Surface Analysis of Nanomaterials
(나노소재표면분석)

:Surface and Thin Film Analysis (표면 및 박막분석)

장소: E6, Room 116

시간: 월7A–8A, 수7A–8A

1. Why Surfaces Matter

Why Surfaces Matter

Wherever the properties of a solid surface are important, it is also i mportant to have the means to measure those properties.

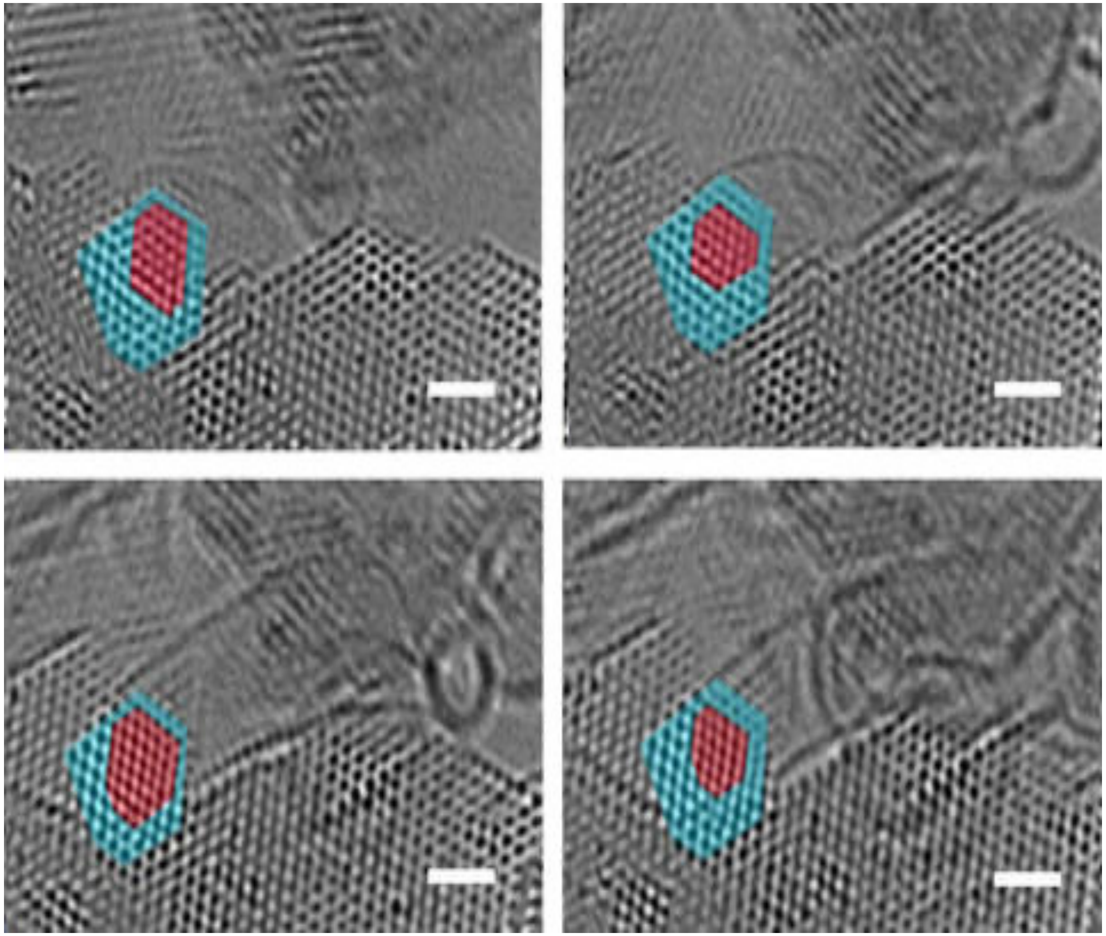
The surfaces of solids

play an overriding part in a remarkably large number of **processes**, **phen omena**, and **materials** of technological importance.

- Catalysis
- Corrosion, passivation, and rusting adhesion
- Tribology, friction, and wear
- Brittle fracture of metals and ceramics microelectronics
- Composites
- Surface treatments of polymers and plastics
- Protective coatings
- Superconductors
- Solid – surface reactions of all types with gases, liquids, or othe r solids.

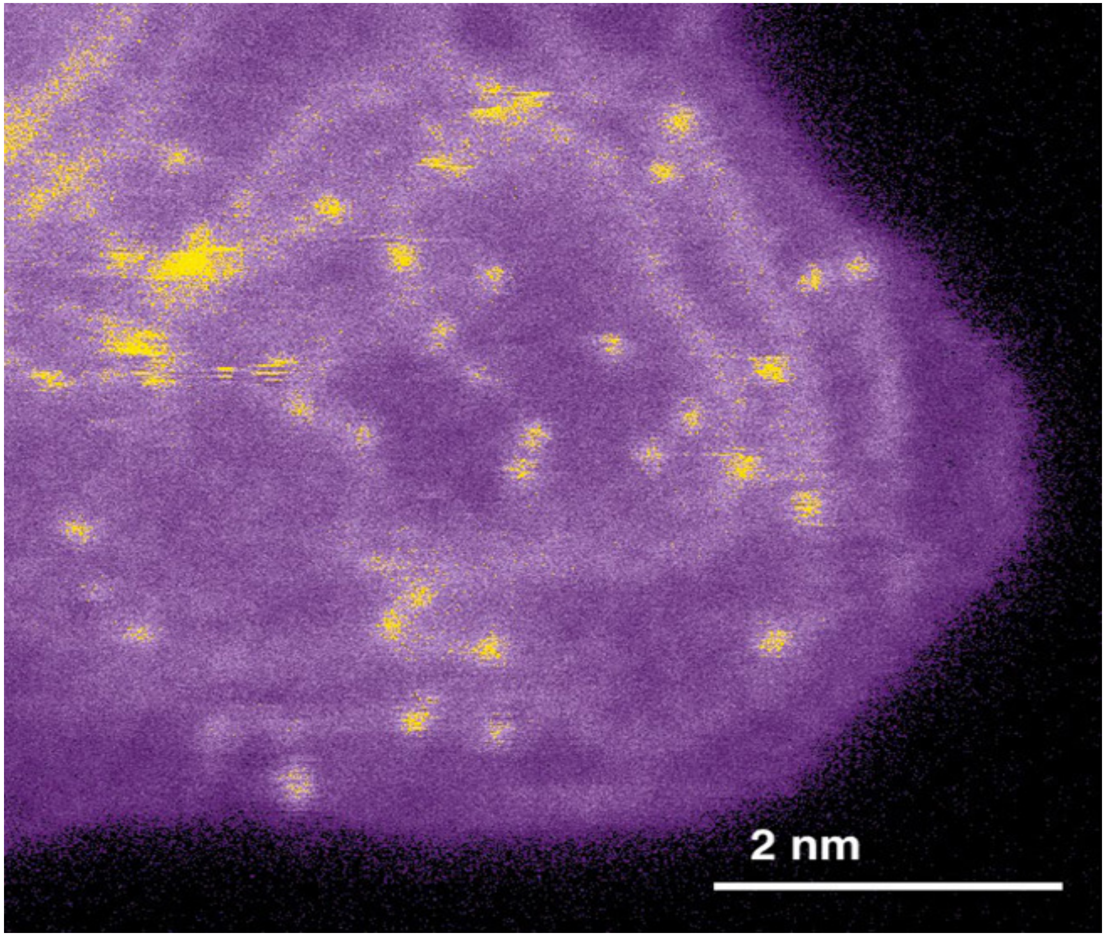
Why Surfaces Matter

A nanoscale surface can reorganize during reaction and thereby cont rol the behavior of the entire particle.



Why Surfaces Matter

Edges, steps, vacancies, and interfaces often dominate adsorption an d reaction because their coordination differs from terraces.



Why Surfaces Matter

The surfaces in question are not always external !!

The processes occurring at inner surfaces such as **interfaces and grain boundaries** are often just as critical to the behavior of the material

Required information

- Surface composition
  - (i.e., the types of atoms present and their concentrations)
- Surface chemistry
  - (i.e., the chemical states of the atoms)
- Arrangement of surface atoms
  - (i.e., the surface structure)

Analysis of Solid Surface

What is meant by a solid surface?

Definition of the surface

the plane at which the solid terminates

– the last atom layer before the adjacent phase (vacuum, vapor, liquid, or another solid) begins

⟶ Impractical!!

the effect of termination extends into the solid beyond the outermost atom layer

➡ Definition of the surface again

– Consisting of that number of atom layers over which the effect of termination of the solid decays until bulk properties are reached

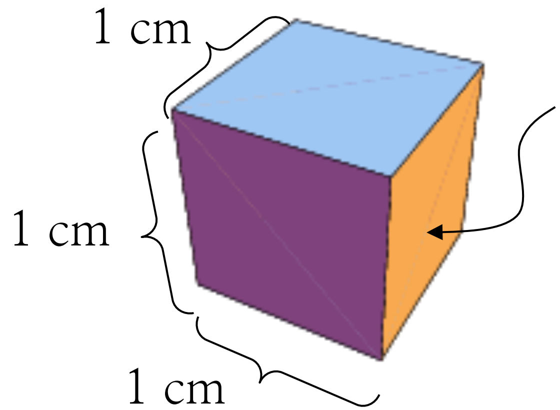
–> Decay distance is of the order of 5 – 20 nm depending on kind of materials

Why Surfaces Matter

How many atoms in a Surface?

How many atoms are we dealing with at the surface and in the bulk of a solid?

i.e Consider a 1cm cube of metal



1 cm^2 surfaces has roughly 10^{15} atoms

Thus the total number of atoms in the cube will be $\approx 10^{23}$

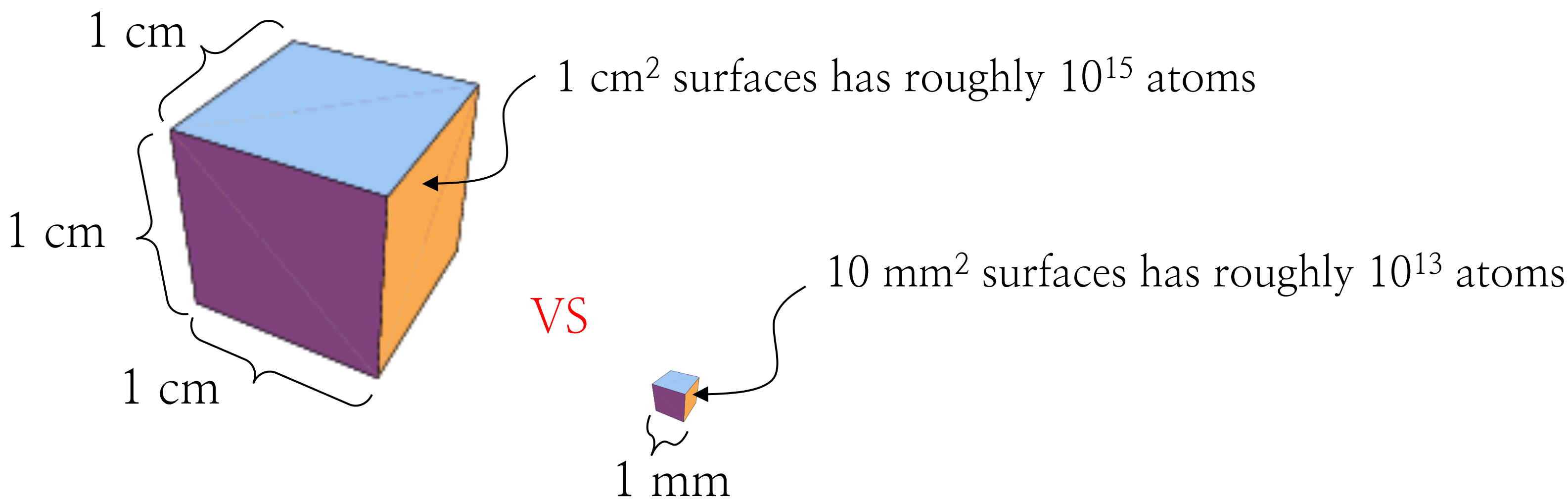
the percentage of surface to bulk atoms

$$\longrightarrow \quad s/b \approx 10^{-8} \times 100 \approx 10^{-6}\,\%$$

Why Surfaces Matter

How sensitive?

General probing area of surface analysis technique -> 1mm^2



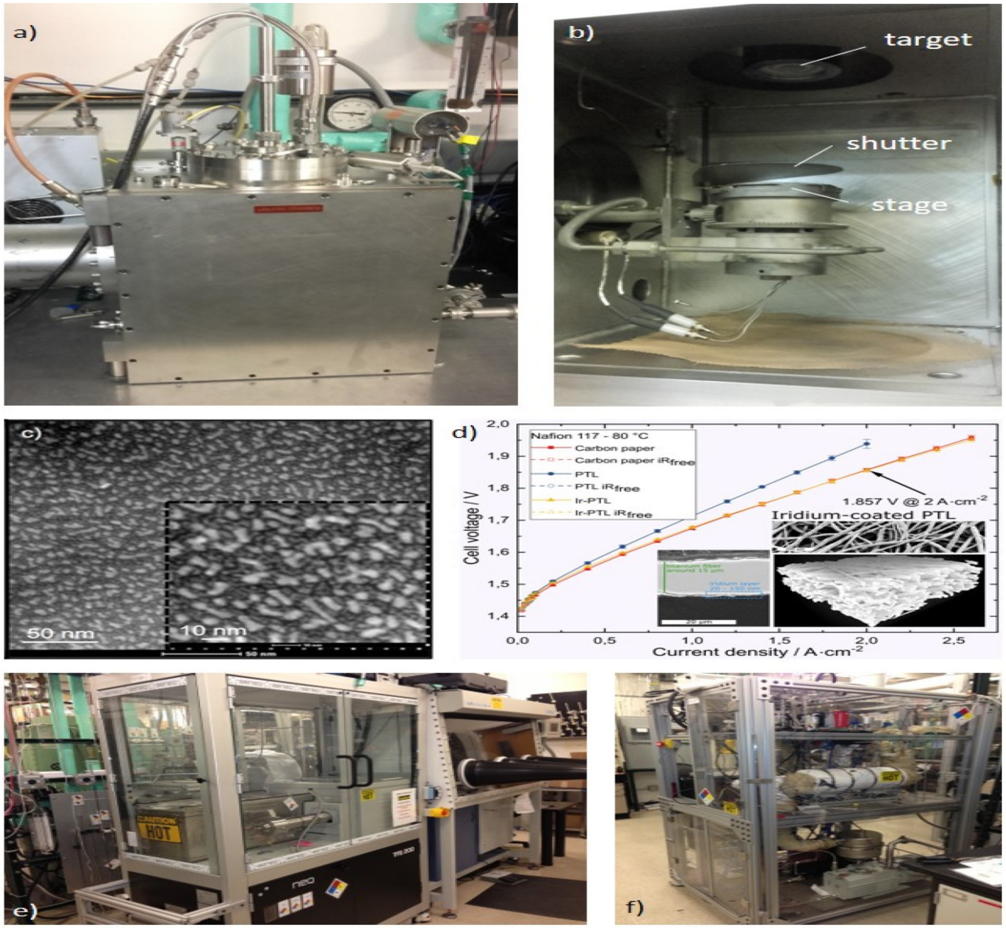
-> Top 10 layer contain 10^{14} atoms or 10^{-10} mol

Therefore, One should consider very low concentration compare to conventional chemical analysis for bulk

More important in nanoscale analysis

Why Surfaces Matter

Surface modification changes adsorption, charge transfer, corrosion resistance, and interfacial kinetics without replacing the bulk material.

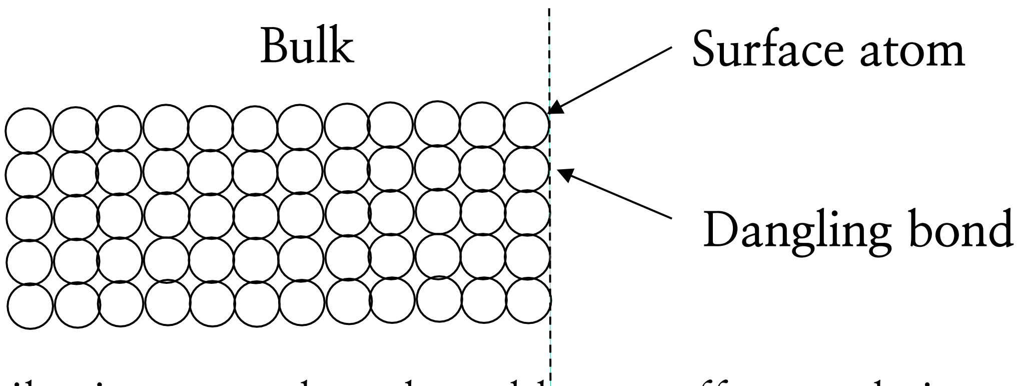


Why Surfaces Matter

Why should surfaces be so important?

First, the properties of surface atoms are usually different from those of the sa me atoms in the bulk

i.e. Even at the surface of a perfect single crystal the surface at oms behave differently from those in the bulk, simply becaus e <u>they do not have the same number of nearest neighbors</u>;



–> Electronic distributions are altered, and hence affect to their reactivity

Why Surfaces Matter

A surface–analysis experiment must answer two linked questions

What is present?

Elemental composition, chemical state, molecular identity, structure, morphology, and their lateral or depth distributions.

What is causally relevant?

Relate the measured surface state to processing history, environment, function, degradation, and uncertainty. No single method supplies every observable.

Why Surfaces Matter

Information Required for surface analysis

To understand the properties and reactivity of a surface, the following informa tion is required:

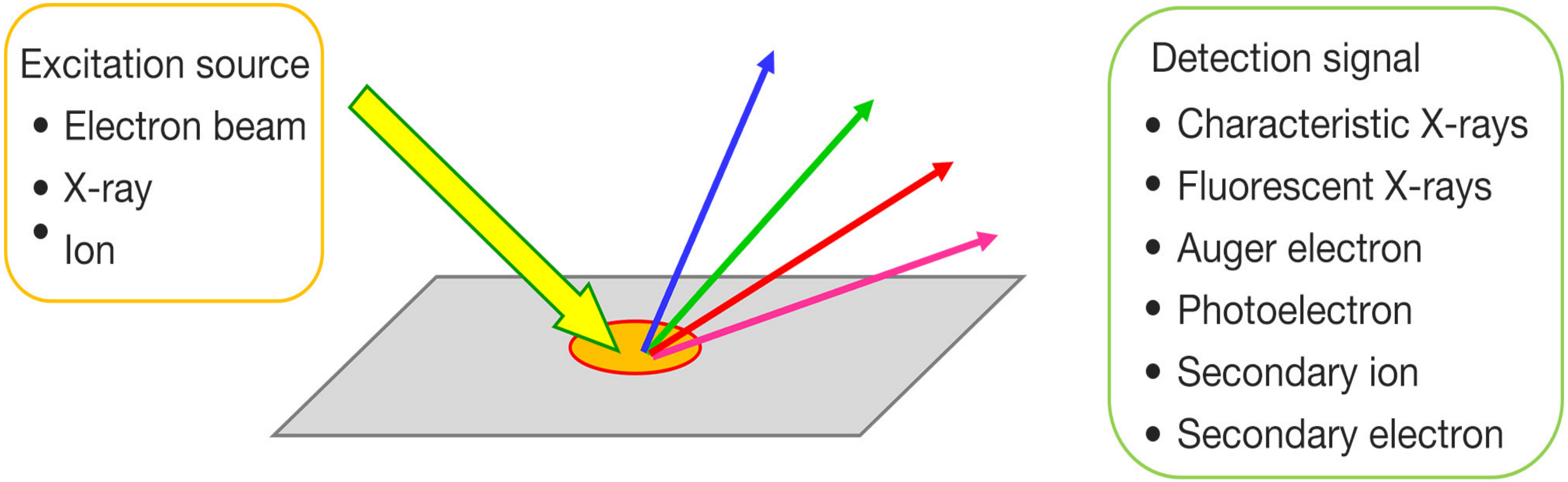
- the physical topography,
- the chemical composition,
- The chemical structure,
- the atomic structure,
- the electronic state
- a detailed description of bonding of molecules at the surface.

-> No one technique can provide all these different pieces of information. A full investigation of a surface phenomenon will always require several techniques.

2. How Surface Analysis Generates Information

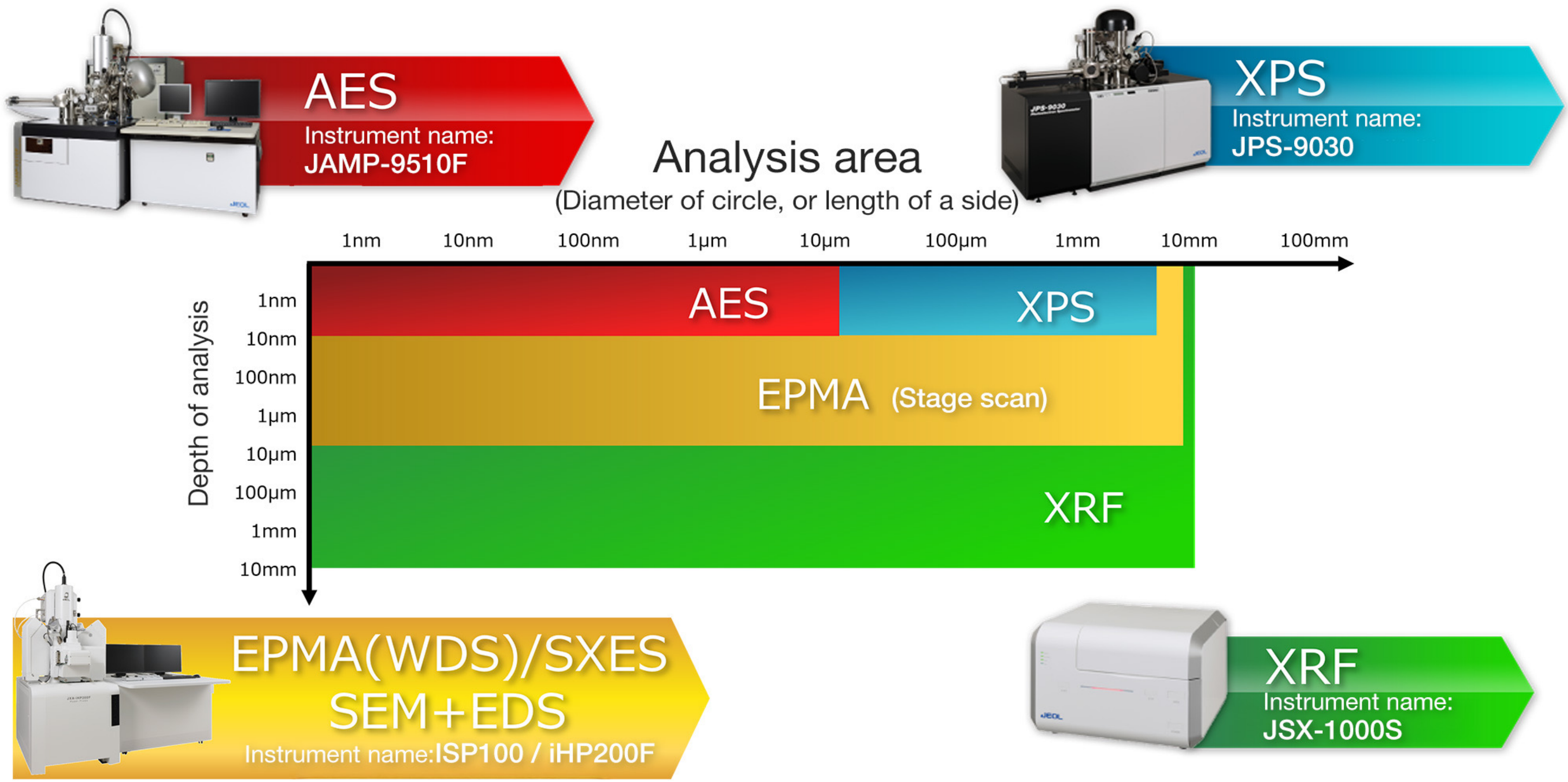
How Surface Analysis Generates Information

An incident probe creates signals that encode composition, bonding, structure, and position.



How Surface Analysis Generates Information

Information depth and lateral resolution are independent experimental dimensions.



How Surface Analysis Generates Information

Five independent dimensions define an experiment

1. Information type

Composition, chemical state, electronic structure, crystallography, topography, or molecular fragments.

2. Sampling geometry

Information depth, lateral resolution, analyzed area, detection limit, and whether the result is local or ensemble averaged.

How Surface Analysis Generates Information

Surface sensitivity comes from signal escape

Inelastic mean free path

Electrons generated deeper in a solid lose energy before escape.
The useful signal is therefore weighted strongly toward the near surface region.

Effective attenuation length

Quantification and angle−dependent measurements require geometry and scatte
ring aware attenuation models, not a universal depth number.

How Surface Analysis Generates Information

Vacuum and specimen history are part of the measurement

Adsorption during handling

Hydrocarbons, water, and oxygen can alter the outermost layers before analysis; transfer time and storage atmosphere must be reported.

Vacuum is not a cleaning step

Ultra-high vacuum slows recontamination but does not restore the as-prepared surface.

Preserve the relevant state

Use inert transfer, cryogenic handling, or controlled exposure when the scientific question requires it.

How Surface Analysis Generates Information

The measurement can modify the surface

Charging and energy referencing

Insulators can shift and broaden electron spectra. Neutralization and transparent referencing rules are essential.

Beam-induced change

X-rays, electrons, ions, and scanning tips can heat, reduce, desorb, amorphize, or displace material.

Depth profiling is destructive

Sputtering can mix layers, preferentially remove elements, and change oxidation states; interpret reconstructed profiles cautiously.

How Surface Analysis Generates Information

Choose the method by the decision criteria

Required observable

Chemistry: XPS/AES/SIMS.

Structure: LEED/RHEED.

Morphology and local properties: AFM/STM.

Constraints and validation

Match depth, area, resolution, vacuum compatibility, damage tolerance, standards, and an orthogonal method to the hypothesis.

3. Representative Surface Analysis Methods

Surface Analysis Methods

Surface analysis techniques and the information they can provide

Radiation IN Radiation DETECTED	photon electron	photon photon	electron electron	ion ion	neutron neutron
SURFACE INFORMATION					
Physical topography			SEM STM (9)		
Chemical composition	ESCA/XPS (3)		AES (2)	SIMS (5) ISS (6)	
Chemical structure	ESCA/XPS (3)	EXAFS (8) IR & SFG (7)	EELS (7)	SIMS (4)	INS (7)
Atomic structure		EXAFS (8)	LEED RHEED (8)	ISS (6)	
Adsorbate bonding		EXAFS (8) IR (7)	EELS (7)	SIMS (4)	INS (7)

Surface Analysis Methods

Basic principal of surface analysis techniques

➡ Interrogation of the surface with a particle probe

Use various energetic particles that are come from the probe

Primary particles used in the probing beam

i.e. electrons, photons, ions, neutron or their combination

Function of the probe

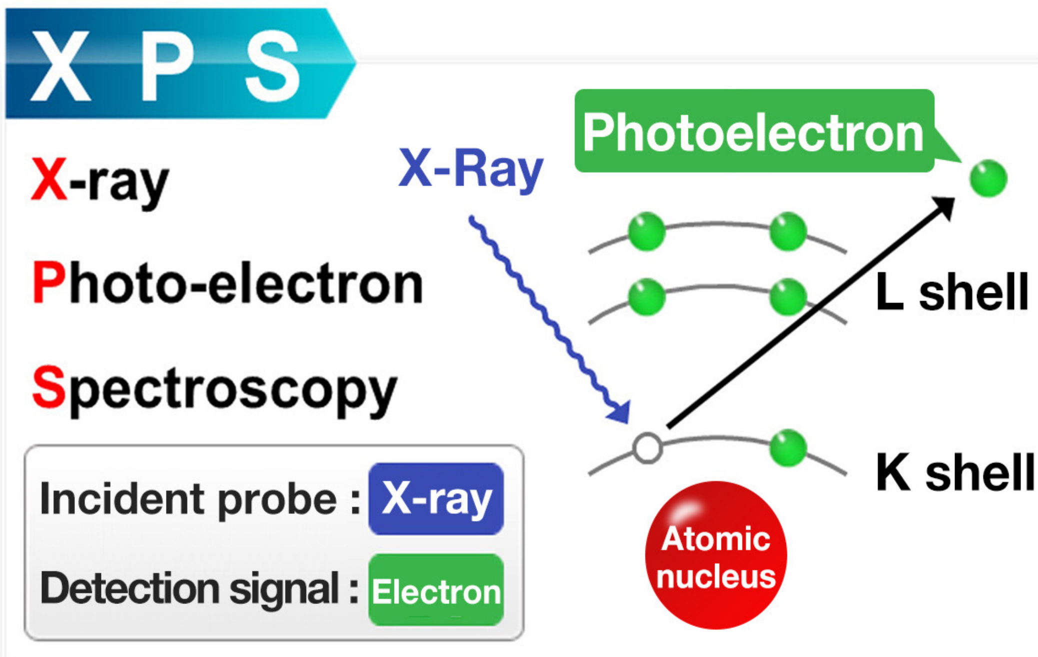
Excite surface atoms

➡ emission of one or more of a variety of sec
ondary particles such as electrons, photons
, ions, and neutrals

Surface Analysis Methods

X-ray Photoelectron Spectroscopy (XPS)

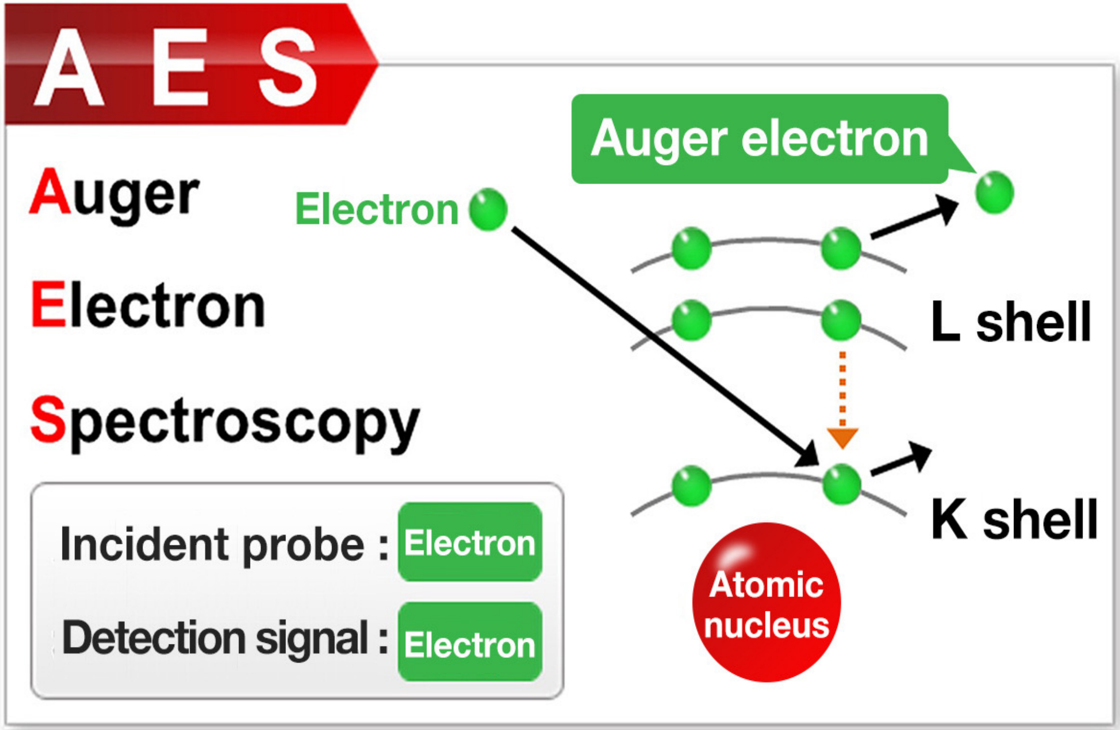
Photoelectron energies reveal binding energy; peak areas and line shapes support composition and chemical-state analysis.



Surface Analysis Methods

Auger Electron Spectroscopy (AES)

A focused electron beam produces element-specific Auger electrons for near-surface composition and mapping.



Surface Analysis Methods

XPS: from spectrum to defensible interpretation

Survey and quantify

Identify elements, select regions, subtract a justified background, fit constrained components, and apply appropriate sensitivity factors.

Validate chemical-state claims

Use spin-orbit structure, peak widths, satellites, reference materials, charge consistency, and complementary evidence; avoid fitting beyond resolution.

Surface Analysis Methods

AES and XPS are complementary electron spectroscopies

XPS strengths

Chemical–state interpretation, broad materials compatibility, and ensemble –average composition over a relatively large area.

AES strengths

High lateral resolution and elemental mapping using a focused electron beam, with greater sensitivity to charging and beam damage.

Surface Analysis Methods

SIMS and ISS emphasize different surface observables

Secondary Ion Mass Spectrometry

Extremely sensitive elemental, isotopic, and molecular–fragment detection matrix effects complicate quantification and sputtering is usually destructive.

Ion Scattering Spectroscopy

Energy and angle of scattered ions probe the outermost atomic layer and near–surface composition with exceptional surface selectivity.

Interpretation requirement

Use standards, dose control, and a physically justified collision or sputter model.

Surface Analysis Methods

Structure probes address different length scales

LEED

Low−energy electron diffraction reveals two−dimensional surface periodicity and reconstruction on clean, ordered surfaces.

RHEED

Grazing−incidence high−energy electrons monitor crystalline surfaces and thin−film growth, often in situ.

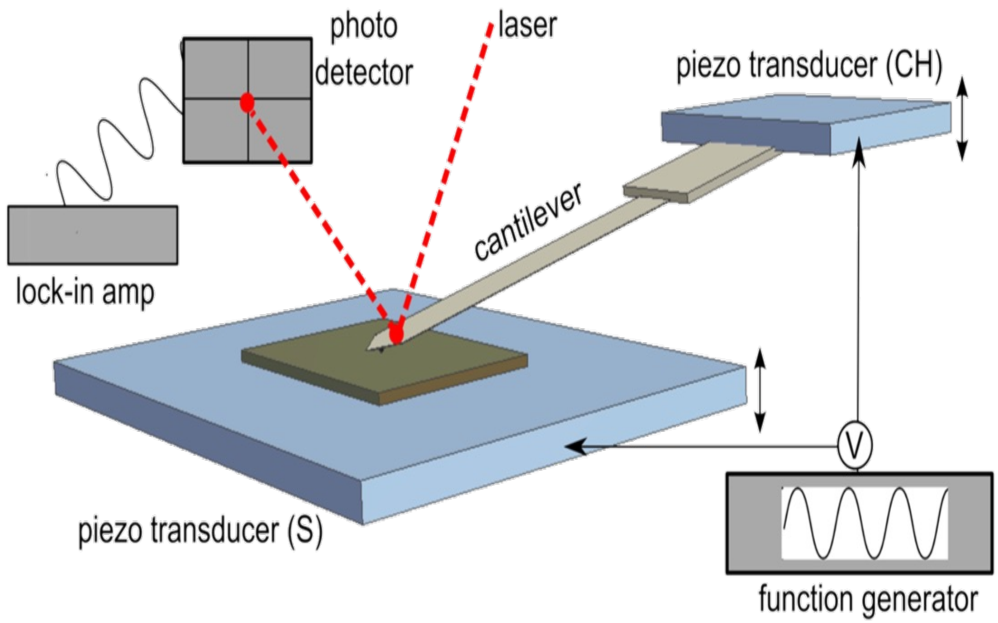
X−ray absorption fine structure

EXAFS probes element−specific local coordination and bond distances; it is not intrinsically limited to the outermost surface.

Surface Analysis Methods

Atomic Force Microscopy (AFM)

Feedback tracks tip–surface interaction; contrast depends on tip geometry, mode, and force setpoint.



Surface Analysis Methods

STM and AFM map different interactions

Scanning Tunneling Microscopy

Tunneling current reflects separation and electronic states; conductive specimens and vibration control are required.

Atomic Force Microscopy

Tip–surface force enables conductive or insulating specimens and diverse environments, but topography is not automatically chemical identity.

Surface Analysis Methods

Surface–specific analytical techniques using particle or photon excitation

Detection	Excitation a)		
	Electrons, e^-	Ions, neutrals, A^+, A^-, A^0	Photons, $h\nu$
e^-	AES SAM EELS EFTEM LEED RHEED	IAES INS	XPS UPS
A^+, A^-, A^0	ESD ESDIAD	SIMS SNMS GDMS FABMS RBS LEIS ERDA NRA	
$h\nu$	EDXS SXAPS IPES BIS	GD-OES IBSCA	TXRF XRD LA LIBS RAIRS SERS SHG SFG ELL SNOM

a) Some of the techniques in Table 1.1 have angle-resolved variants, with the prefix AR (e.g., ARUPS), or use Fourier-transform methods, with the prefix FT (e.g., FT-RAIRS).

Surface Analysis Methods

Surface-specific analytical techniques <u>using non – particle excitation</u>

Detection	Excitation		
	Heat, *kT*	High electrical field, *F*	Mechanical force
A^+	TDS	FIM AP	
A^-	TDS		
e^-		IETS STM, STS	
(Displacement)			AFM

Surface Analysis Methods

Surface analysis acronyms

1. **Electron Excitation**

AES, Auger electron spectroscopy

BIS, Bremsstrahlung isochromat spectroscopy (or ILS, ionization loss spectroscopy)

EDXS, Energy-dispersive X-ray spectroscopy

EELS, Electron energy loss spectroscopy

EFTEM, Energy-filtered transmission electron microscopy

ESD, Electron-stimulated desorption (or EID, electron-induced desorption)

ESDIAD, Electron-stimulated desorption ion angular distribution

IPES, Inverse photoemission spectroscopy

LEED, Low-energy electron diffraction

RHEED, Reflection high-energy electron diffraction

SXAPS, Soft X-ray appearance potential spectroscopy (or APS, appearance potential spectroscopy)

SAM, Scanning Auger microscopy

Surface Analysis Methods

Surface analysis acronyms

2. Ion Excitation

ERDA, Elastic recoil detection analysis

GDMS, Glow discharge mass spectrometry

GD-OES, Glow discharge optical emission spectroscopy

IAES, Ion (excited) Auger electron spectroscopy

IBSCA, Ion beam spectrochemical analysis (or SCANIIR, surface composition by analysis of neutral and ion impact radiation or BLE, bombardment-induced light emission)

INS, Ion neutralization spectroscopy

LEIS, Low-energy ion scattering (or ISS, Ion-scattering spectroscopy)

NRA, Nuclear reaction analysis

RBS, Rutherford back-scattering spectroscopy (or HEIS, high-energy ion scattering)

SIMS, Secondary-ion mass spectrometry (SSIMS, static secondary-ion mass spectrometry) (DSIMS, dynamic secondary-ion mass spectrometry)

SNMS, Secondary neutral mass spectrometry

Surface Analysis Methods

Surface analysis acronyms

3. Photon Excitation

ELL, Ellipsometry

LA, Laser ablation

LIBS, Laser-induced breakdown spectroscopy (or LIPS, Laser-induced plasma spectroscopy)

RAIRS, Reflection–absorption infrared spectroscopy (or IRRAS, infrared reflection–absorption spectroscopy, or IRAS, infrared absorption spectroscopy, or ERIRS, external reflection infrared spectroscopy)

SERS, Surface-enhanced Raman scattering

SFG, Sum frequency generation

SHG, (optical) Second harmonic generation

SNOM, Scanning near-field optical microscopy

TXRF, Total reflection X-ray fluorescence analysis

UPS, Ultraviolet photoelectron spectroscopy

XPS, X-ray photoelectron spectroscopy (or ESCA, electron spectroscopy for chemical analysis)

XRD, X-ray diffraction

Surface Analysis Methods

Surface analysis acronyms

4. **Neutral Excitation**

   FABMS, Fast-atom bombardment mass spectrometry

5. **Thermal Excitation**

   TDS, Thermal desorption spectroscopy

6. **High-Field Excitation**

   AP, Atom probe

   FIM, Field ion microscopy

   IETS, Inelastic electron tunneling spectroscopy

   STM, Scanning tunneling microscopy

   STS, Scanning tunneling spectroscopy

7. **Mechanical Force**

   AFM, Atomic force microscopy

Surface Analysis Methods

Build complementary evidence, not a single-technique story

1. State the hypothesis and target length scale

   Match information depth and lateral resolution to the target feature.

2. Control surface state and perturbation

   Document preparation, transfer, environment, acquisition order, and dose.

3. Triangulate the conclusion

   Combine orthogonal observables

   - ➡ Composition/chemistry + structure + morphology
     ; require agreement within uncertainty.

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