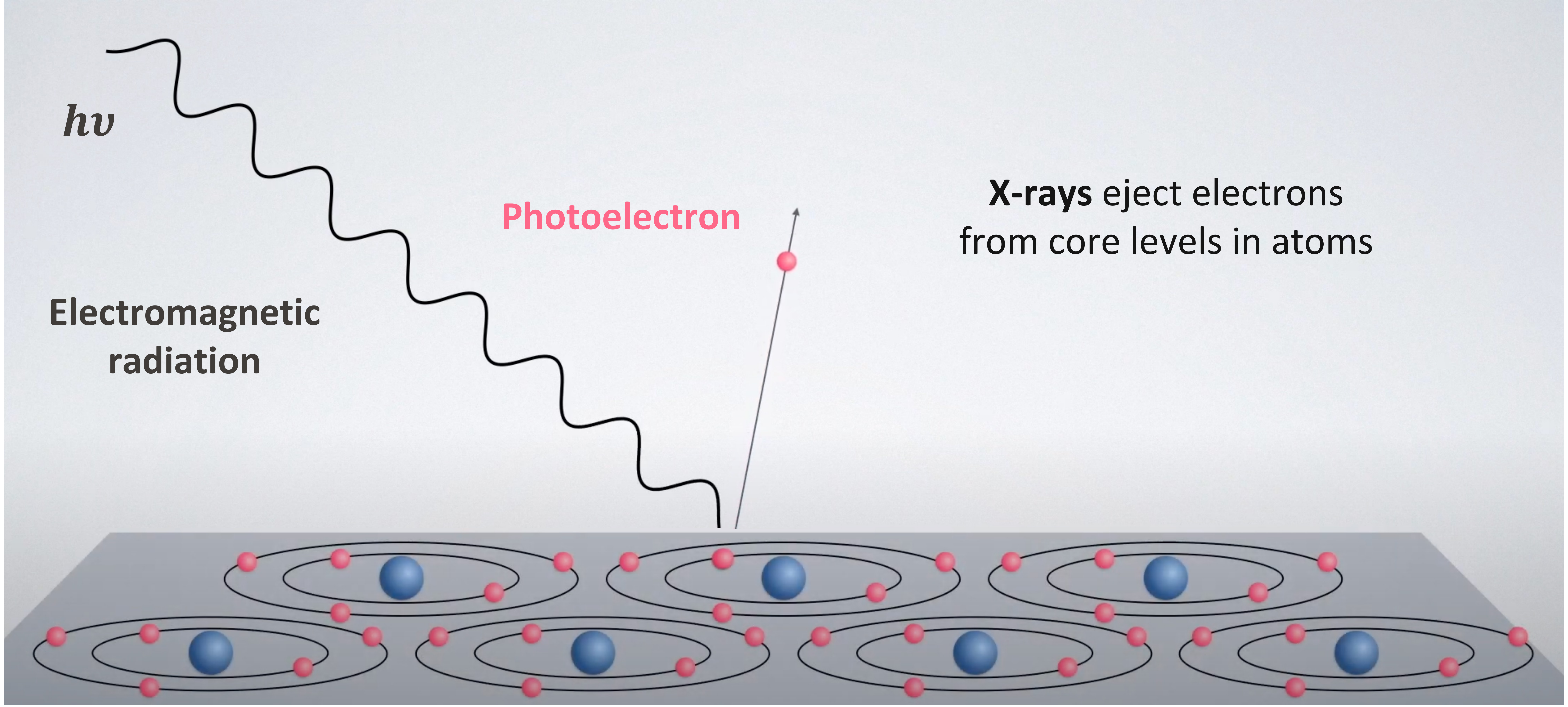


Albert Einstein

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

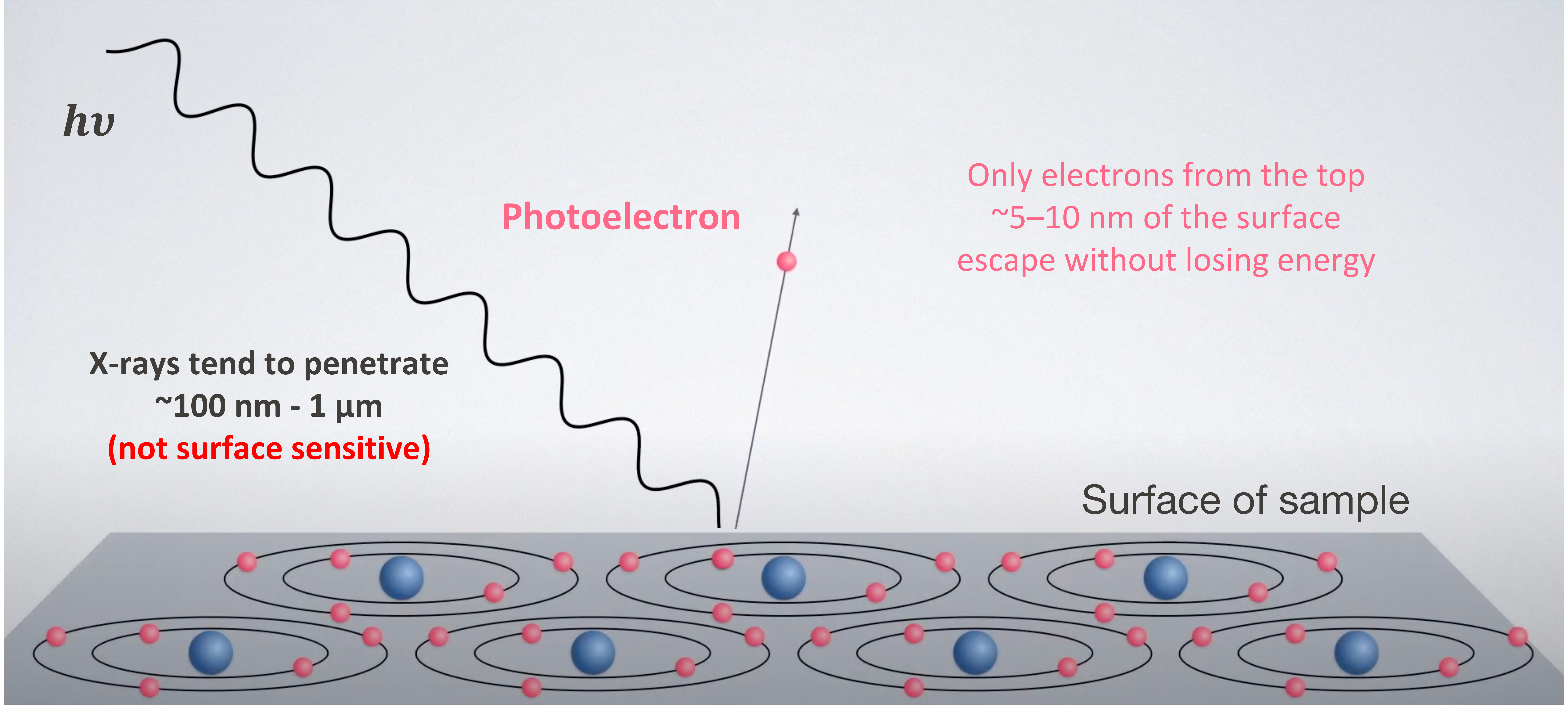
Nobel Prize in Physics for his discovery of the Photoelectric Effect (1921)

Photoelectric Effect



Surface of sample

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



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

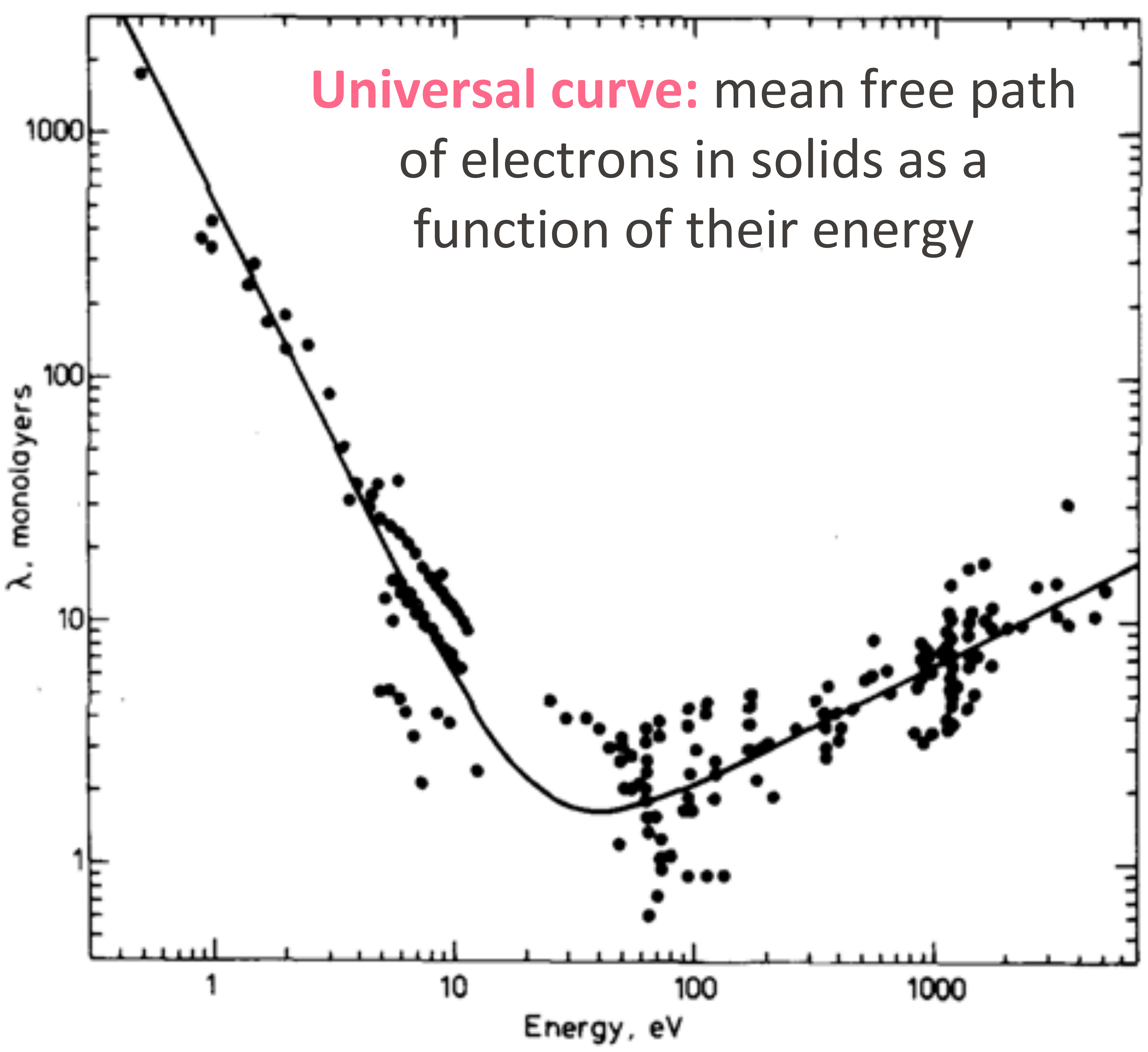
Only electrons from the top
~5–10 nm of the surface
escape without losing energy

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 ~3 nm



Universal curve: mean free path of electrons in solids as a function of their energy

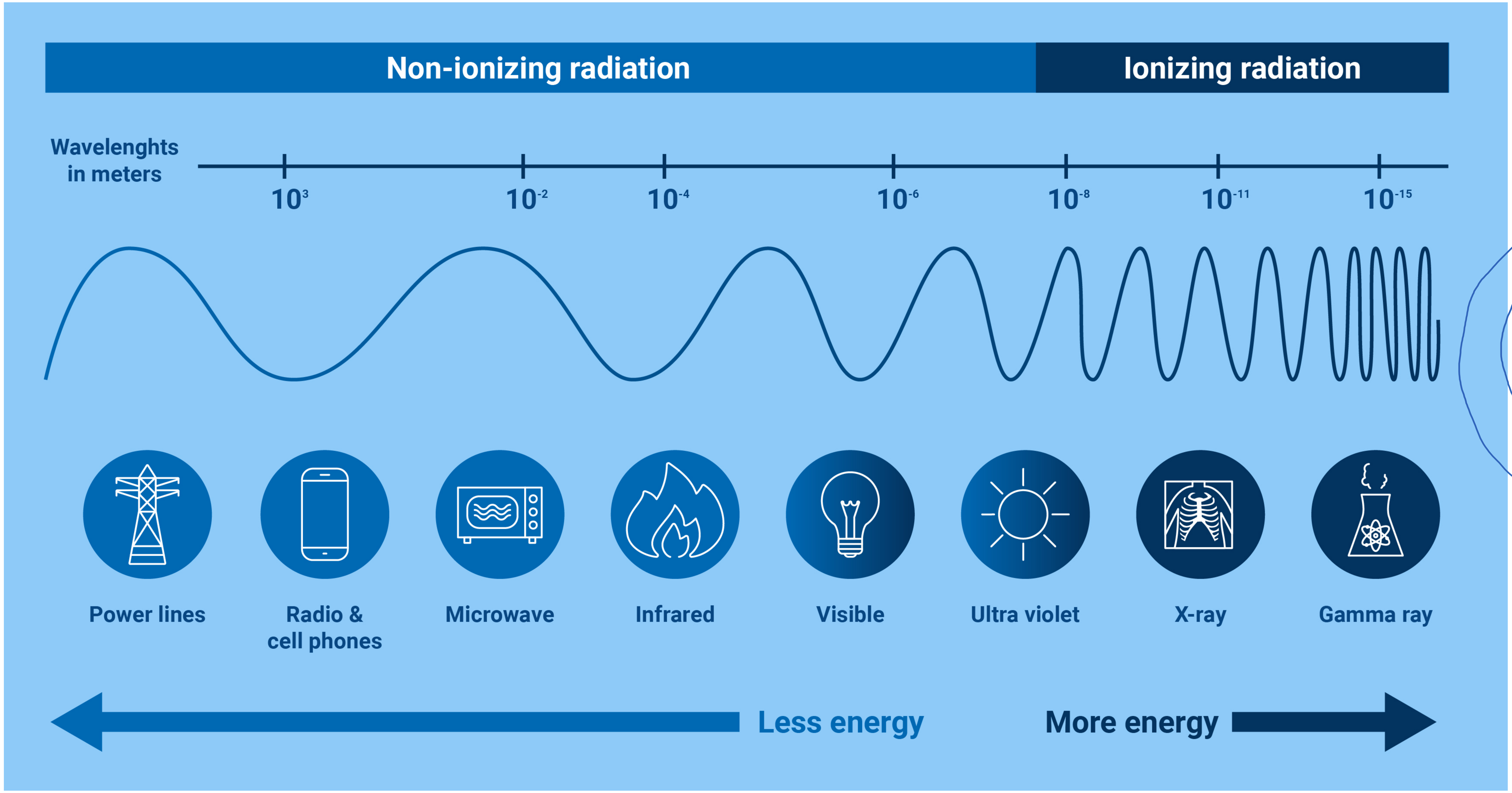
Each data point represents a measurement of the inelastic mean free path of electrons in some material at a particular kinetic energy

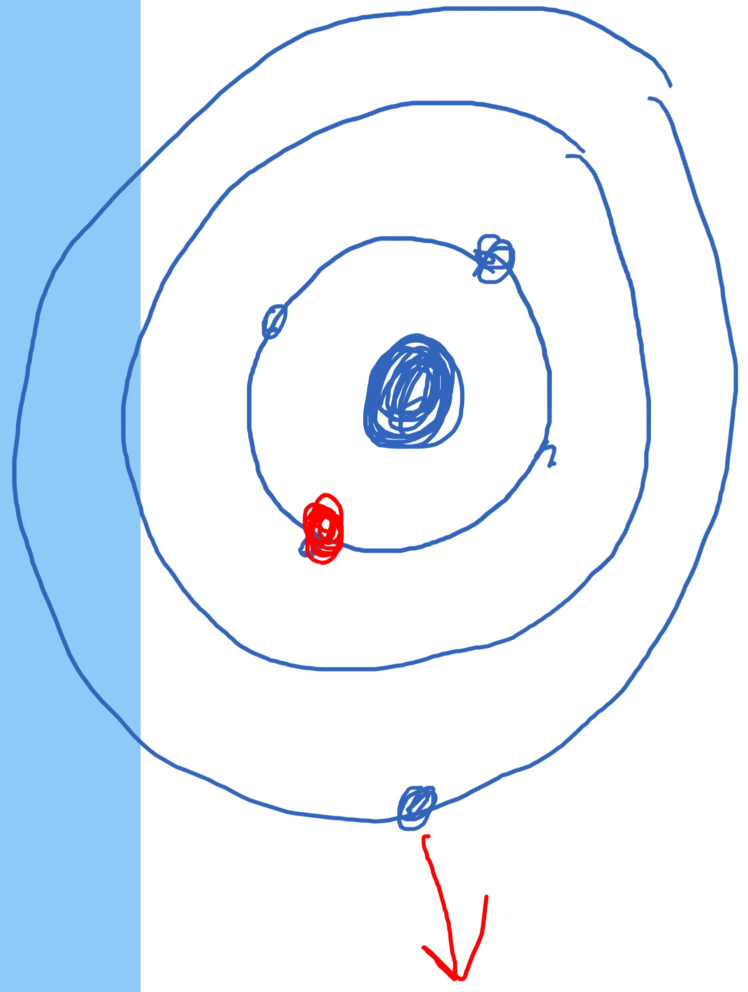
Seah & Dench. Surf. Interf. Anal.| 1979

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)

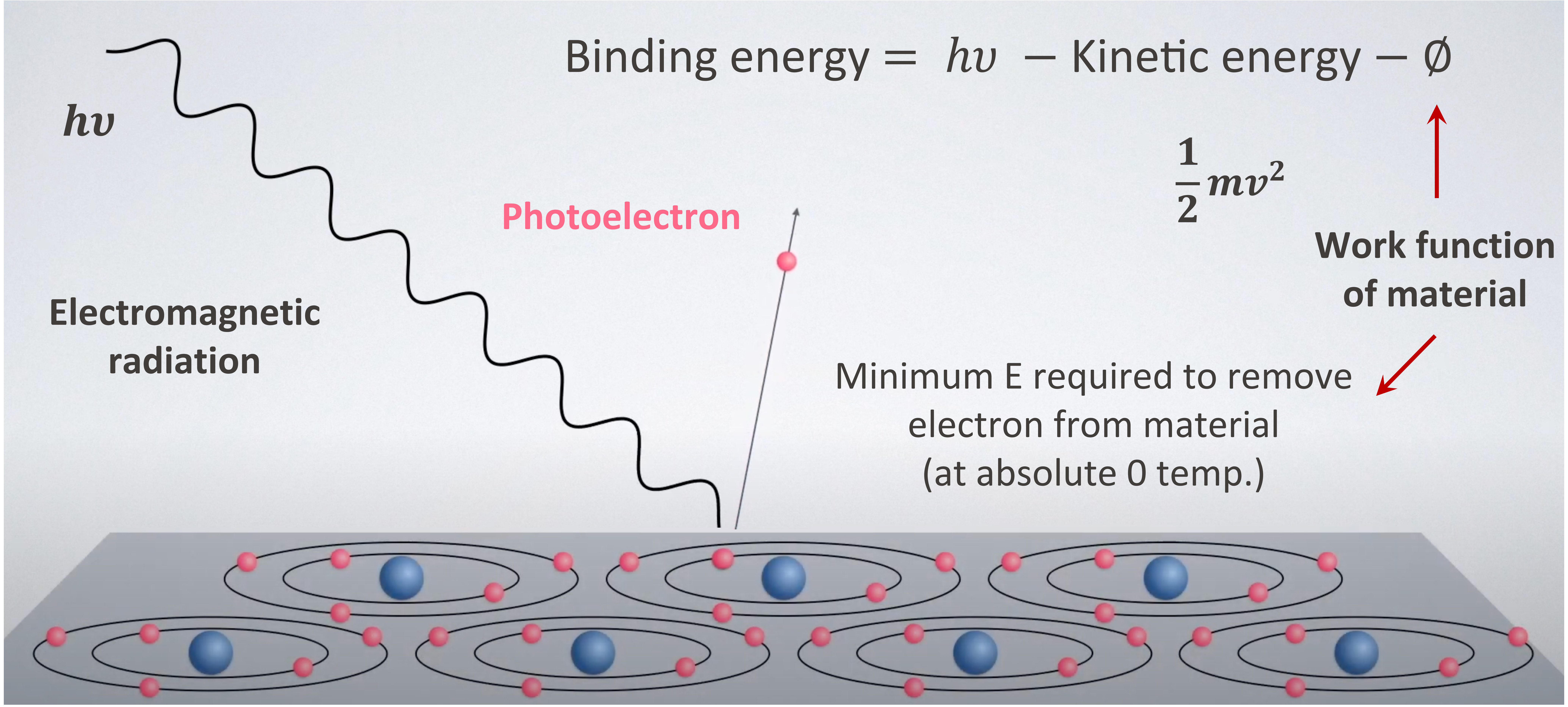
Electromagnetic Radiation – Ionizing Radiation for XPS





Valence electrons : UV light
Core electrons: X-rays

Photoelectric Effect Equation



$$\text{Binding energy} = h\upsilon - \text{Kinetic energy} - \emptyset$$

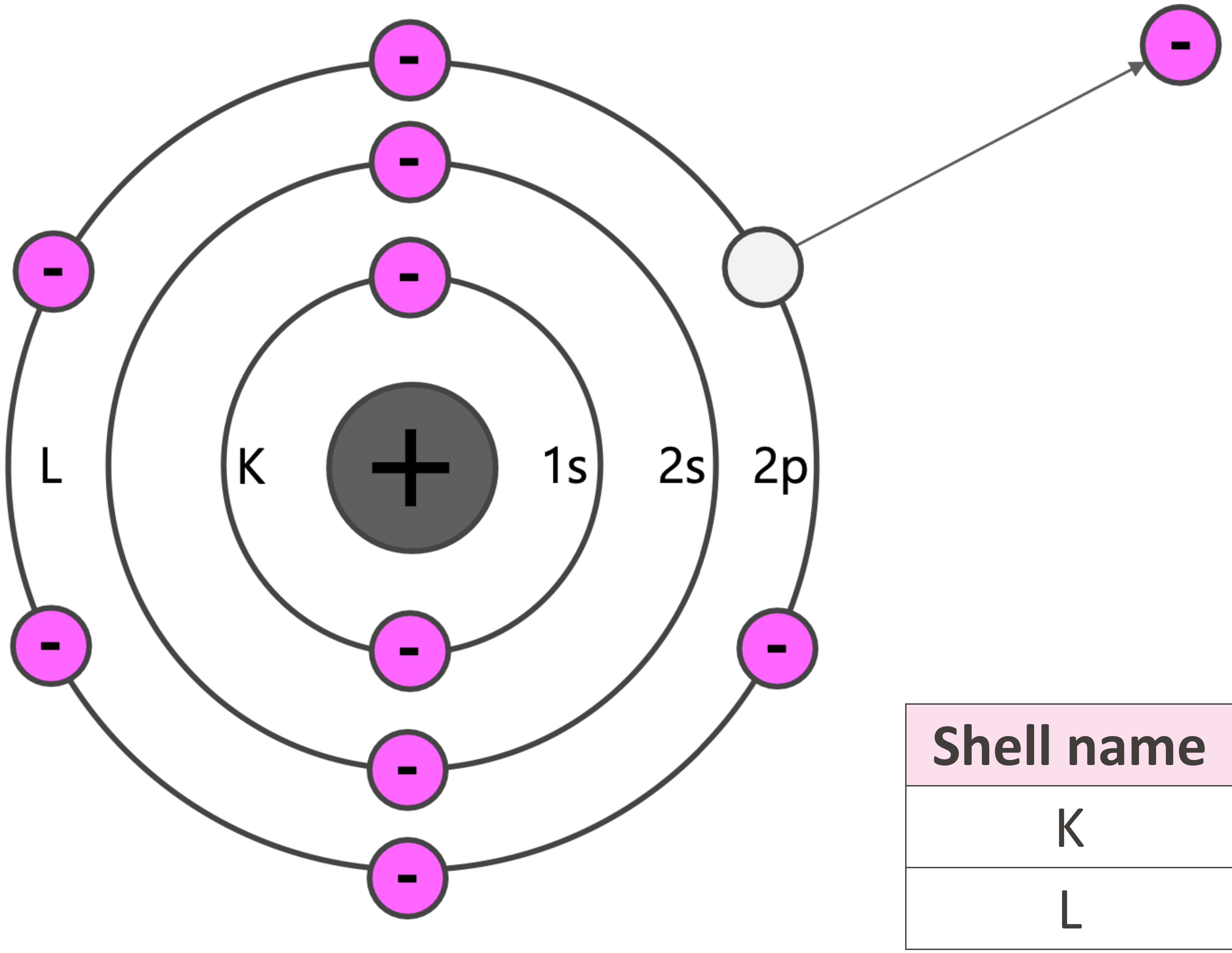
$$\frac{1}{2}mv^2$$

Work function of material

Minimum E required to remove electron from material (at absolute 0 temp.)

Surface of sample

What is Binding Energy?

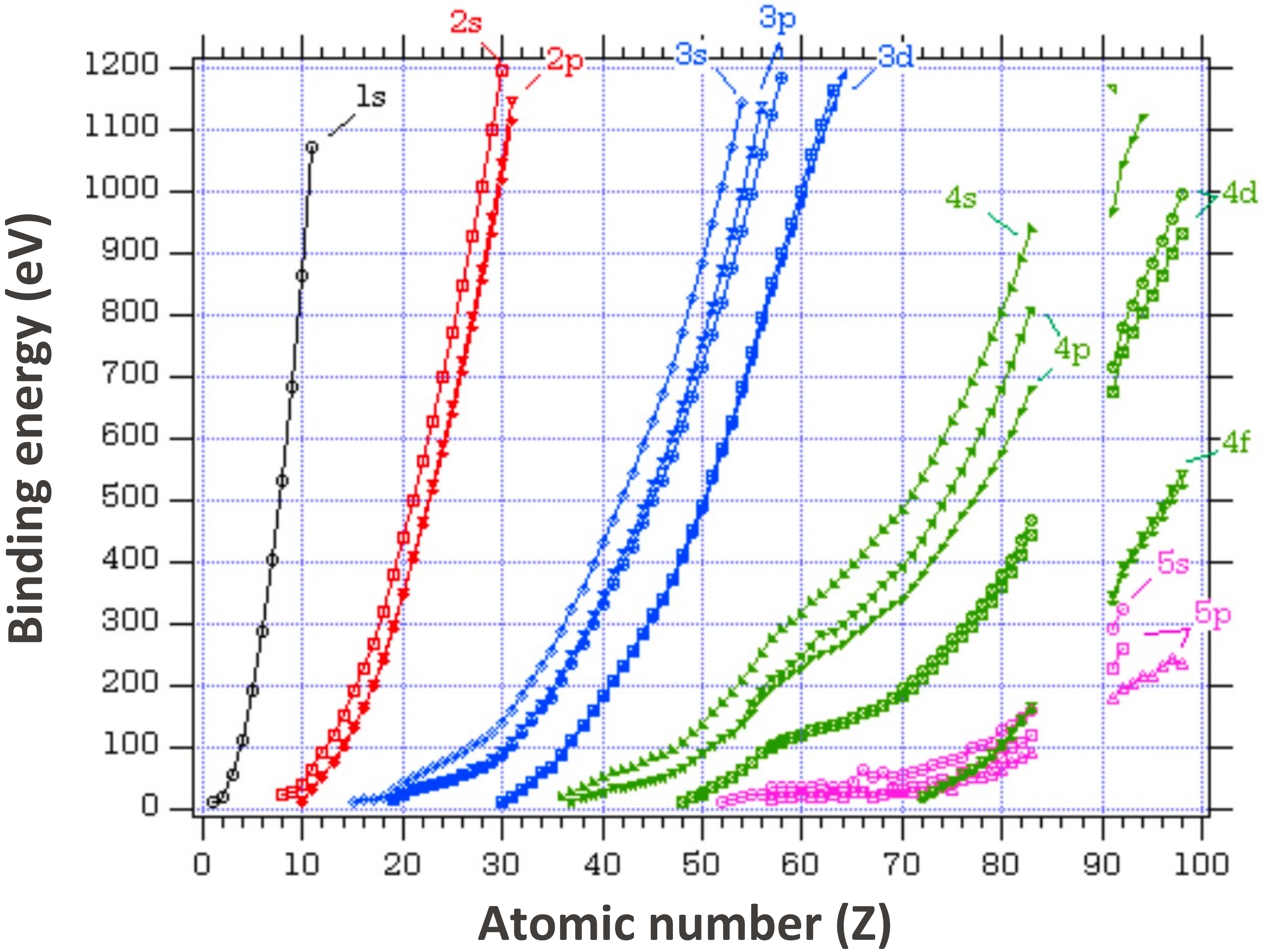


Binding energy = energy an electron needs to overcome the attraction of the nucleus

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

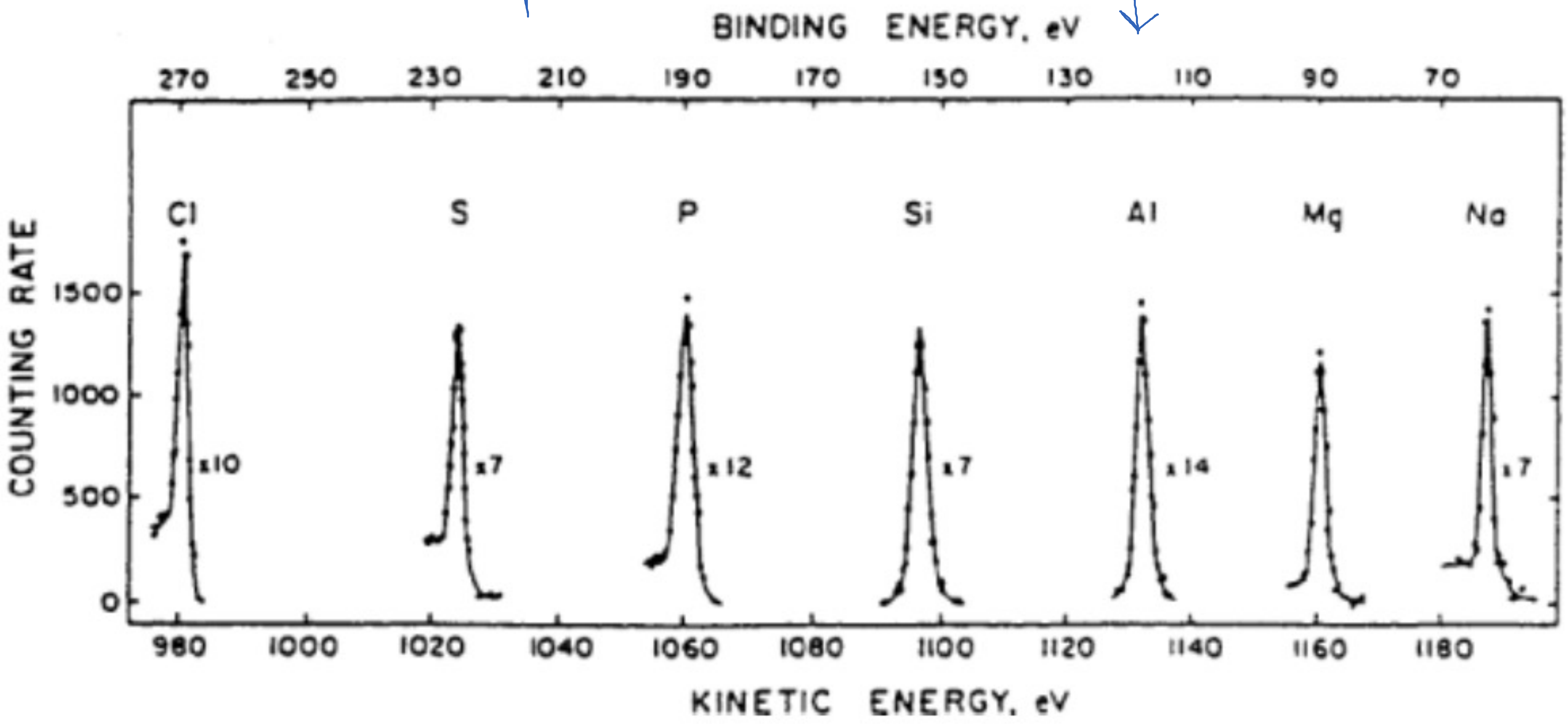
Each element has a unique set of core levels, **binding energies can be used to fingerprint element**

Core-Level Binding Energies are Element Specific

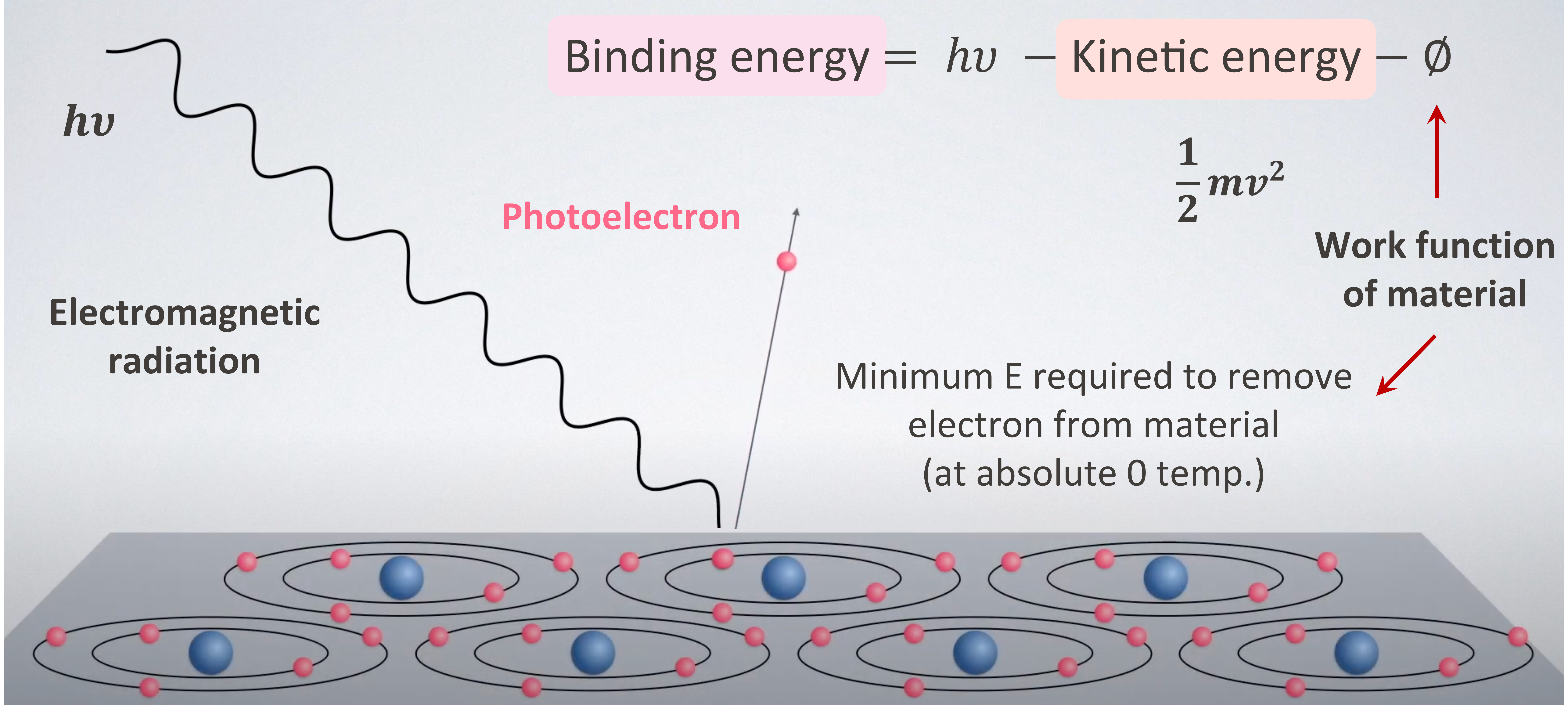
In XPS, higher binding energies correspond to lower kinetic energies and vice-versa

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

$\uparrow$ $\downarrow$



Photoelectric Effect Equation



$$\text{Binding energy} = h\upsilon - \text{Kinetic energy} - \emptyset$$

$$\frac{1}{2}mv^2$$

Work function of material

Minimum E required to remove electron from material (at absolute 0 temp.)

Surface of sample

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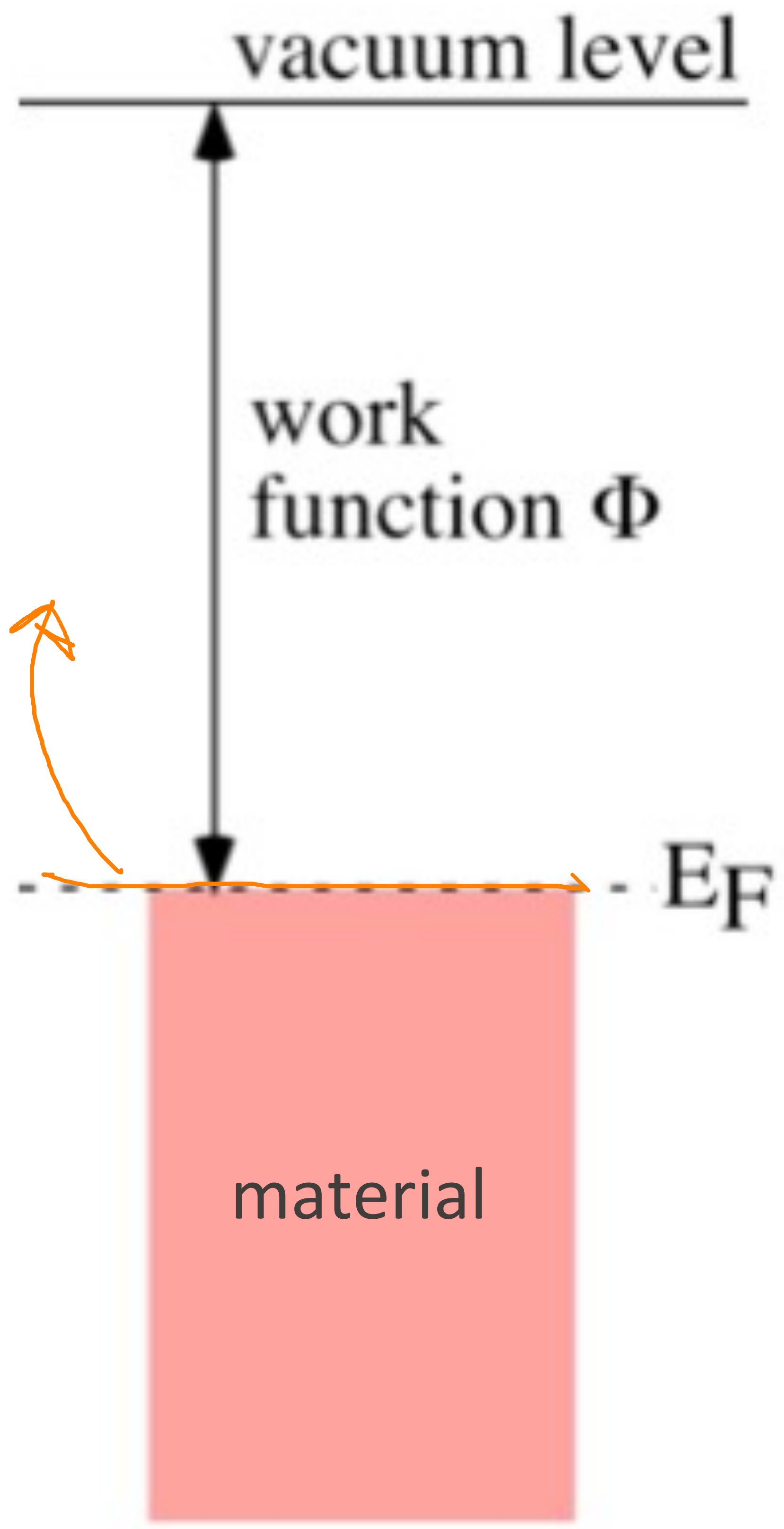
Work Function of Different Materials

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

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



~ 10 nm from the surface

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

Work Function of Different Materials

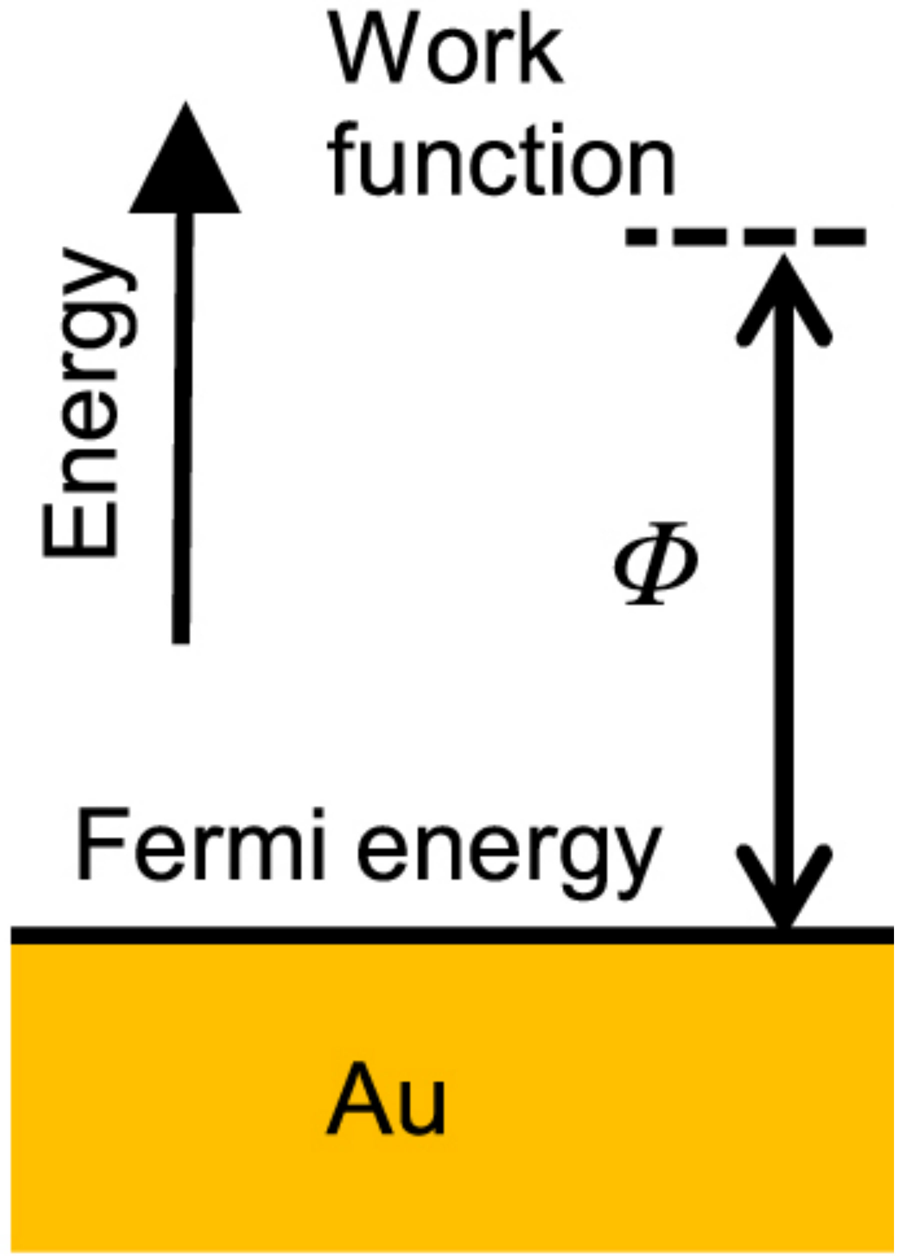
Φ is an inherent material property but it is not fixed – it strongly depends on the surface property of the material (crystallographic orientation/contamination)

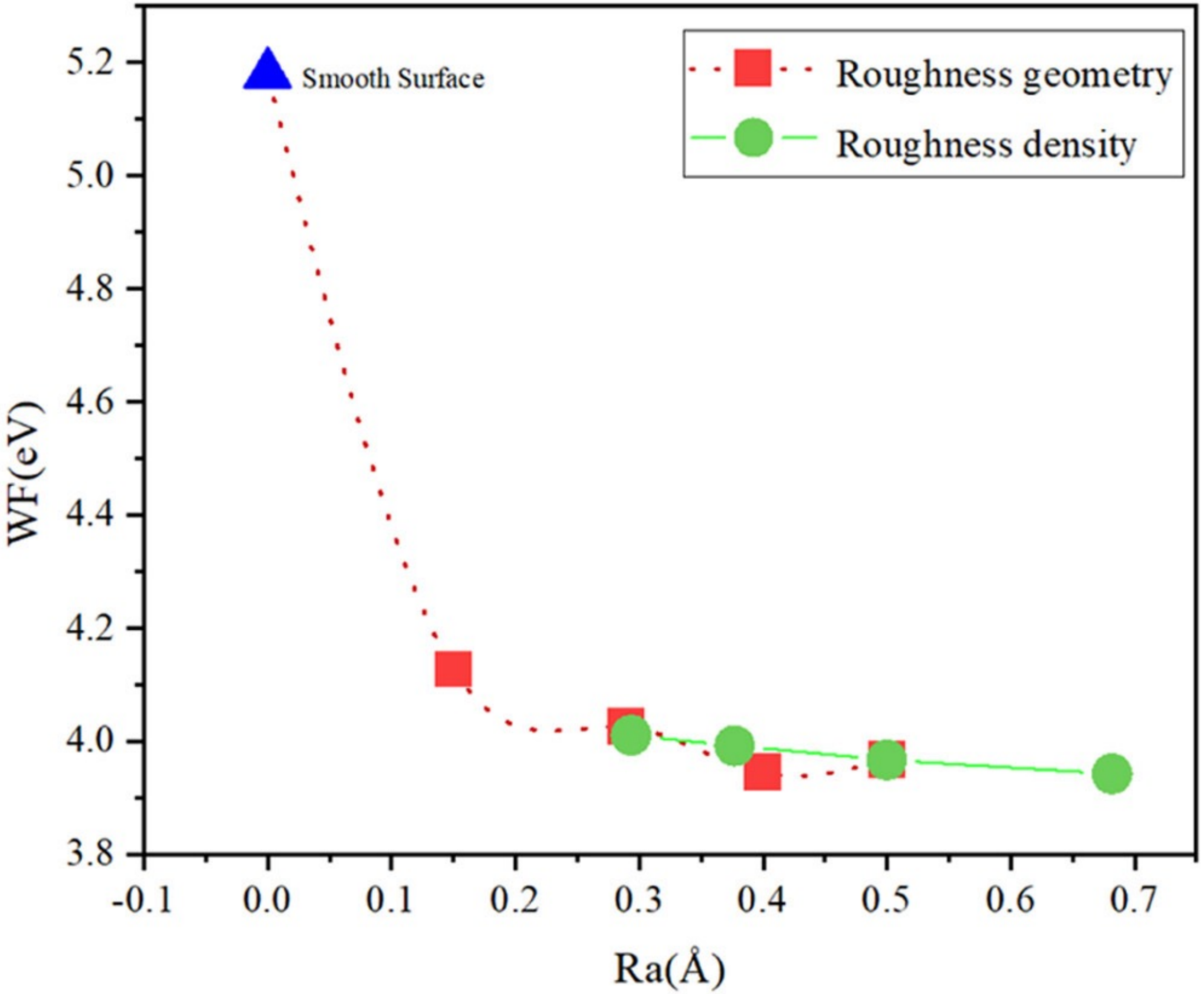
Element	Surface plane	Work Function in eV
Ag	(110)	4.52
Ag	(100)	4.64
Ag	(111)	4.74
Cs	polycrystalline	2.14
Cu	(110)	4.48
Cu	(100)	4.59
Cu	(111)	4.98
Ge	(111)	4.80
Ni	(110)	5.04
Ni	(100)	5.22
Ni	(111)	5.35
W	(111)	4.47
W	(100)	4.63
W	(110)	5.25

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

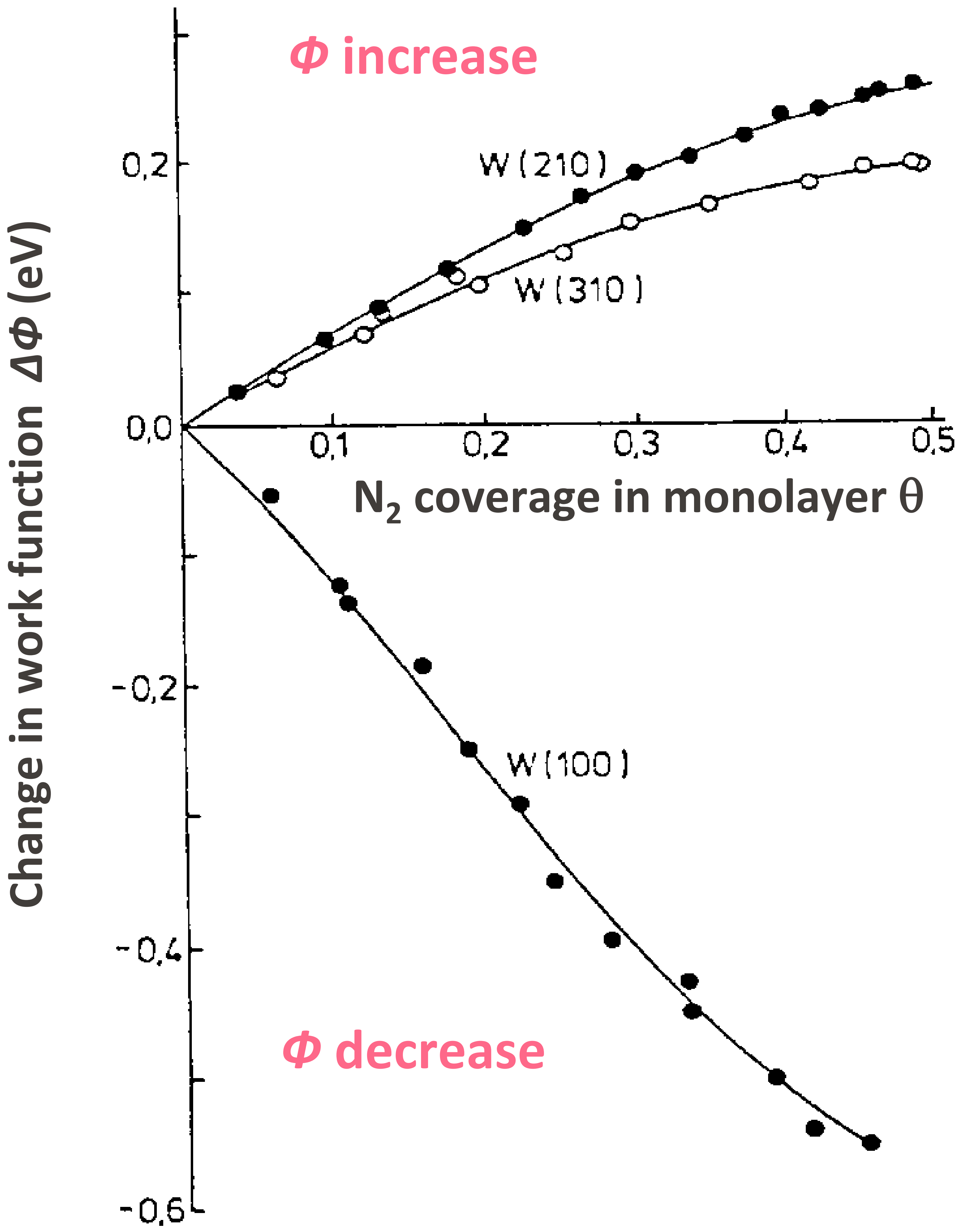
Increasing surface roughness decreases the work function of gold and renders it chemically reactive





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

Adsorbates Alters the Work Function of Materials



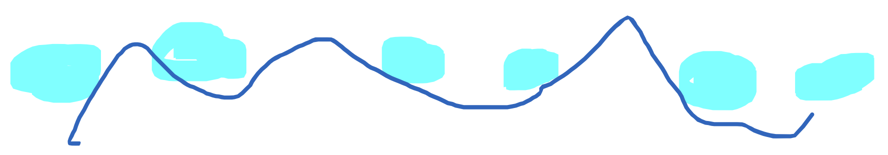
W(210) rougher

↓

Adsorbate atoms located in same plane as metal atoms

↓

Smoothening effect



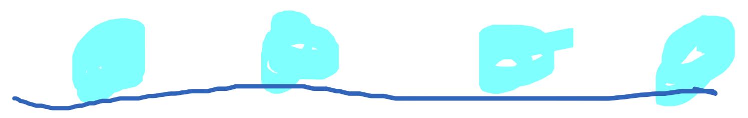
↓

Work function increases

W(100) smoother

↓

Adsorbates stick out



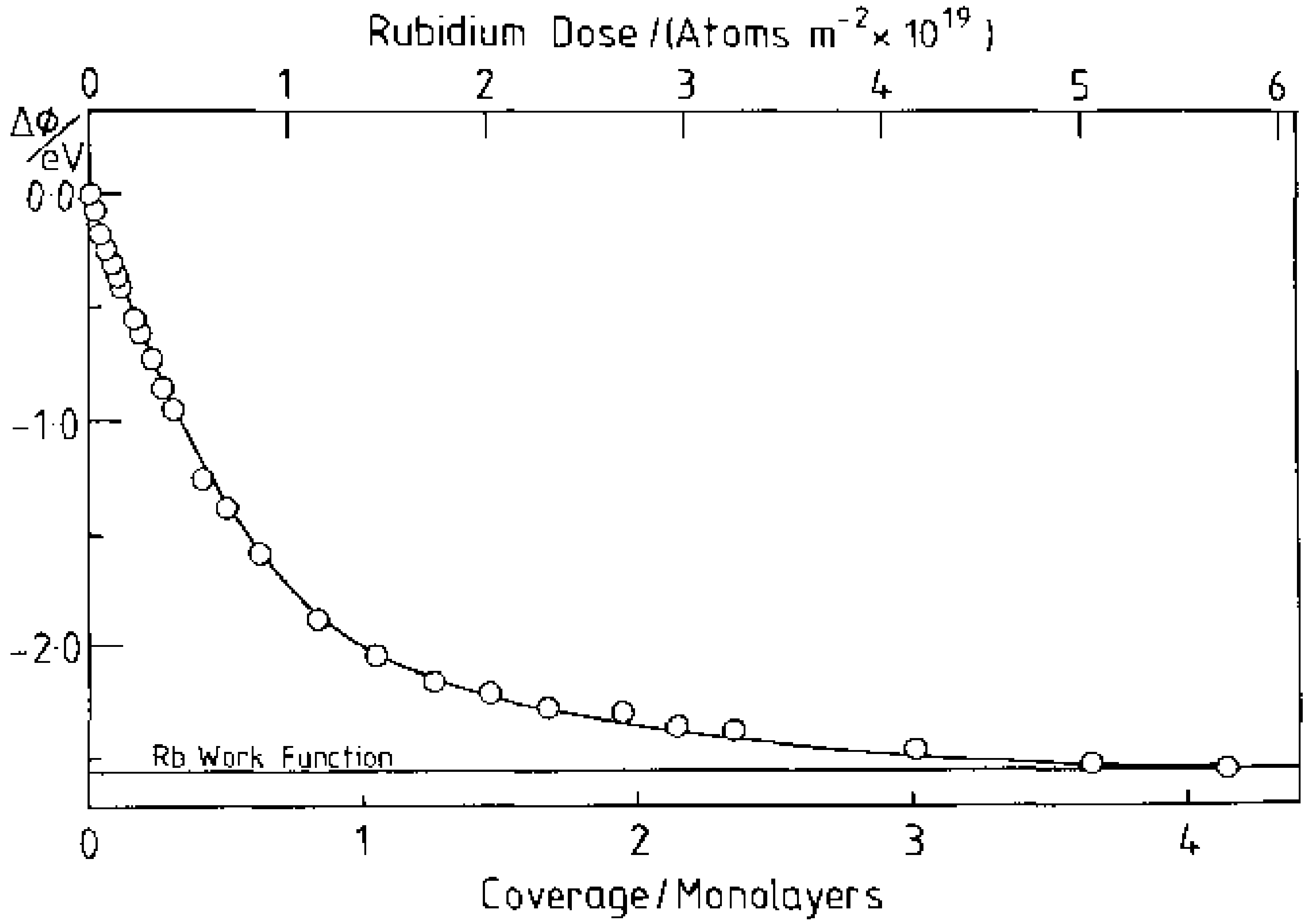
↓

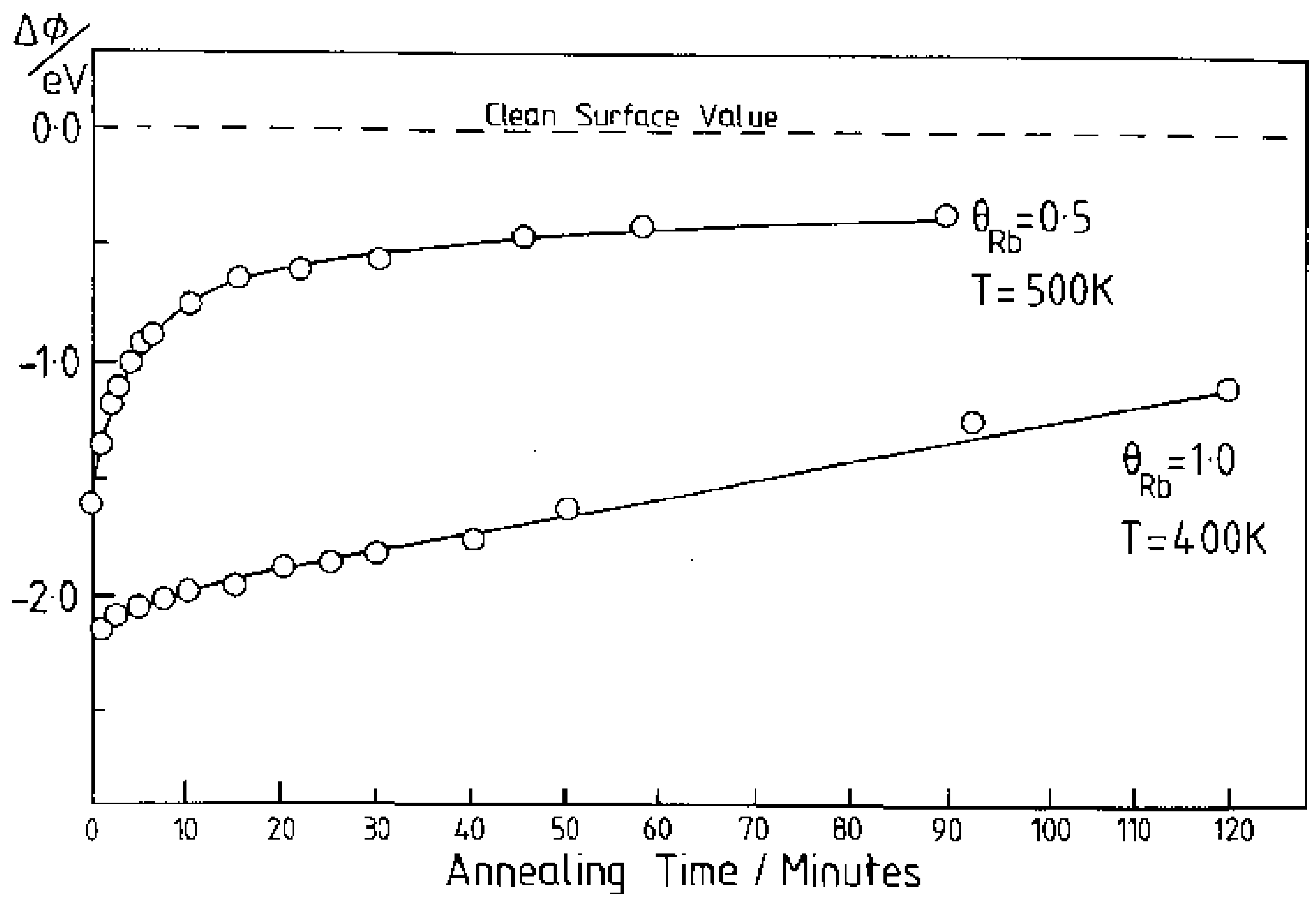
work function decreases upon adsorption

Source: Nic Spencer

Work Function Changes Reflect Surface Composition

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





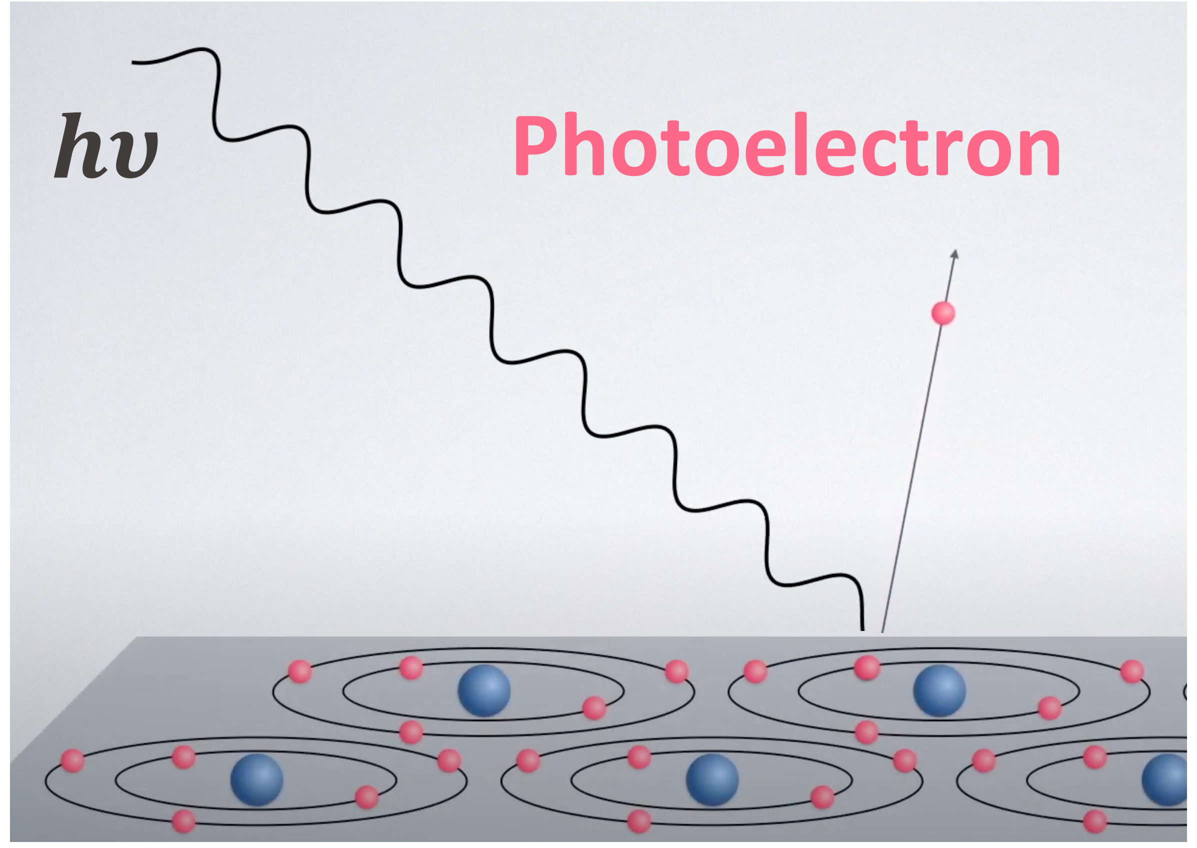
Φ decrease of Ag(111) surface by adsorption of Rb atoms (donates electrons to metal)

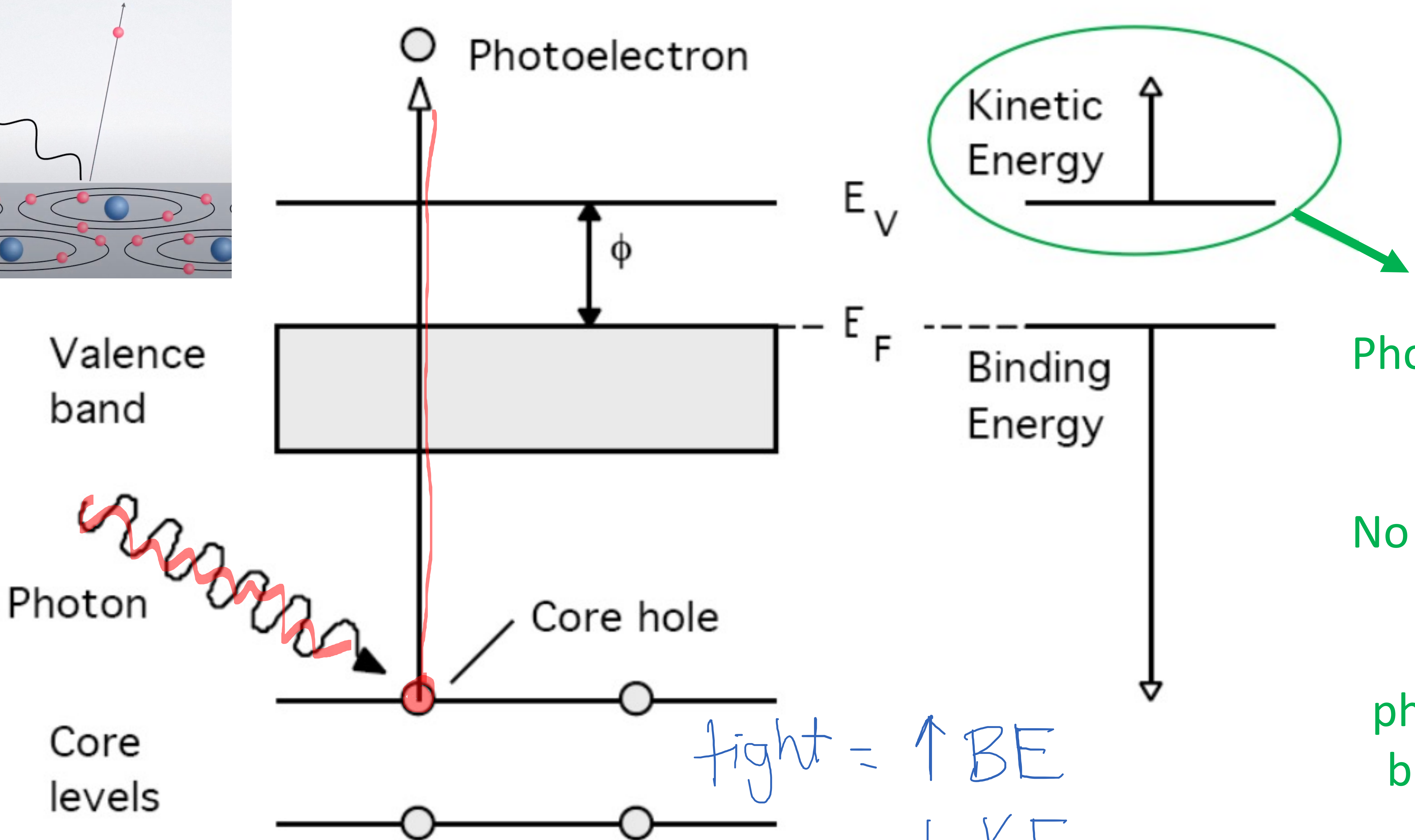
ΔΦ increase upon annealing Rb-covered surface → Rb atoms diffuse into bulk of Ag crystal and no longer sit on surface

Eventually, reaches *Φ* of clean silver

Source: Nic Spencer

Relating the Work Function and Fermi Level to XPS





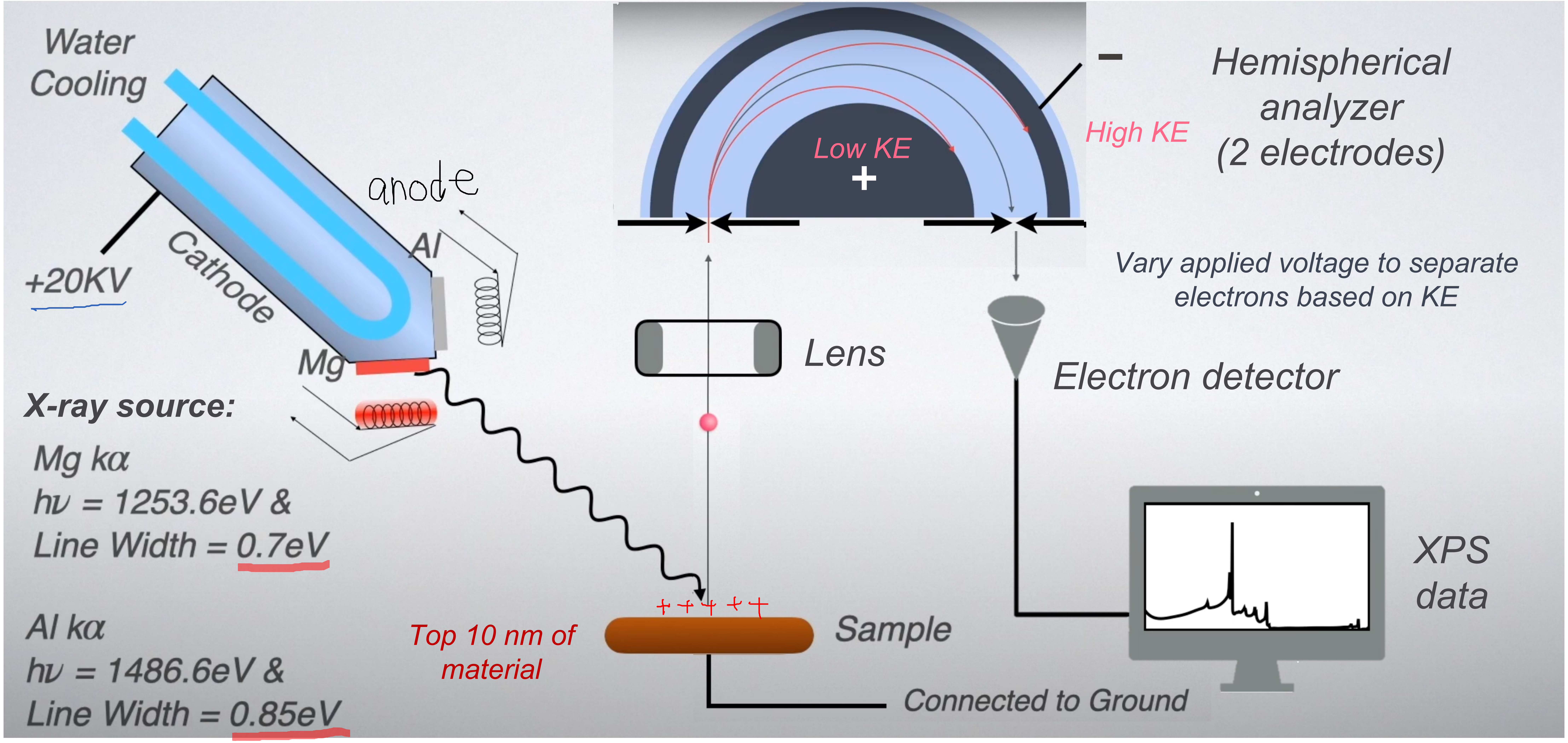
tight = ↑BE
↓KE

Photoelectron kinetic energy can be measured

No photoemission for hν < Φ

Kinetic energy of photoelectron increases as binding energy decreases

How Does XPS Analyze Surface Elements?

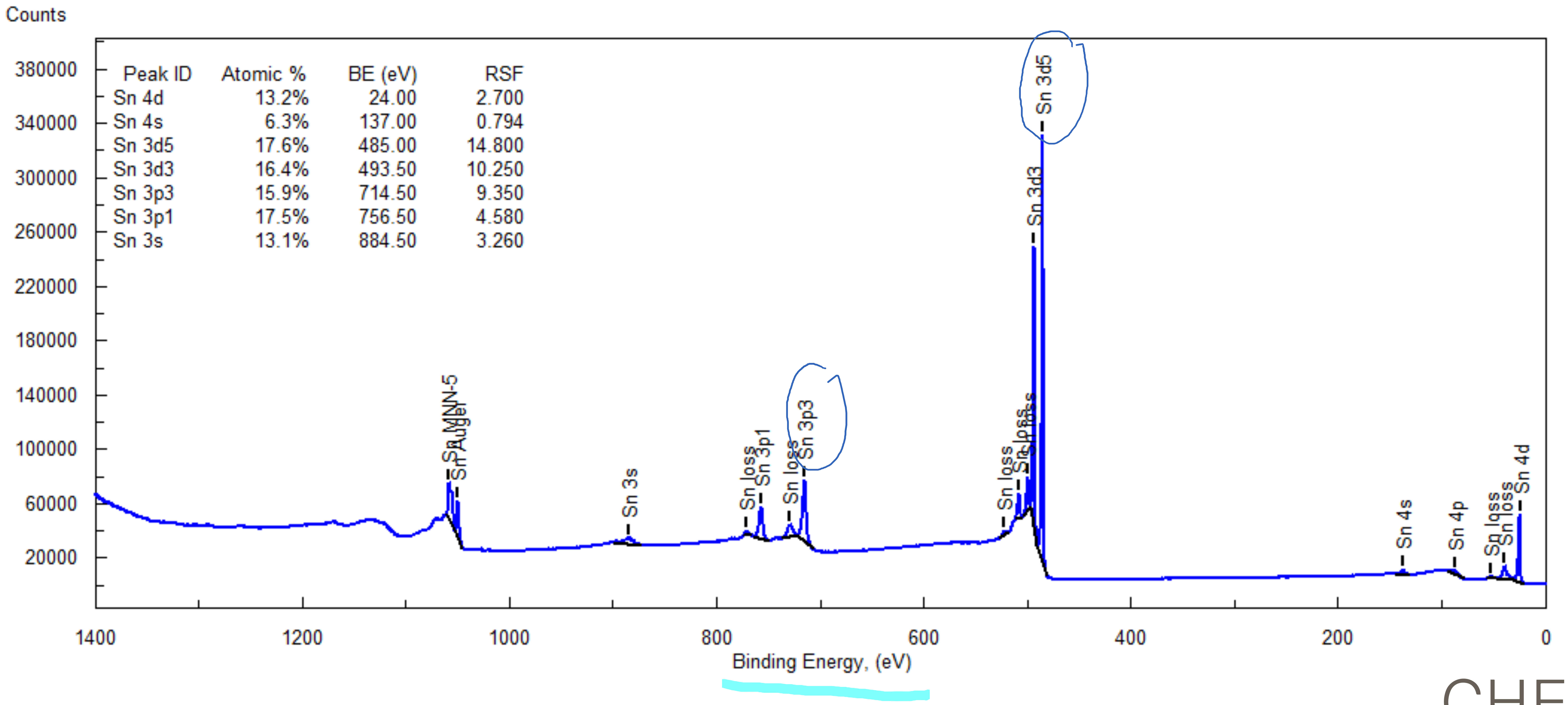


Binding Energy (eV) vs. Number of Electrons Counted

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

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

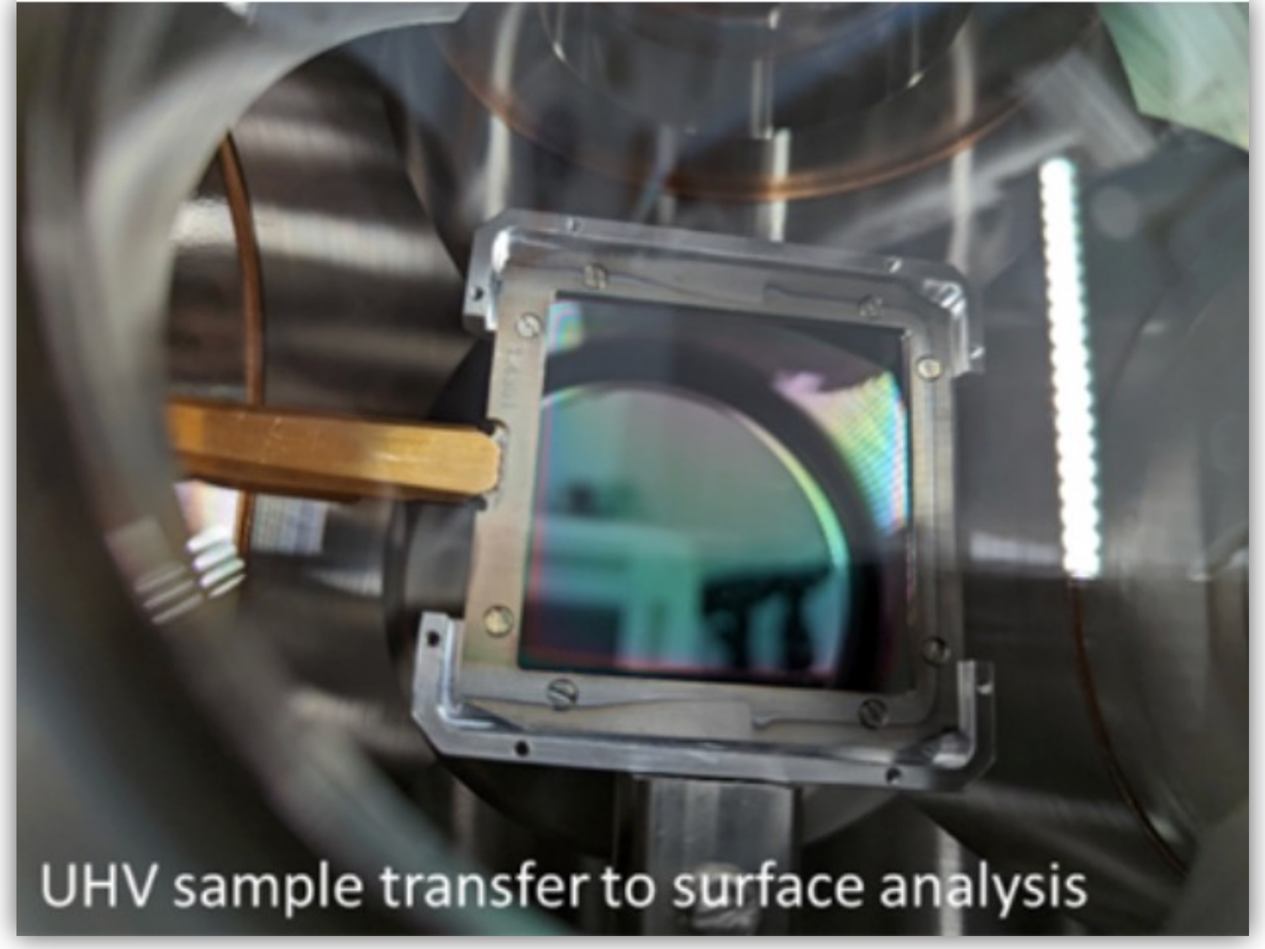
Sample Description: Sn, tin



Peak ID	Atomic %	BE (eV)	RSF
Sn 4d	13.2%	24.00	2.700
Sn 4s	6.3%	137.00	0.794
Sn 3d5	17.6%	485.00	14.800
Sn 3d3	16.4%	493.50	10.250
Sn 3p3	15.9%	714.50	9.350
Sn 3p1	17.5%	756.50	4.580
Sn 3s	13.1%	884.50	3.260

Limitations of XPS – General Challenges

- Requires UHV and clean surfaces – complex sample handling
- H^{1} and He^{2} cannot be detected (no core levels accessible)
- Slow analysis and expensive instrumentation


UHV sample transfer to surface analysis

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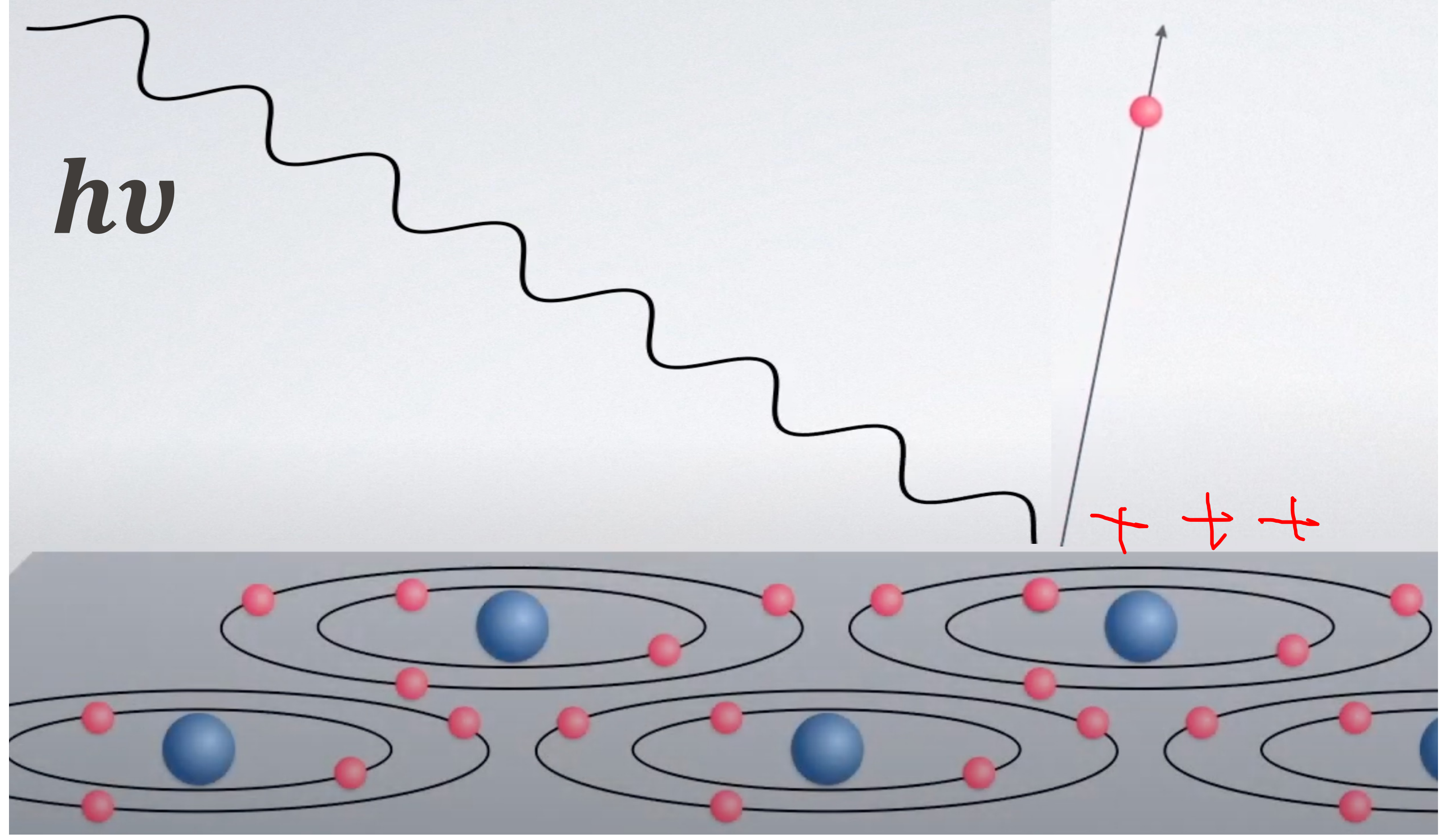
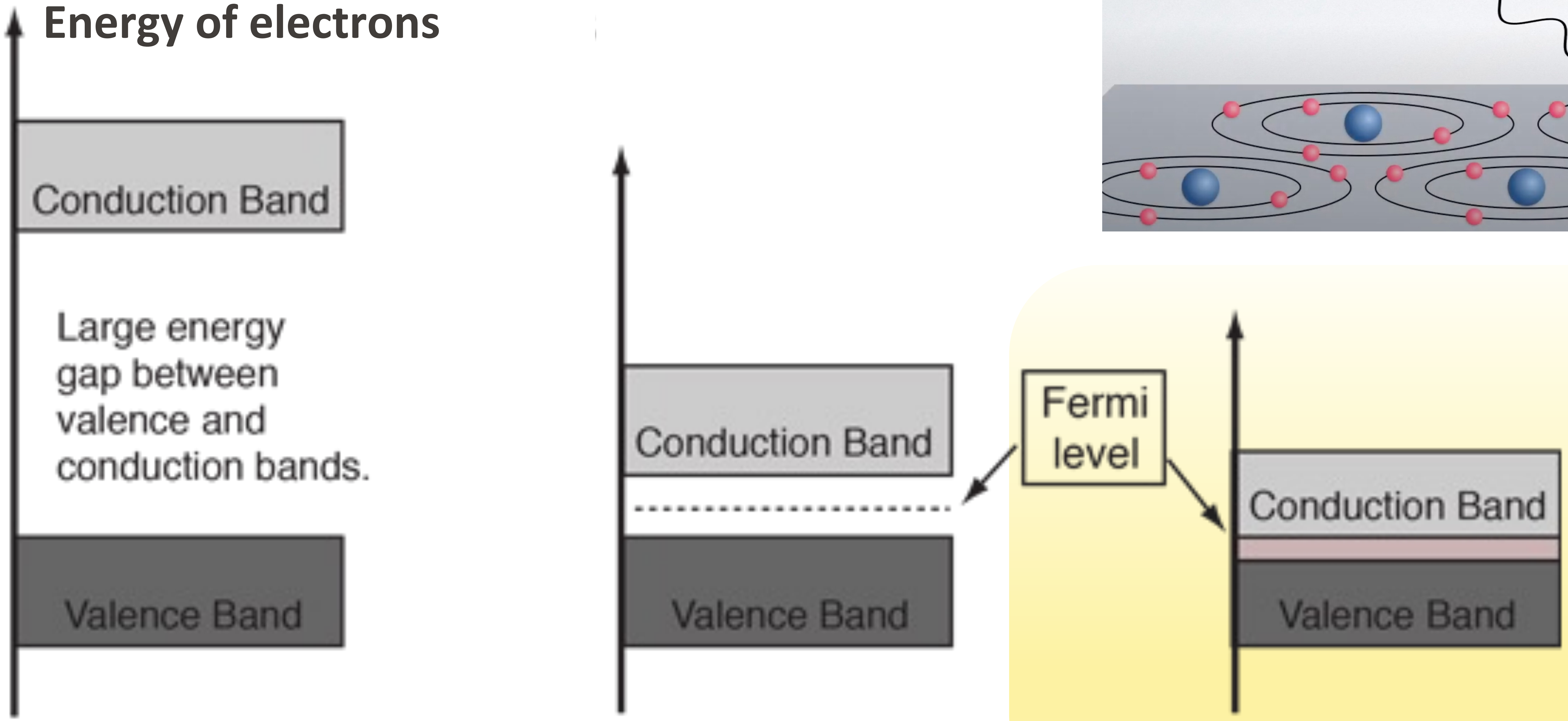
Limitations of XPS – Charging Effects on Insulators

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





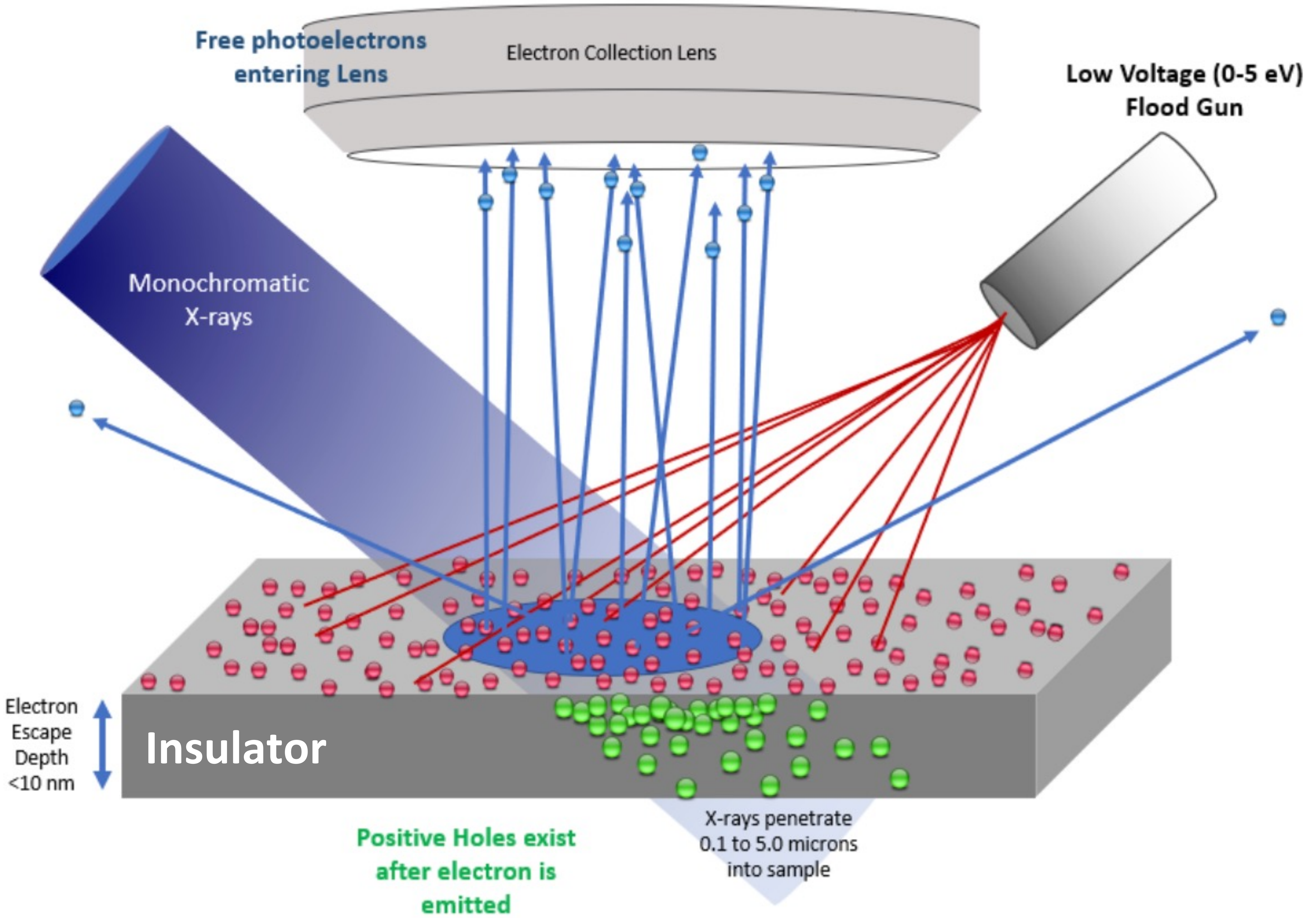
Insulator

Semiconductor

Conductor

Electrons can flow freely to replace ejected ones

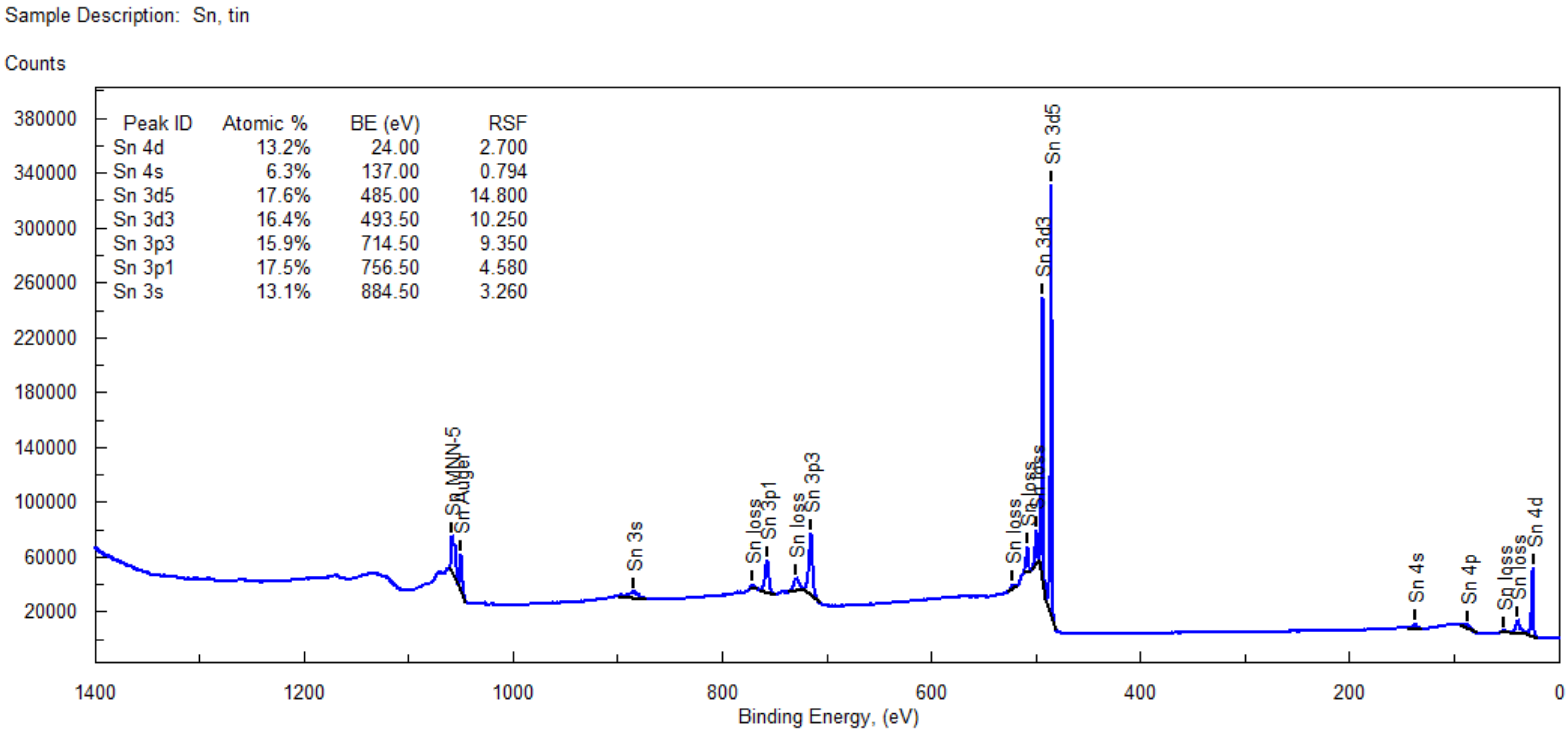
Limitations of XPS – Neutralization Using Flood Gun



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

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Sn 3d5	17.6%	485.00	14.800
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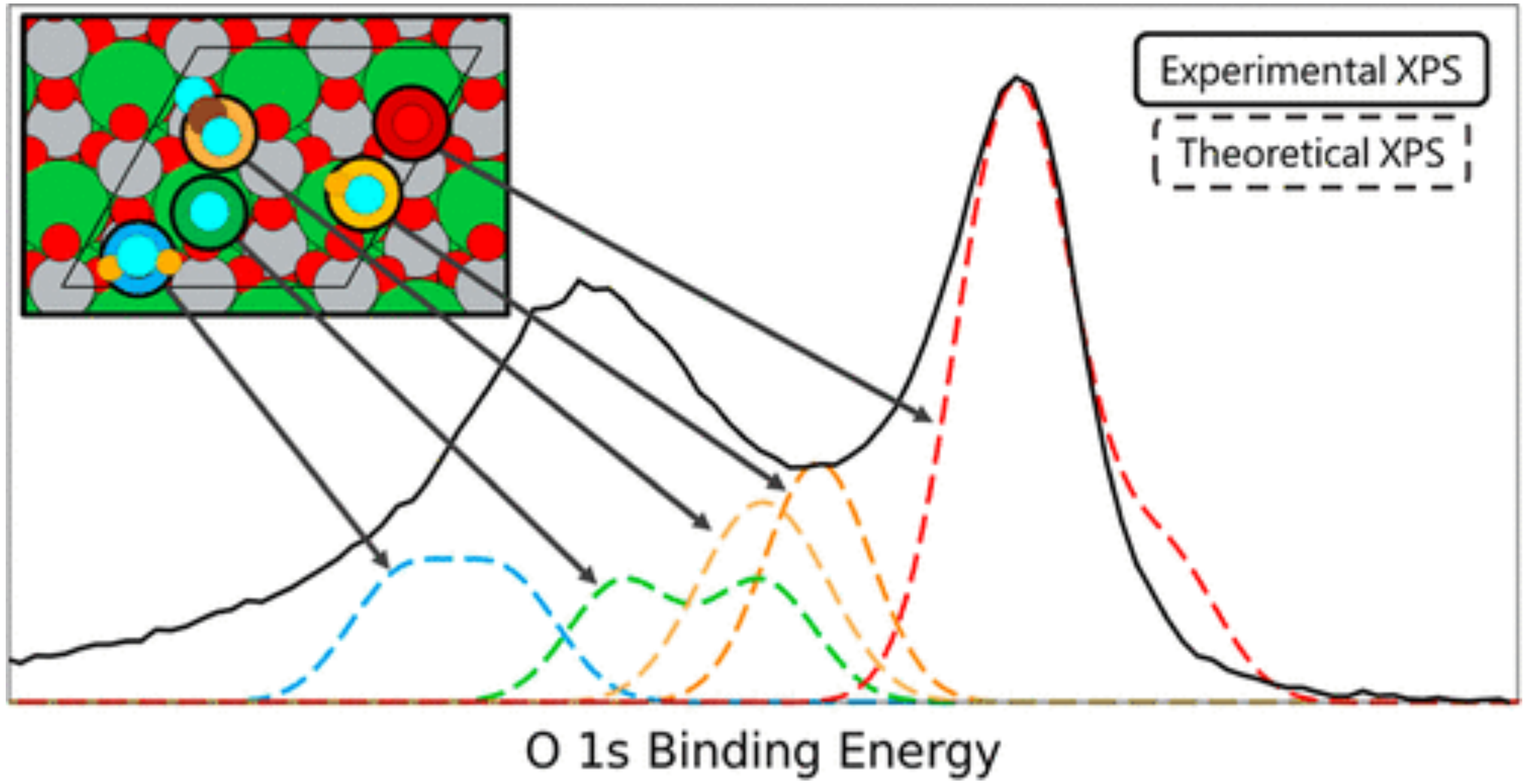
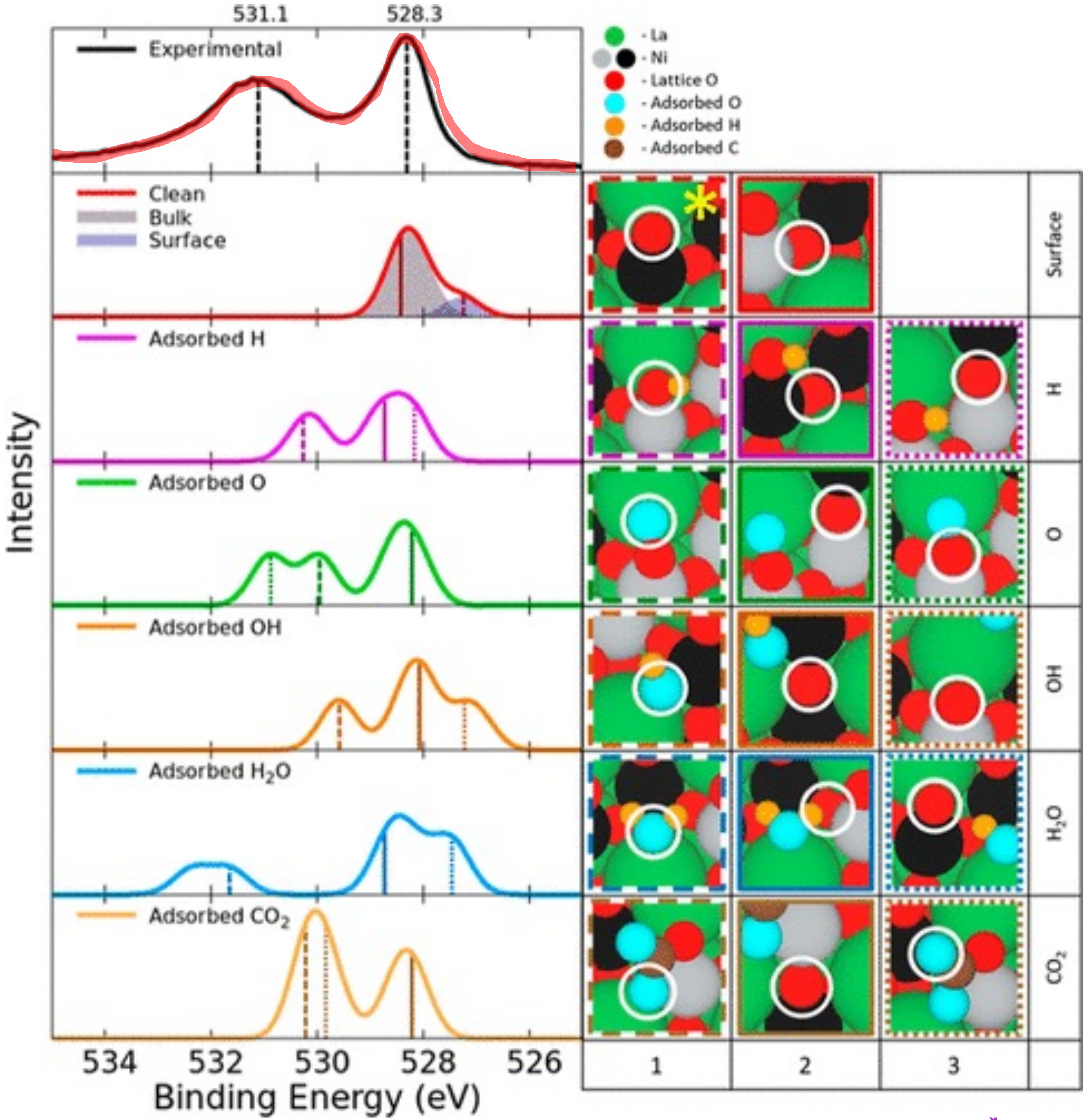
Sn 3p3	15.9%	714.50	9.350
Sn 3p1	17.5%	756.50	4.580
Sn 3s	13.1%	884.50	3.260

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

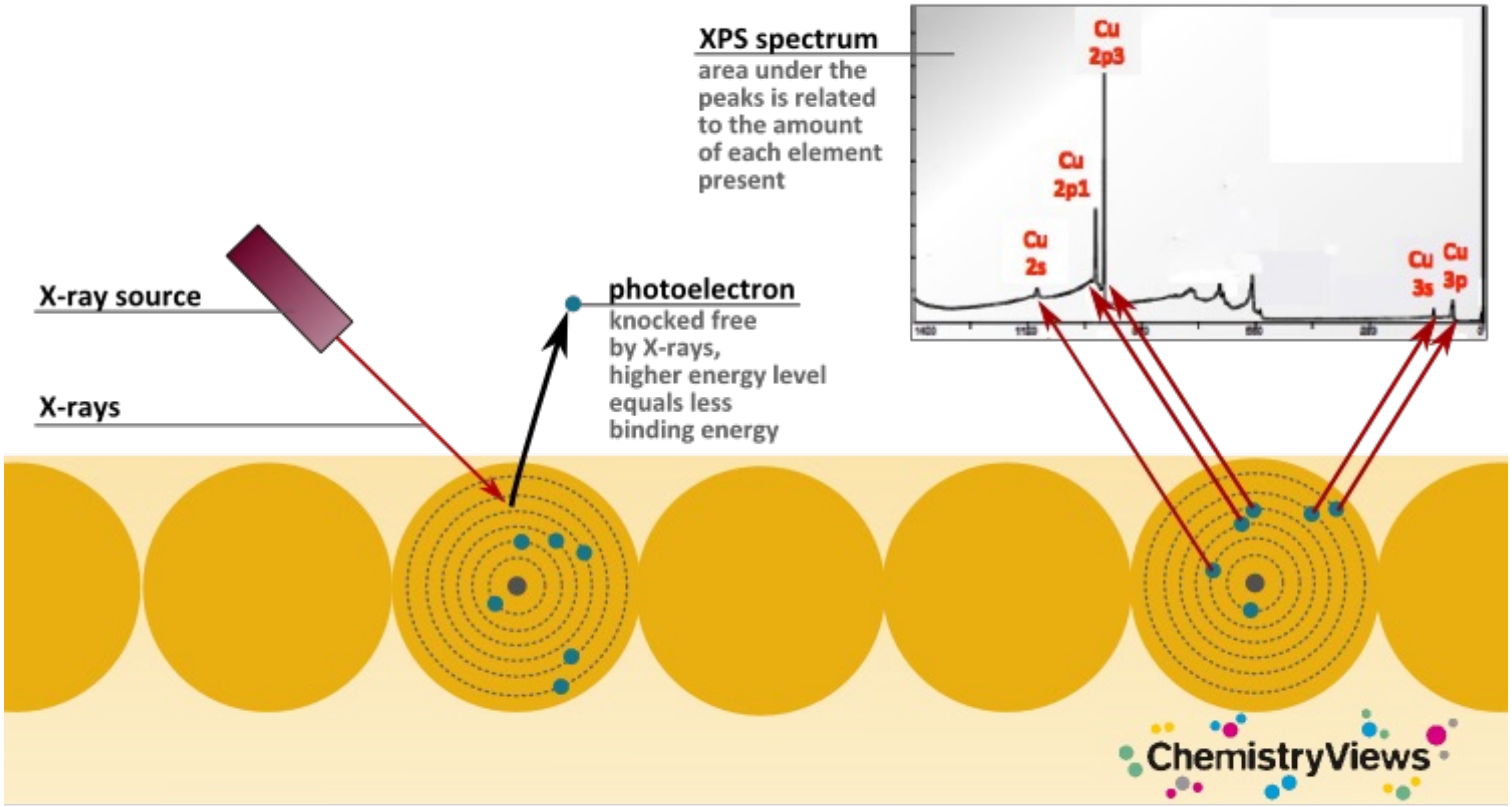
Perovskite-based oxides for electrochemical cells





Whitten *et al.* | JACS Au | 2024

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



XPS spectrum: area under the peaks is related to the amount of each element present

photoelectron: knocked free by X-rays, higher energy level equals less binding energy

Key Takeaways

- XPS can identify elements on the surface of materials
- XPS relies on the photelectric 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?

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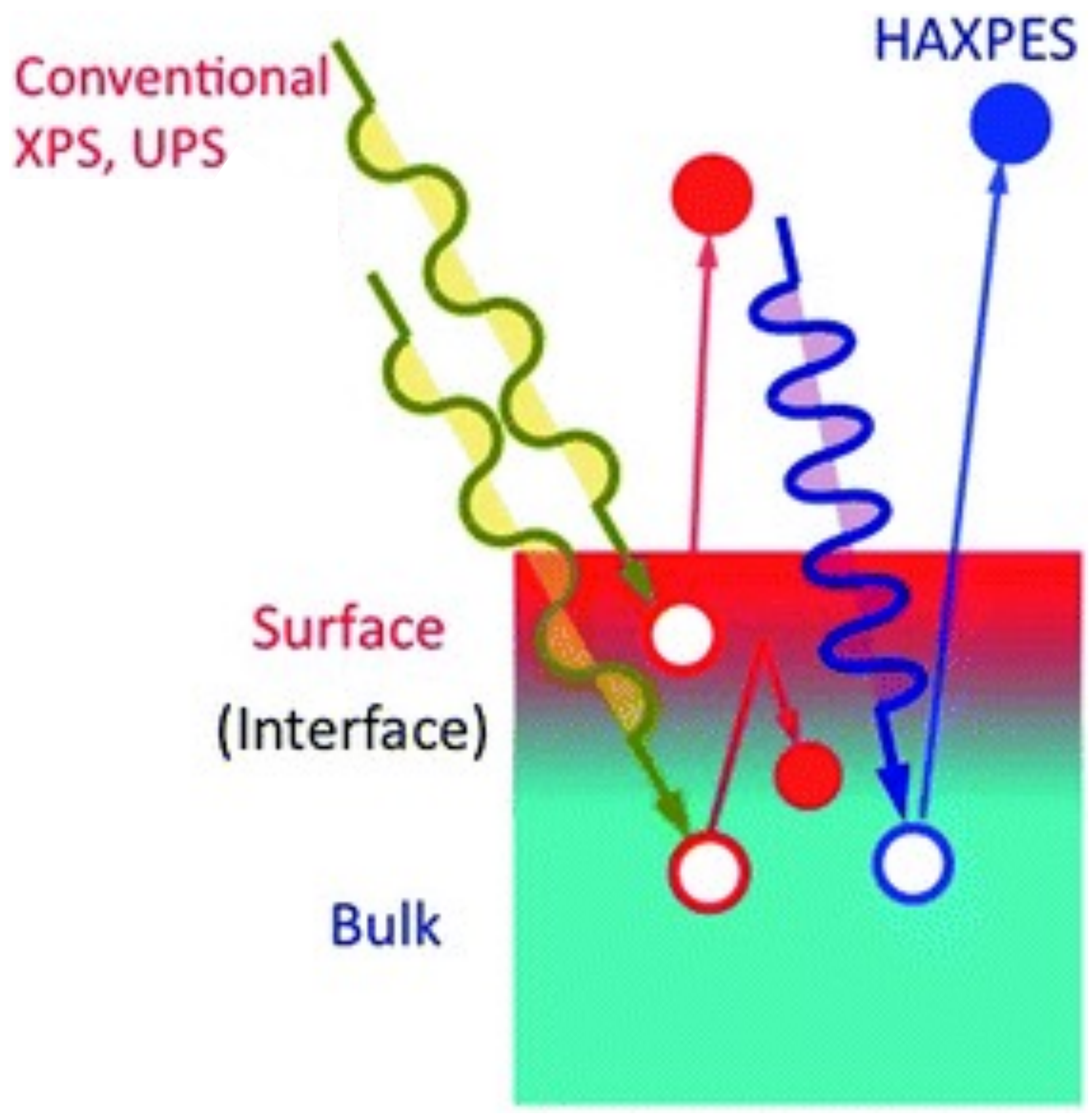
Various Forms of Photoelectron Spectroscopy to Probe Materials

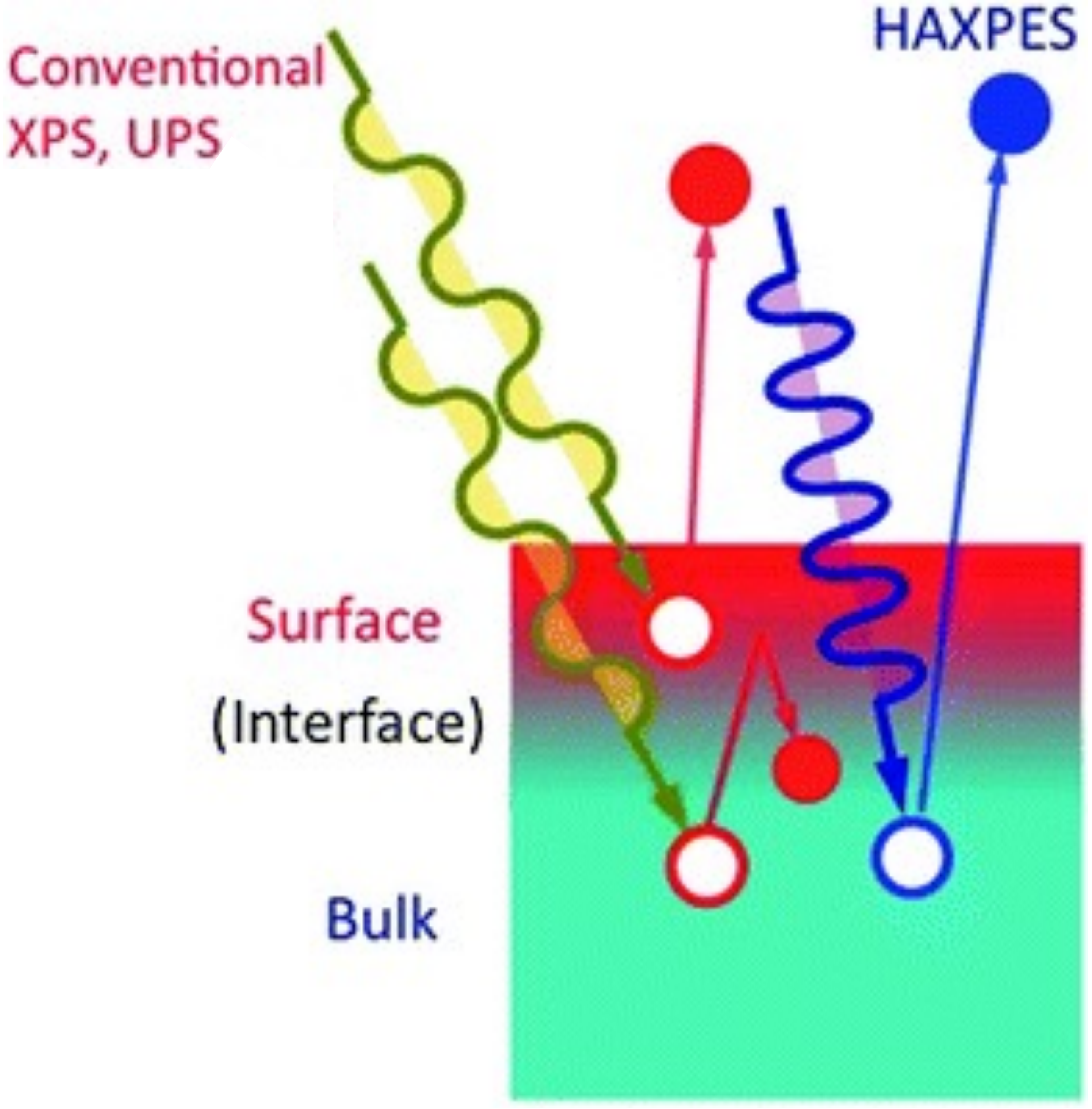
Kinetic energy of emitted electrons determines how deep into the material the technique can “see”

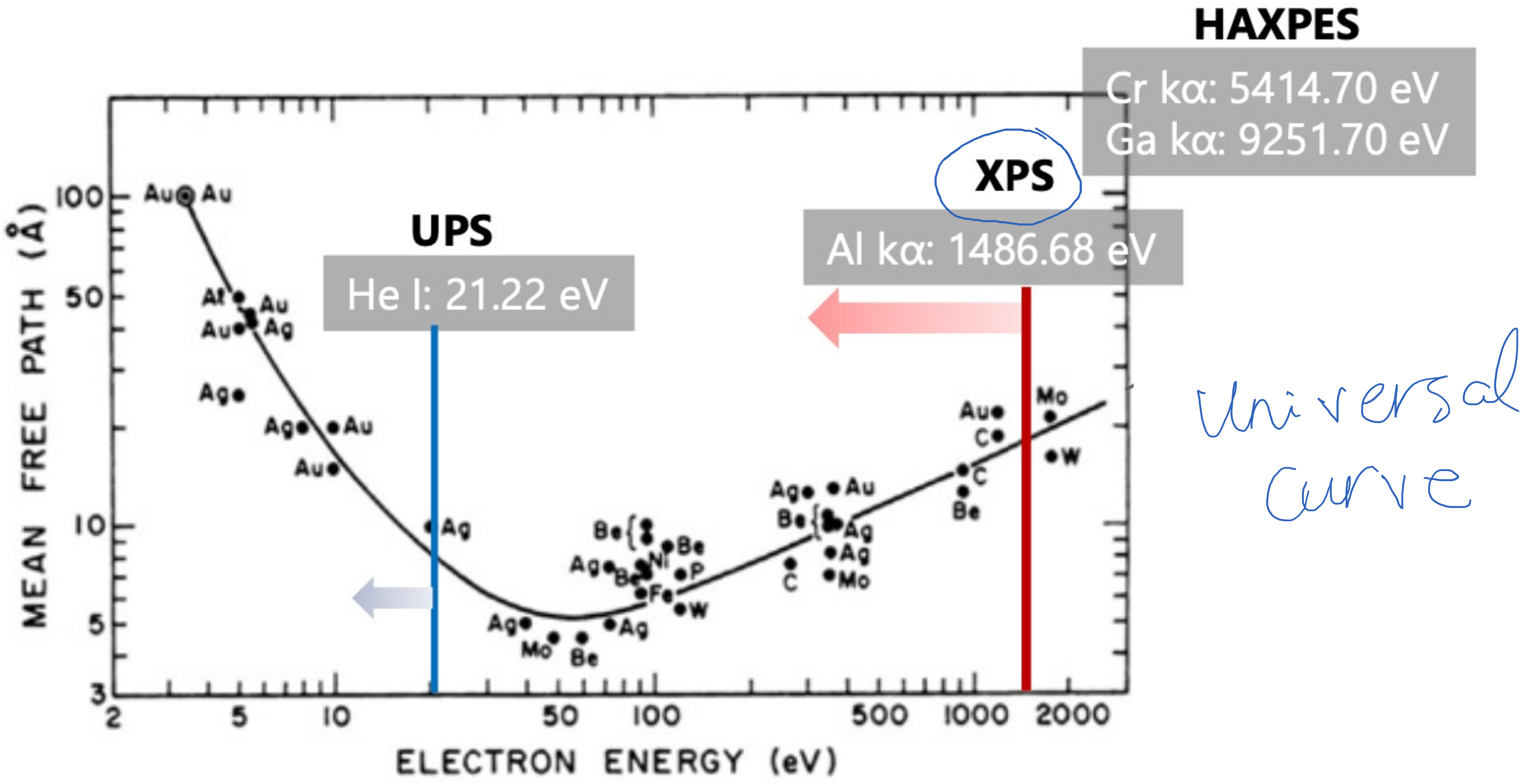


Technique	Photon source	Measures	Main use
UV Photoelectron Spectroscopy (UPS)	UV (20–50 eV)	Valence electrons	Electronic structure, work function, bonding at surface
X-ray Photoelectron Spectroscopy (XPS)	Soft X-rays (≈ 1.5 keV)	Core electrons	Elemental ID + chemical states at the surface
Hard X-ray 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





HAXPES

Cr kα: 5414.70 eV
Ga kα: 9251.70 eV

XPS

Al kα: 1486.68 eV

UPS

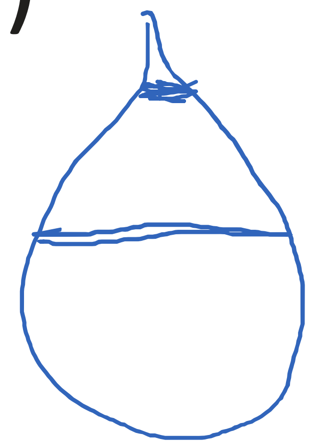
He I: 21.22 eV

Universal curve

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

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