

Surface Characterization by Spectroscopy and Microscopy

- ✓ *The surface of a solid in contact with a liquid or gaseous phase usually differs substantially from the interior of the solid both in chemical composition and physical properties.*
- ✓ *Characterization of these surface properties is of vital importance in a number of fields,*
 - ✓ *heterogeneous catalysis,*
 - ✓ *sensor development and application, and*
 - ✓ *semiconductor thin-film technology*

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- ✓ *Such characterization also aids in understanding*
 - ✓ *corrosion and adhesion mechanisms,*
 - ✓ *activity of metal surfaces,*
 - ✓ *embrittlement properties, and*
 - ✓ *behavior and functions of biological membranes.*
- *This chapter deals with the investigation of solid surfaces by spectroscopic and microscopic methods. Although the emphasis is on solid surfaces, some of the techniques are also applicable to other interfaces, such as liquid-liquid and liquid-gas interfaces.*

Solid surface:

- ✓ *the boundary layer between a solid and a vacuum, a gas, or a liquid*
- ✓ *a part of the solid that differs in composition from the average composition of the bulk of the solid.*
- ✓ *Comprise not only the top layer of atoms or molecules of a solid but also a transition layer with a non uniform composition that varies continuously from that of the outer layer to that of the bulk.*
- ✓ *a surface may be several or even several tens of atomic layers deep.*
- ✓ *surface layer is generally only a tiny fraction of the total solid therefore, the difference in composition of the surface layer does not significantly affect the measured overall average composition of the bulk.*
- ✓ *an operational definition of a surface is that volume of the solid that is sampled by a specific measurement technique.*
- ✓ *This definition recognizes that if we use several surface techniques, we may in fact be sampling different surfaces and may obtain different, albeit useful, results.*

Why is surface analysis important?

- ✓ *The composition of the outer most atomic layers of a material plays a critical role in properties such as:*
 - ✓ *chemical activity, adhesion, wettability, electrostatic behavior, corrosion resistance, bio-compatibility, etc.*
 - ✓ *In addition, contaminants, process residues, diffusion products, and impurities are typically present at the surface of solid samples or at the interfaces of thin film structures.*
- ✓ *The ability to characterize thin film structures, via sputter depth profiling, provides a unique opportunity to examine materials used in thin layers and to study their interaction with materials in adjacent layers.*
- ✓ **Surface analysis techniques** *are routinely applied to a broad range of materials systems and high technology industrial products.*

Surface measurements:

- 1) Classical methods:
- 2) Spectroscopic methods:
- 3) Microscopic methods:

1) *Classical methods:*

- *These provide useful information about the physical nature of surfaces but less about their chemical nature.*
- *They involve;*
 - *obtaining optical and electron microscopic images,*
 - *as well as measurements of adsorption isotherms,*
 - *surface areas,*
 - *surface roughness,*
 - *pore sizes and*
 - *reflectivity.*

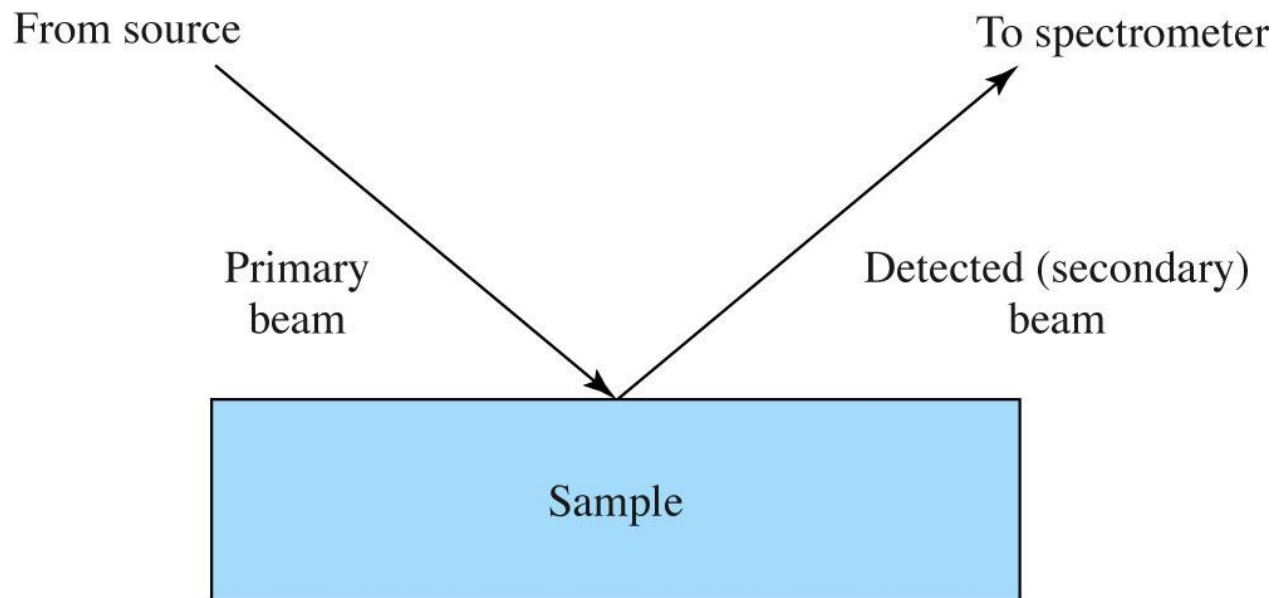
2) Spectroscopic Methods:

Provide both qualitative and quantitative chemical information about the composition of a surface layer of a solid that is a few angstroms to hundreds of angstroms in thickness.

Spectroscopic techniques can be;

- electron spectroscopic techniques,*
- ion spectroscopic techniques and*
- photon spectroscopic techniques*

The general principle of surface analysis



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FIGURE 21-1 General scheme for surface spectroscopy. Beams may be photons, electrons, ions, or neutral molecules.

- The solid surface is irradiated with a primary beam. Beam may be photons, electrons, ions, or neutral molecules.
- Impact of these primary beams on a surface results in formation of a secondary beam (photons, ions, e^- or molecules) that are scattered, sputtered or emitted from the solid surface

Photons vs. electrons, ions, or neutral molecules

- *Photons have larger penetration depth,*
 - *1 keV photon: 10^4 °A (= 1micron)penetration depth*
 - *1 keV e⁻ or ion: 25 °A penetration depth*
- *Therefore, the most effective surface methods are those in which the primary / secondary beam is made up of*

Electrons, ions or molecules **→** *NOT PHOTONS*

➤ *Because this assures that the measurements are restricted to the uppermost surface layer not to its bulk, so that bulk interference is eliminated*

TABLE 21-1 Some Common Spectroscopic Techniques for Analysis of Surfaces

Method and Acronym	Primary Beam	Detected Beam	Information
X-ray photoelectron spectroscopy (XPS), or electron spectroscopy for chemical analysis (ESCA)	X-ray photons	Electrons	Chemical composition Chemical structure
Auger electron spectroscopy (AES)	Electrons or X-ray photons	Electrons	Chemical composition
Electron energy-loss spectroscopy (EELS)	Electrons	Electrons	Chemical structure Adsorbate binding
Electron microprobe (EM)	Electrons	X-ray photons	Chemical composition
Secondary-ion mass spectrometry (SIMS)	Ions	Ions	Chemical composition Chemical structure
Ion-scattering spectroscopy (ISS) and Rutherford backscattering	Ions	Ions	Chemical composition Atomic structure
Laser-microprobe mass spectrometry (LMMS)	Photons	Ions	Chemical composition Chemical structure
Surface plasmon resonance (SPR)	Photons	Photons	Composition and concentration of thin films
Sum frequency generation (SFG)	Photons	Photons	Interface structure, adsorbate binding
Ellipsometry	Photons	Photons	Thin-film thickness

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Electron spectroscopy:

- The first three methods listed in the above table are based upon the analysis of emitted electrons produced by various incident beams.
- In electron spectroscopy, the spectroscopic measurement consists of the determination of the power of the electron beam as a function of the energy (or frequency $h\nu$) of the electrons.
- In electron spectroscopy the photon energies range from 20 -1500 eV (even higher in the case of Auger, up to 10,000eV) much greater than any typical work function values (2-5 eV).
- There are three types of electron spectroscopy for the study of surfaces. XPS, Auger, and UPS

Electron spectroscopy:

1. The most common type is based upon the irradiation of the sample surface with monochromatic X-Ray radiation. This is called X-ray photoelectron spectroscopy (XPS). This method is also known as Electron spectroscopy for chemical analysis (ESCA), using soft x-ray (200 - 1500 eV) radiation to examine core-levels.
2. The second type of electron spectroscopy is called Auger electron spectroscopy (AES), using energetic electron (1000 – 10,000 eV) to examine core-levels. Auger spectra are most commonly excited by a beam of electrons, although X-rays are also used.
3. The third type of electron spectroscopy is ultraviolet photoelectron spectroscopy (UPS), by using vacuum UV (10 - 45 eV) radiation to examine valence levels. In this method, a monochromatic beam of ultraviolet radiation causes the ejection of electrons from the analyte. This method is not as common as the first two methods.

- Synchrotron radiation sources have enabled high resolution studies to be carried out with radiation spanning a much wider and more complete energy range (5 - 5000+ eV) but such work will remain, a very small minority of all photoelectron studies due to the expense, complexity and limited availability of such sources.
- Electron spectroscopy can be used for the identification of all of the elements in the periodic table except for helium and hydrogen. (low 'Photoionisation cross-section' ∴ probability of an electron being emitted...)
- The method also permits the determination of the oxidation state of an element and the type of species to which it is bonded.
- This technique also provides useful information about the electronic structure of molecules.

- X-Ray Photoelectron Spectroscopy (XPS), not only provided information about the atomic composition of the a sample, but also information about the structure and oxidation state of the compounds being examined
- The kinetic energy of the emitted electron E_k is measured in an electron spectrometer. The binding energy of the electron E_b can be calculated

$$E_b = h\nu - E_k - w$$

where, w is the work function of the spectrometer, a factor that corrects for the electrostatic environment in which the electron is formed and measured.

Secondary-ion mass spectrometry (SIMS)

- Secondary-ion mass spectrometry (SIMS) is the most highly developed of the mass spectrometric surface methods, with several manufacturers offering instruments for this technique.
- SIMS is useful for determining both the atomic and the molecular composition of solid surfaces.
- In secondary-ion mass analyzers that serve for general surface analysis and depth profiling, the primary ion beam diameter is from 0.3 to 0.5mm.
- Double-focusing, single-focusing, time-of-flight, and quadrupole spectrometers are used for mass determination.

3) Microscopic Methods:

- For imaging surfaces and determining their morphology and their physical features.
- In the fields of chemistry, material science, geology, and biology, detailed knowledge of the physical nature of the surface of solids is of great importance, therefore, the classical method of obtaining this information was optical microscopy.
- The resolution of optical microscopy that uses light to form an image is limited by diffraction effects to about the wavelength of light.

Method	Resolution	Magnification (x)
Human Eye	0.1-0.2 mm	-
Optical Microscopy	0.1-0.2 μm	~1200
Electron Microscopy	30-50 \AA	10 - 75,000
Probe Microscopy	<1 \AA	> 500,000

Some Common Microscopic Techniques for Analysis of Surfaces

- Scanning electron microscopy (SEM)
- Scanning probe microscopy
 - Scanning tunneling microscopy (STM)
 - Atomic force microscopy (AFM)

Scanning Electron Microscope

- The Scanning Electron Microscope (SEM) is a microscope that uses electrons rather than light to form an image.
- A high energy (typically 10keV) electron beam is scanned across the surface. The incident electrons cause low energy secondary electrons to be generated, and some escape from the surface.
- The secondary electrons emitted from the sample are detected by attracting them onto a phosphor screen. This screen will glow and the intensity of the light is measured with a photomultiplier.

Scanning Probe Microscope

- Scanning probe microscopes (SPMs) are capable of resolving details or surfaces down to the atomic level. Unlike optical and electron microscopes, scanning probe microscopes reveal details not only on the lateral x and y -axis of a sample but also the z -axis.
- The atomic force microscope (AFM) is a widely used scanning probe microscope, which was invented in 1986 and permits the resolution of individual atoms on both conducting and insulating surfaces

Desired Information	Techniques
Imaging, profilometry and/or quantitative measurements of film thickness	<p>Atomic force microscopy (AFM)</p> <p>Scanning tunneling microscopy (STM)</p> <p>Transmission electron microscopy (TEM)</p> <p>Scanning electron microscopy (SEM)</p> <p>Scanning transmission electron microscopy (STEM)</p> <p>Variable angle spectroscopic ellipsometry (VASE)</p> <p>Light microscopy (RBF, FM and CLSM)</p>
Elemental composition and chemical state measurements	<p>Auger electron spectroscopy (AES)</p> <p>Energy-dispersive X-ray spectroscopy (EDS)</p> <p>X-ray photoelectron spectroscopy (XPS)</p> <p>High-resolution electron energy-loss spectroscopy (EELS)</p> <p>Fourier transform infrared spectroscopy (FTIR)</p> <p>Fourier transform Raman spectroscopy (FT Raman)</p> <p>UV-Visible spectroscopy (UV/Vis)</p>
Microstructure, crystallography, and defects measurement	<p>High-resolution transmission electron microscopy (HRTEM)</p> <p>Low-energy electron diffraction (LEED)</p> <p>X-ray diffraction (XRD)</p>
Real-time measurements of surface interactions	<p>Surface plasmon resonance (SPR)</p>

SAMPLING SURFACES: Methodology

Three types of sampling methods are used regardless of the spectroscopic surface method.

- 1) Focussing the primary beam on a single small area of the sample and observing the secondary beam.
- 2) Mapping the surface, by moving the primary beam across the surface in a raster pattern of measured increments and observing changes in the secondary beam.
- 3) Etching a hole in the surface by sputtering by using a beam of ions from an ion gun. During this process a finer primary beam is used to produce a secondary beam from the center of the hole. This provides analytical data on the surface composition as a function of depth. This method is known as **depth profiling**.

SURFACE ENVIRONMENT

- Most of the surface spectroscopic techniques require a "vacuum" environment.
- High vacuum conditions ensure that the particles used have long mean free paths to interact with the surface of interest.
- The vacuum environment also keeps the surface free from adsorbed gases during the surface analysis experiment.
- The exceptions to the high vacuum requirement are the photon-photon techniques given in the last three rows of Table 21-1.
- These allow examination of surfaces under conditions more akin to those used in applications such as catalysis, sensing, and corrosion studies.
- A problem frequently encountered in surface analyses is contamination of the surface

SURFACE CONTAMINATION

- Adsorption of atmospheric components :
 - oxygen, water, carbondioxide
- Even in vacuum contamination occurs
 - At 10^{-6} torr → monolayer of gas molecules → 3 sec.
 - At 10^{-8} torr → monolayer of gas molecules → 1 hr.
 - At 10^{-10} torr → monolayer of gas molecules → 10 hr.
- Cleaning required by
 - baking at high temp.
 - sputtering with an inert gas ions
 - polishing / mech. scrappingwith an abrasive
 - Ultrasonic washing in various solvents
 - Bathing the sample in a reducing atmosphere to remove oxides

- In addition to atmospheric contamination, the primary beam itself can alter the surface as a measurement progresses.
- Damage caused by the primary beam depends on the momentum of the primary beam particles. Thus, of the beams listed in Table 21-1, ions are the most damaging and photons the least.