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INTRODUCTION AND SUMMARIES

1.0 INTRODUCTION

Though a wide range of analytical techniques is covered in this volume there are certain traits common to many of them. Most involve either electrons, photons, or ions as a probe beam striking the material to be analyzed. The beam interacts with the material in some way, and in some of the techniques the changes induced in the beam (energy, intensity, and angular distribution) are monitored after the interaction, and analytical information is derived from the observation of these changes. In other techniques the information used for analysis comes from electrons, photons, or ions that are ejected from the sample under the stimulation of the probe beam. In many situations several connected processes may be going on more or less simultaneously, with a particular analytical technique picking out only one aspect, e.g., the extent of absorption of incident light, or the kinetic energy distribution of ejected electrons.

The range of information provided by the techniques discussed here is also wide, but again there are common themes. What types of information are provided by these techniques? Elemental composition is perhaps the most basic information, followed by chemical state information, phase identification, and the determination of structure (atomic sites, bond lengths, and angles). One might need to know how these vary as a function of depth into the material, or spatially across the material, and many techniques specialize in addressing these questions down to very fine dimensions. For surfaces, interfaces, and thin films there is often very little material at all to analyze, hence the presence of many microanalytical methods in this volume. Within this field (microanalysis) it is often necessary to identify trace components down to extremely low concentration (parts per trillion in some cases) and a number of techniques specialize in this aspect. In other cases a high degree of accuracy in measuring the presence of major components might be the issue. Usually the techniques that are good for trace identification are not the same ones used to accurately quantify major components. Most complete analyses require the use of

multiple techniques, the selection of which depends on the nature of the sample and the desired information.

This first chapter contains one-page summaries of each of the 50 techniques covered in the following chapters. All summaries have the same format to allow easy comparison and quick access to the information. Further comparative information is provided in the introductions to the chapters. Finally, a table is provided at the end of this introduction, in which many of the important parameters describing the capabilities for all 50 techniques are listed.

The subtitle of this Series is "Surfaces, Interfaces, and Thin Films." The definition of a "surface" or of a "thin film" varies considerably from person to person and with application area. The academic discipline of "Surface Science" is largely concerned with chemistry and physics at the atomic monolayer level, whereas the "surface region" in an engineering or applications sense can be much more extensive. The same is true for interfaces between materials. The practical consideration in distinguishing "surface" from "bulk" or "thin" from "thick" is usually connected to the property of interest in the application. Thus, for a catalytic reaction the presence of half a monolayer of extraneous sulfur atoms in the top atomic layer of the catalyst material might be critical, whereas for a corrosion protection layer (for example, Cr segregation to the surface region in steels) the important region of depth may be several hundred Å. For interfaces the epitaxial relationship between he last atomic layer of a single crystal material and the first layer of the adjoining material may be critical for the electrical properties of a device, whereas diffusion barrier interfaces elsewhere in the same device may be 1000 Å thick. In thin-film technology requirements can range from layers μm thick, which for the majority of analytical techniques discussed in this volume constitute bulk material, to layers as thin as 50 Å or so in thin-film magnetic recording technology. Because of these different perceptions of "thick" and "thin," actual numbers are used whenever discussing the depth an analytical technique examines. Thus in Ion Scattering Spectroscopy the signals used in the analysis are generated from only the top atomic monolayer of material exposed to a vacuum, whereas in X-ray photoemission up to 100 Å is probed, and in X-ray fluorescence the signal can come from integrated depths ranging up to 10 μm. Note that in these three examples, two are quoted as having ranges of depths. For many of the techniques it is impossible to assign unique values because the depth from which a signal originates may depend both on the particular manner in which the technique is used, and on the nature of the material being examined. Performing measurements at grazing angles of incidence of the probe beam, or grazing exit angles for the detected signal, will usually make the technique more surface sensitive. For techniques where X-ray, electron, or high-energy ion scattering is the critical factor in determining the depth analyzed, materials consisting of light elements are always probed more deeply than materials consisting of heavy elements.

Another confusing issue is that of "depth resolution." It is a measurement of the technique's ability to clearly distinguish a property as a function of depth. For example a depth resolution of 20 Å, quoted in an elemental composition analysis, means that the composition at one depth can be distinguished from that at another depth if there is at least 20 Å between them.

A depth profile is a record of the variation of a property (such as composition) as a function of depth. Some of the techniques in this volume have essentially no intrinsic depth profiling capabilities; the signal is representative of the material integrated over a fixed probing depth. Most, however, can vary the depth probed by varying the condition of analysis, or by removing the surface, layer by layer, while collecting data.

By varying the angle of incidence, the X-ray, electron, or ion beam energy, etc. many techniques are capable of acquiring depth profiles. Those profiles are generated by combining several measurements, each representative of a different integrated depth. The higher energy ion scattering techniques (Medium Energy Ion Scattering, MEIS, and Rutherford Backscattering, RBS), however, are unique in that the natural output of the methods is composition as a function of depth. By far the most common way of depth profiling is the destructive method of removing the surface, layer by layer, while also taking data. For the mass spectrometry-based techniques of Chapter 10, removal of surface material is intrinsic to the sputtering and ionization process. Other methods, such as Auger Electron Spectroscopy, AES, or X-Ray Photoemission, XPS, use an ancillary ion beam to remove material while constantly ionizing the newly exposed surface. Under the most favorable conditions depth resolutions of around 20 Å can be achieved this way, but there are many artifacts to be aware of and the depth resolution usually degrades rapidly with depth. Some aspects of sputter depth profiling are touched upon in the article "Surface Roughness" in Chapter 12, but for a more complete discussion of the capabilities and limitations of sputter depth profiling the reader is referred to a paper by D. Marton and J. Fine in *Thin Solid Films*, **185**, 79, 1990 and to other articles cited there.

Compilation of Comparative Information on the Analytical Techniques Discussed in This Volume

Article No.	Technique	Elemental	Chem. state	Phase	Defects	Structure	Image	Other	Depth probed (typical)	Width probed (typical)	Trace capability (typical)	Types of solid sample (typical)	Vacuum needed?	Commercial Instrument cost	Usage	Service available
2.1	Light Microscopy				•		•	•	Variable	0.2 µm	—	All	N	1	1	Y
2.2	SEM				•		•		sub µm	10 nm	—	Cond., coated ins.	Y	2	1	Y
2.3	STM				•	•	•		sub Å	1 Å	—	Conductors	N	2	3	Y
2.3	SFM				•	•	•		sub Å	1 nm	—	All	N	2	2	Y
2.4	TEM			•	•	•	•		200 nm*	5 nm	—	All; <200 nm thick	Y	3	2	Y
3.1	EDS	•					•		1 µm	0.5 µm	500 ppm	All; $Z > 5$	Y	2	2	Y
3.2	EELS	•	•				•		20 nm*	1 nm	Few %	All; <30 nm thick	Y	2	3	N
3.3	Cathodo-luminescence	•			•			•	10 nm–µm	1 µm	ppm	All; semicond. usually	Y	1	3	N
3.4	STEM			•	•	•	•		100 nm*	1 nm	—	All; <200 nm thick	Y	3	3	N
3.5	EPMA	•				•			1 µm	0.5 µm	100 ppm	All; flat best	Y	3	2	Y
4.1	XRD			•	•	•			10 µm	mm	3%	Crystalline	N	2	1	Y
4.2	EXAFS	•				•			Bulk*	mm	Few %	All	Y/N	—	3	N
4.3	SEXAFS	•				•			1 nm	mm	Few %	Surface and adsorbate	Y	—	3	N
4.3	NEXAFS	•	•			•			1 nm	mm	Few %	Surface and adsorbate	Y	—	3	N
4.4	XPD	•	•			•			3 nm	150 µm	1%	Single crystal	Y	3	3	N
4.5	LEED				•	•			1 nm	0.1 mm	—	Single crystal	Y	—	2	N
4.6	RHEED				•	•			1 nm	0.02 mm	—	Single crystal	Y	—	2	N
5.1	XPS	•	•						3 nm	150 µm	1%	All	Y	3	1	Y
5.2	UPS		•			•			1 nm	mm	—	All	Y	—	3	N
5.3	AES	•	•				•		2 nm	100 nm	0.1%	All, inorganic usually	Y	3	1	Y

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Article No.	Technique	Elemental	Chem. state	Phase	Defects	Structure	Image	Other	Depth probed (typical)	Width probed (typical)	Trace capability (typical)	Types of solid sample (typical)	Vacuum needed?	Commercial Instrument cost	Usage	Service available
5.4	REELS	•	•				•		2 nm	100 nm	—	All	Y	—	3	N
6.1	XRF	•							10 µm	mm	0.1%	All	N	2	1	Y
6.2	TXRF	•					•		3 nm	cm	ppb–ppm	Trace heavy metals	Y	3	3	Y
6.3	PIXE	•					•		Few µm	100 µm	10 ppm	All	Y	3	3	Y
7.1	Photo-luminescence		•		•	•	•		Few µm	Few µm	ppb	All, semicond. usually	N	1	2	N
7.2	Modulation Spectroscopy		•		•	•	•		1 µm	100 µm	ppm	All, semicond. usually	N	2	3	N
7.3	VASE					•			1 µm	cm	—	Flat thin films	N	2	3	Y
8.1	FTIR		•		•	•			Few µm	20 µm	Variable	All	N	2	1	Y
8.2	Raman Scattering		•		•	•			Few µm	1 µm	Variable	All	N	2	2	Y
8.3	HREELS		•			•			2 nm	mm	1%	All; flat cond. best	Y	3	3	N
8.4	NMR		•	•		•			Bulk	—	—	All; not all elements	N	3	3	N
9.1	RBS	•				•	•		To 2 µm	mm	0.01–10%	All	Y/N	3	2	Y
9.2	ERS						•		1 µm	mm	0.01%	H containing	Y	—	3	N
9.3	MEIS	•				•	•		1 nm	mm	0.1%–10%	All; usually single crystal	Y	3	3	N
9.4	ISS	•							3 Å	150 µm	50 ppm–1%	All	Y	—	3	Y
10.1	Dynamic SIMS	•					•		2 nm	1 µm	ppb–ppm	All, mostly semicond.	Y	3	1	Y
10.2	Static SIMS	•	•				•		3 Å	100 µm	Few %	All, mostly polymer	Y	3	2	Y
10.3	SALI	•	•						3 Å	100 nm	ppb–ppm	All, mostly inorg.	Y	3	3	N

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Article No.	Technique	Main information: Elemental	Chem. state	Phase	Defects	Structure	Image	Other	Depth probed (typical)	Width probed (typical)	Trace capability (typical)	Types of solid sample (typical)	Vacuum needed?	Commercial Instrument cost	Usage	Service available
10.4	SNMS	•							1.5 nm	cm	50 ppm	Flat conductors	Y	2	2	Y
10.5	LIMS	•	•						100 nm	2 µm	1–100 ppm	All	Y	3	2	Y
10.6	SSMS	•							3 µm	cm	0.05 ppm	Sample forms electrode	Y	—	2	Y
10.7	GDMS	•							100 nm	cm	ppt–ppb	Sample forms electrode	Y	3	2	Y
10.8	ICPMS	•							5 µm	mm	ppt	All	Y	2	1	Y
10.9	ICPOES	•							5 µm	mm	ppb	All	Y	1	1	Y
11.1	Neutron Diffraction			•		•			Bulk	—	—	Crystalline	N	—	3	N
11.2	Neutron Reflectivity						•		Up to mm	—	—	Flat polymer films	N	—	3	N
11.3	NAA	•							Bulk	—	ppt–ppm	Trace metals	N	2	3	Y
11.4	NRA	•							10–100 nm	10 µm	10–100 ppm	All; $Z < 21$	Y	—	3	Y
12.2	Optical Scatterometry						•		—	mm	—	Flat smooth films	N	1	3	Y
12.3	MOKE						•	•	30 nm	0.5 µm	—	Magnetic films	N	1	2	N
12.4	Adsorption							•	Outer atoms	—	—	Large surface area	Y	—	2	N

Notes: This table should be used as a "quick reference" guide only.

* Measured in transmission.

Commercial Instrument cost: These are typical costs; large ranges depending on sophistication and accessories: 1 means < $50k; 2 means $50–300k; 3 means >$300k. "—" means no complete commercial instrument.

Usage: Numbers refer to usage for anaylsis of solid materials. 1 means Extensive; 2 means medium; 3 means not common.

Trace capability: Guide only. Often very material/conditions dependent. "—" means not used for trace components.

Light Microscopy

The light microscope uses the visible or near visible portion of the electromagnetic spectrum; light microscopy is the interpretive use of the light microscope. This technique, which is much older than other characterization instruments, can trace its origin to the 17th century. Modern analytical and characterization methods began about 150 years ago when thin sections of rocks and minerals, and the first polished metal and metal-alloy specimens were prepared and viewed with the intention of correlating their structures with their properties. The technique involves, at its very basic level, the simple, direct visual observation of a sample with white-light resolution to 0.2 μm. The morphology, color, opacity, and optical properties are often sufficient to characterize and identify a material.

Range of samples characterized	Almost unlimited for solids and liquid crystals
Destructive	Usually nondestructive; sample preparation may involve material removal
Quantification	Via calibrated eyepiece micrometers and image analysis
Detection limits	To sub-ng
Resolving power	0.2 μm with white light
Imaging capabilities	Yes
Main use	Direct visual observation; preliminary observation for final characterization, or preparative for other instrumentation
Instrument cost	$2,500–$50,000 or more
Size	Pocket to large table

Scanning Electron Microscopy (SEM) 1.2.2

The Scanning Electron Microscope (SEM) is often the first analytical instrument used when a "quick look" at a material is required and the light microscope no longer provides adequate resolution. In the SEM an electron beam is focused into a fine probe and subsequently raster scanned over a small rectangular area. As the beam interacts with the sample it creates various signals (secondary electrons, internal currents, photon emission, etc.), all of which can be appropriately detected. These signals are highly localized to the area directly under the beam. By using these signals to modulate the brightness of a cathode ray tube, which is raster scanned in synchronism with the electron beam, an image is formed on the screen. This image is highly magnified and usually has the "look" of a traditional microscopic image but with a much greater depth of field. With ancillary detectors, the instrument is capable of elemental analysis.

Main use	High magnification imaging and composition (elemental) mapping
Destructive	No, some electron beam damage
Magnification range	$10\times$–$300,000\times$; $5000\times$–$100,000\times$ is the typical operating range
Beam energy range	500 eV–50 keV; typically, 20–30 keV
Sample requirements	Minimal, occasionally must be coated with a conducting film; must be vacuum compatible
Sample size	Less than 0.1mm, up to 10 cm or more
Lateral resolution	1–50 nm in secondary electron mode
Depth sampled	Varies from a few nm to a few µm, depending upon the accelerating voltage and the mode of analysis
Bonding information	No
Depth profiling capabilities	Only indirect
Instrument cost	$100,000–$300,000 is typical
Size	Electronics console 3 ft. $\times$ 5 ft.; electron beam column 3 ft. $\times$ 3 ft.

Scanning Tunneling Microscopy and Scanning Force Microscopy (STM and SFM) 1.2.3

In Scanning Tunneling Microscopy (STM) or Scanning Force Microscopy (SFM), a solid specimen in air, liquid or vacuum is scanned by a sharp tip located within a few Å of the surface. In STM, a quantum-mechanical tunneling current flows between atoms on the surface and those on the tip. In SFM, also known as Atomic Force Microscopy (AFM), interatomic forces between the atoms on the surface and those on the tip cause the deflection of a microfabricated cantilever. Because the magnitude of the tunneling current or cantilever deflection depends strongly upon the separation between the surface and tip atoms, they can be used to map out surface topography with atomic resolution in all three dimensions. The tunneling current in STM is also a function of local electronic structure so that atomic-scale spectroscopy is possible. Both STM and SFM are unsurpassed as high-resolution, three-dimensional profilometers.

Parameters measured	Surface topography (SFM and STM); local electronic structure (STM)
Destructive	No
Vertical resolution	STM, 0.01 Å; SFM, 0.1 Å
Lateral resolution	STM, atomic; SFM, atomic to 1 nm
Quantification	Yes; three-dimensional
Accuracy	Better than 10% in distance
Imaging/mapping	Yes
Field of view	From atoms to > 250 μm
Sample requirements	STM—solid conductors and semiconductors, conductive coating required for insulators; SFM—solid conductors, semiconductors and insulators
Main uses	Real-space three-dimensional imaging in air, vacuum, or solution with unsurpassed resolution; high-resolution profilometry; imaging of nonconductors (SFM).
Instrument cost	$65,000 (ambient) to $200,000 (ultrahigh vacuum)
Size	Table-top (ambient), 2.27–12 inch bolt-on flange (ultrahigh vacuum)

Transmission Electron Microscopy (TEM)　1.2.4

In Transmission Electron Microscopy (TEM) a thin solid specimen ($\leq$ 200 nm thick) is bombarded in vacuum with a highly-focused, monoenergetic beam of electrons. The beam is of sufficient energy to propagate through the specimen. A series of electromagnetic lenses then magnifies this transmitted electron signal. Diffracted electrons are observed in the form of a diffraction pattern beneath the specimen. This information is used to determine the atomic structure of the material in the sample. Transmitted electrons form images from small regions of sample that contain contrast, due to several scattering mechanisms associated with interactions between electrons and the atomic constituents of the sample. Analysis of transmitted electron images yields information both about atomic structure and about defects present in the material.

Range of elements	TEM does not specifically identify elements measured
Destructive	Yes, during specimen preparation
Chemical bonding information	Sometimes, indirectly from diffraction and image simulation
Quantification	Yes, atomic structures by diffraction; defect characterization by systematic image analysis
Accuracy	Lattice parameters to four significant figures using convergent beam diffraction
Detection limits	One monolayer for relatively high-Z materials
Depth resolution	None, except there are techniques that measure sample thickness
Lateral resolution	Better than 0.2 nm on some instruments
Imaging/mapping	Yes
Sample requirements	Solid conductors and coated insulators. Typically 3-mm diameter, < 200-nm thick in the center
Main uses	Atomic structure and Microstructural analysis of solid materials, providing high lateral resolution
Instrument cost	$300,000–$1,500,000
Size	100 ft.^{2} to a major lab

Energy-Dispersive X-Ray Spectroscopy (EDS) 1.3.1

When the atoms in a material are ionized by a high-energy radiation they emit characteristic X rays. EDS is an acronym describing a technique of X-ray spectroscopy that is based on the collection and energy dispersion of characteristic X rays. An EDS system consists of a source of high-energy radiation, usually electrons; a sample; a solid state detector, usually made from lithium-drifted silicon, Si (Li); and signal processing electronics. EDS spectrometers are most frequently attached to electron column instruments. X rays that enter the Si (Li) detector are converted into signals which can be processed by the electronics into an X-ray energy histogram. This X-ray spectrum consists of a series of peaks representative of the type and relative amount of each element in the sample. The number of counts in each peak may be further converted into elemental weight concentration either by comparison with standards or by standardless calculations.

Range of elements	Boron to uranium
Destructive	No
Chemical bonding information	Not readily available
Quantification	Best with standards, although standardless methods are widely used
Accuracy	Nominally 4–5%, relative, for concentrations > 5% wt.
Detection limits	100–200 ppm for isolated peaks in elements with $Z > 11$, 1–2% wt. for low-Z and overlapped peaks
Lateral resolution	.5–1 μm for bulk samples; as small as 1 nm for thin samples in STEM
Depth sampled	0.02 to μm, depending on Z and keV
Imaging/mapping	In SEM, EPMA, and STEM
Sample requirements	Solids, powders, and composites; size limited only by the stage in SEM, EPMA and XRF; liquids in XRF; 3 mm diameter thin foils in TEM
Main use	To add analytical capability to SEM, EPMA and TEM
Cost	$25,000–$100,000, depending on accessories (not including the electron microscope)

Electron Energy-Loss Spectroscopy in the Transmission Electron Microscope (EELS)   1.3.2

In Electron Energy-Loss Spectroscopy (EELS) a nearly monochromatic beam of electrons is directed through an ultrathin specimen, usually in a Transmission (TEM) or Scanning Transmission (STEM) Electron Microscope. As the electron beam propagates through the specimen, it experiences both elastic and inelastic scattering with the constituent atoms, which modifies its energy distribution. Each atomic species in the analyzed volume causes a characteristic change in the energy of the incident beam; the changes are analyzed by means of a electron spectrometer and counted by a suitable detector system. The intensity of the measured signal can be used to determine quantitatively the local specimen concentration, the electronic and chemical structure, and the nearest neighbor atomic spacings.

Range of elements	Lithium to uranium; hydrogen and helium are sometimes possible
Destructive	No
Chemical bonding information	Yes, in the near-edge structure of edge profiles information
Depth profiling capabilities	None, the specimen is already thin
Quantification	Without standards $\sim\pm10$–20% at.; with standards $\sim$1–2% at.
Detection limits	$\sim10^{-21}$ g
Depth probed	Thickness of specimen (≤ 2000 Å)
Lateral resolution	1 nm–10 μm, depending on the diameter of the incident electron probe and the thickness of the specimen
Imaging capabilities	Yes
Sample requirements	Solids; specimens must be transparent to electrons and $\sim$100–2000 Å thick
Main use	Light element spectroscopy for concentration, electronic, and chemical structure analysis at ultrahigh lateral resolution in a TEM or STEM
Cost	As an accessory to a TEM or STEM: $50,000–$150,000 (does not include electron microscope cost)

Cathodoluminescence (CL) 1.3.3

In Cathodoluminescence (CL) analysis, electron-beam bombardment of a solid placed in vacuum causes emission of photons (in the ultraviolet, visible, and near-infrared ranges) due to the recombination of electron–hole pairs generated by the incident energetic electrons. The signal provides a means for CL microscopy (i.e., CL images are displayed on a CRT) and spectroscopy (i.e., luminescence spectra from selected areas of the sample are obtained) analysis of luminescent materials using electron probe instruments. CL microscopy can be used for uniformity characterization (e.g., mapping of defects and impurity segregation studies), whereas CL spectroscopy provides information on various electronic properties of materials.

Range of elements	Not element specific
Chemical bonding information	Sometimes
Nondestructive	Yes; caution—in certain cases electron bombardment may ionize or create defects
Detection limits	In favorable cases, dopant concentrations down to 10^{14} atoms/cm^3
Depth profiling	Yes, by varying the range of electron penetration (between about 10 nm and several μm), which depends on the electron-beam energy (1–40 keV).
Lateral resolution	On the order of 1 μm; down to about 0.1 μm in special cases
Imaging/mapping	Yes
Sample requirements	Solid, vacuum compatible
Quantification	Difficult, standards needed
Main use	Nondestructive qualitative and quantitative analysis of impurities and defects, and their distributions in luminescent materials
Instrument cost	$25,000–$250,000
Size	Small add-on item to SEM, TEM

Scanning Transmission Electron Microscopy (STEM)   1.3.4

In Scanning Transmission Electron Microscopy (STEM) a solid specimen, 5–500 nm thick, is bombarded in vacuum by a beam (0.3–50 nm in diameter) of monoenergetic electrons. STEM images are formed by scanning this beam in a raster across the specimen and collecting the transmitted or scattered electrons. Compared to the TEM an advantage of the STEM is that many signals may be collected simultaneously: bright- and dark-field images; Convergent Beam Electron Diffraction (CBED) patterns for structure analysis; and energy-dispersive X-Ray Spectrometry (EDS) and Electron Energy-Loss Spectrometry (EELS) signals for compositional analysis. Taken together, these analysis techniques are termed Analytical Electron Microscopy (AEM). STEM provides about 100 times better spatial resolution of analysis than conventional TEM. When electrons scattered into high angles are collected, extremely high-resolution images of atomic planes and even individual heavy atoms may be obtained.

Range of elements	Lithium to uranium
Destructive	Yes, during specimen preparation
Chemical bonding information	Sometimes, from EELS
Quantification	Quantitative compositional analysis from EDS or EELS, and crystal structure analysis from CBED
Accuracy	5–10% relative for EDS and EELS
Detection limits	0.1–3.0% wt. for EDS and EELS
Lateral resolution	Imaging, 0.2–10 nm; EELS, 0.5–10 nm; EDS, 3–30 nm
Imaging/mapping capabilities	Yes, lateral resolution down to < 5 nm
Sample requirements	Solid conductors and coated insulators typically 3 mm in diameter and < 200 nm thick at the analysis point for imaging and EDS, but < 50 nm thick for EELS
Main uses	Microstructural, crystallographic, and compositional analysis; high spatial resolution with good elemental detection and accuracy; unique structural analysis with CBED
Instrument cost	$500,000–$2,000,000
Size	3 m × 4 m × 3 m

Electron Probe X-Ray Microanalysis (EPMA)   1.3.5

Electron Probe X-Ray Microanalysis (EPMA) is an elemental analysis technique based upon bombarding a specimen with a focused beam of energetic electrons (beam energy 5–30 keV) to induce emission of characteristic X rays (energy range 0.1–15 keV). The X rays are measured by Energy-Dispersive (EDS) or Wavelength-Dispersive (WDS) X-ray spectrometers. Quantitative matrix (interelement) correction procedures based upon first principles physical models provide great flexibility in attacking unknown samples of arbitrary composition; the standards suite can be as simple as pure elements or binary compounds. Typical error distributions are such that relative concentration errors lie within ±4% for 95% of cases when the analysis is performed with pure element standards. Spatial distributions of elemental constituents can be visualized qualitatively by X-ray area scans (dot maps) and quantitatively by digital compositional maps.

Range of elements	Beryllium to the actinides
Destructive	No, except for electron beam damage
Chemical bonding	In rare cases: from light-element X-ray peak shifts
Depth profiling	Rarely, by changing incident beam energy
Quantification	Standardless or; pure element standards
Accuracy	±4% relative in 95% of cases; flat, polished samples
Detection limits	WDS, 100 ppm; EDS, 1000 ppm
Sampling depth	Energy and matrix dependent, 100 nm–5 μm
Lateral resolution	Energy and matrix dependent, 100 nm–5 μm
Imaging/mapping	Yes, compositional mapping and SEM imaging
Sample requirements	Solid conductors and insulators; typically, < 2.5 cm in diameter, and < 1 cm thick, polished flat; particles, rough surfaces, and thin films
Major uses	Accurate, nondestructive quantitative analysis of major, minor, and trace constituents of materials
Instrument cost	$300,000–$800,000
Size	3 m × 1.5 m × 2 m high

X-Ray Diffraction (XRD) 1.4.1

In X-Ray Diffraction (XRD) a collimated beam of X rays, with wavelength $\lambda \sim 0.5$–2 Å, is incident on a specimen and is diffracted by the crystalline phases in the specimen according to Bragg's law ($\lambda = 2d\sin\theta$, where d is the spacing between atomic planes in the crystalline phase). The intensity of the diffracted X rays is measured as a function of the diffraction angle 2θ and the specimen's orientation. This diffraction pattern is used to identify the specimen's crystalline phases and to measure its structural properties, including strain (which is measured with great accuracy), epitaxy, and the size and orientation of crystallites (small crystalline regions). XRD can also determine concentration profiles, film thicknesses, and atomic arrangements in amorphous materials and multilayers. It also can characterize defects. To obtain this structural and physical information from thin films, XRD instruments and techniques are designed to maximize the diffracted X-ray intensities, since the diffracting power of thin films is small.

Range of elements	All, but not element specific. Low-Z elements may be difficult to detect
Probing depth	Typically a few μm but material dependent; monolayer sensitivity with synchrotron radiation
Detection Limits	Material dependent, but ~3% in a two phase mixture; with synchrotron radiation can be ~0.1%
Destructive	No, for most materials
Depth profiling	Normally no; but this can be achieved.
Sample requirements	Any material, greater than ~0.5 cm, although smaller with microfocus
Lateral resolution	Normally none; although ~10 μm with microfocus
Main use	Identification of crystalline phases; determination of strain, and crystallite orientation and size; accurate determination of atomic arrangements
Specialized uses	Defect imaging and characterization; atomic arrangements in amorphous materials and multilayers; concentration profiles with depth; film thickness measurements
Instrument cost	$70,000–$200,000
Size	Varies with instrument, greater than ~70 ft.^{2}

Extended X-Ray Absorption Fine Structure (EXAFS)

An EXAFS experiment involves the irradiation of a sample with a tunable source of monochromatic X rays from a synchrotron radiation facility. As the X-ray energy is scanned from just below to well above the binding energy of a core-shell electron (e.g., K or L) of a selected element, the X-ray photoabsorption process is monitored. When the energy of the incident X-rays is equal to the electron binding energy, X-ray absorption occurs and a steeply rising absorption edge is observed. For energies greater than the binding energy, oscillations of the absorption with incident X-ray energy (i.e., EXAFS) are observed. EXAFS data are characteristic of the structural distribution of atoms in the immediate vicinity (~5 Å) of the X-ray absorbing element. The frequency of the EXAFS is related to the interatomic distance between the absorbing and neighboring atoms. The amplitude of the EXAFS is related to the number, type, and order of neighboring atoms.

Range of elements	Lithium through uranium
Destructive	No
Bonding information	Yes, interatomic distances, coordination numbers, atom types, and structural disorder; oxidation state by inference
Accuracy	1–2% for interatomic distances; 10–25% for coordination numbers
Detection limits	Surface, monolayer sensitivity; bulk, > 100 ppm
Depth probed	Variable, from Å to μm
Depth profiling	Yes, with glancing incidence angles; electron- and ion-yield detection
Lateral resolution	Not yet developed
Imaging/mapping	Not yet developed
Sample requirements	Virtually any material; solids, liquids, gas
Main use	Local atomic environments of elements in materials
Instrument cost	Laboratory facility, < \$300,000; synchrotron beam line, > \$1,000,000
Size	Small attachment to synchrotron beam line

Surface Extended X-Ray Absorption Fine Structure and Near Edge X-Ray Absorption Fine Structure (SEXAFS/NEXAFS) 1.4.3

In Surface Extended X-Ray Absorption Fine Structure and Near Edge X-Ray Absorption Fine Structure (SEXAFS/NEXAFS) a solid sample, usually placed in ultrahigh vacuum, is exposed to a tunable beam of X rays from a synchrotron radiation source. A spectrum is collected by varying the photon energy of the X rays and measuring the yield of emitted electrons or fluorescent X rays. Analysis of the wiggles in the observed spectrum (the SEXAFS features) gives information on nearest neighbor bond lengths and coordination numbers for atoms at or near the surface. Features near an absorption edge (NEXAFS) are often characteristic of the local coordination (octahedral, tetrahedral, etc.) or oxidation state. For adsorbed molecules, NEXAFS resonances characterize the type of bonding. On a flat surface, the angular variation of intensity of the resonances gives the orientation of the molecule.

Range of elements	Almost all, from C to U
Destructive	No
Chemical bonding information	Yes, through NEXAFS
Accuracy	In nearest neighbor distance, ±0.01 Å with care
Surface sensitivity	Top few monolayers
Detection limits	0.05 monolayer
Lateral resolution	~0.5 mm
Imaging/mapping	No
Sample requirements	Vacuum-compatible solids
Main use of SEXAFS	Adsorbate–substrate bond lengths
Main use of NEXAFS	Orientation of molecular adsorbates
Instrument cost	$400,000, plus cost of synchrotron
Size	Small attachment to synchrotron beam line

X-Ray Photoelectron and
Auger Electron Diffraction (XPD and AED)   1.4.4

In X-Ray Photoelectron Diffraction (XPD) and Auger Electron Diffraction (AED), a single crystal or a textured polycrystalline sample is struck by photons or electrons to produce outgoing electrons that contain surface chemical and structural information. The focus of XPD and AED is structural information, which originates from interference effects as the outbound electrons from a particular atom are scattered by neighboring atoms in the solid. The electron–atom scattering process strongly increases the electron intensity in the forward direction, leading to the simple observation that intensity maxima occur in directions corresponding to rows of atoms. An energy dispersive angle-resolved analyzer is used to map the intensity distribution as a function of angle for elements of interest.

Range of elements	All except H and He
Destructive	XPD no; AED may cause e-beam damage
Element specific	Yes
Chemical state specific	Yes, XPD is better than AED
Accuracy	Bond angles to within 1°; atomic positions to within 0.05 Å
Site symmetry	Yes, and usually quickly
Depth Probed	5–50 Å
Depth profiling	Yes, to 30 Å beneath the surface
Detection limits	0.2 at.%
Lateral resolution	150 Å (AED), 150 μm (XPD)
Imaging/mapping	Yes
Sample requirements	Primarily single crystals, but also textured samples
Main use	To determine adsorption sites and thin-film growth modes in a chemically specific manner
Instrument cost	$300,000–$600,000
Size	4 m × 4 m × 3 m

Low-Energy Electron Diffraction (LEED) 1.4.5

In Low-Energy Electron Diffraction (LEED) a collimated monoenergetic beam of electrons in the energy range 10–1000 eV ($\lambda \approx 0.4$–4.0 Å) is diffracted by a specimen surface. In this energy range, the mean free path of electrons is only a few Å, leading to surface sensitivity. The diffraction pattern can be analyzed for the existence of a clean surface or an ordered overlayer structure. Intensities of diffracted beams can be analyzed to determine the positions of surface atoms relative to each other and to underlying layers. The shapes of diffracted beams in angle can be analyzed to provide information about surface disorder. Various phenomena related to surface crystallography and microstructure can be investigated. This technique requires a vacuum.

Range of elements	All elements, but not element specific
Destructive	No, except in special cases of electron-beam damage
Depth probed	4–20 Å
Detection limits	0.1 monolayer; any ordered phase can be detected; atomic positions to 0.1 Å; step heights to 0.1 Å; surface disorder down to ~10% of surface sites
Resolving power	Maximum resolvable distance for detecting disorder: typically 200 Å; best systems, 5 μm
Lateral resolution	Typical beam sizes, 0.1 mm; best systems, ~10 μm
Imaging capability	Typically, no; with specialized instruments (e.g., low-energy electron microscopy), 150 Å
Sample requirements	Single crystals of conductors and semiconductors; insulators and polycrystalline samples under special circumstances; 0.25 cm^2 or larger, smaller with special effort
Main uses	Analysis of surface crystallography and microstructure; surface cleanliness
Cost	≤$75,000; can be home built cheaply
Size	Generally part of other systems; if self-standing, ~8 m^2

Reflection High-Energy
Electron Diffraction (RHEED) 1.4.6

In Reflection High-Energy Electron Diffraction (RHEED), a beam of high-energy electrons (typically 5–50 keV), is accelerated toward the surface of a conducting or semiconducting crystal, which is held at ground potential. The primary beam strikes the sample at a grazing angle ($\sim$1–5°) and is subsequently scattered. Some of the electrons scatter elastically. Since their wavelengths are shorter than interatomic separations, these electrons can diffract off ordered rows of atoms on the surface, concentrating scattered electrons into particular directions, that depend on row separations. Beams of scattered electrons whose trajectories intersect a phosphor screen placed opposite the electron gun will excite the phosphor. The light from the phosphor screen is called the RHEED pattern and can be recorded with a photograph, television camera, or by some other method. The symmetry and spacing of the bright features in the RHEED pattern give information on the surface symmetry, lattice constant, and degree of perfection, i.e., the crystal structure.

Range of elements	All, but not chemical specific
Destructive	No, Except for electron-sensitive materials
Depth probed	2–100 Å
Depth profiling	No
Lateral resolution	200 μm × 4 mm, in special cases 0.3 nm × 6 nm
Structural information	Measures surface crystal structure parameters, sensitive to structural defects
Sample requirements	Usually single crystal conductor or semiconductor surfaces
Main use	Monitoring surface structures, especially during thin-film epitaxial growth; can distinguish two- and three-dimensional defects
Instrument cost	$50,000–$200,000
Size	$\sim$25 sq. ft., larger if incorporated with an MBE chamber

X-Ray Photoelectron Spectroscopy (XPS)   1.5.1

In X-Ray Photoelectron Spectroscopy (XPS) monoenergetic soft X rays bombard a sample material, causing electrons to be ejected. Identification of the elements present in the sample can be made directly from the kinetic energies of these ejected photoelectrons. On a finer scale it is also possible to identify the chemical state of the elements present from small variations in the determined kinetic energies. The relative concentrations of elements can be determined from the measured photoelectron intensities. For a solid, XPS probes 2–20 atomic layers deep, depending on the material, the energy of the photoelectron concerned, and the angle (with respect to the surface) of the measurement. The particular strengths of XPS are semiquantitative elemental analysis of surfaces without standards, and chemical state analysis, for materials as diverse as biological to metallurgical. XPS also is known as electron spectroscopy for chemical analysis (ESCA).

Range of elements	All except hydrogen and helium
Destructive	No, some beam damage to X-ray sensitive materials
Elemental analysis	Yes, semiquantitative without standards; quantitative with standards. Not a trace element method.
Chemical state information	Yes
Depth probed	5–50 Å
Depth profiling	Yes, over the top 50 Å; greater depths require sputter profiling
Depth resolution	A few to several tens of Å, depending on conditions
Lateral resolution	5 mm to 75 μm; down to 5 μm in special instruments
Sample requirements	All vacuum-compatible materials; flat samples best; size accepted depends on particular instrument
Main uses	Determinations of elemental and chemical state compositions in the top 30 Å
Instrument cost	$200,000–$1,000,000, depending on capabilities
Size	10 ft. × 12 ft.

Ultraviolet Photoelectron Spectroscopy (UPS)   1.5.2

If monoenergetic photons in the 10–100 eV energy range strike a sample material, photoelectrons from the valence levels and low-lying core levels (i.e., having lower binding energy than the photon energy) are ejected. Measurement of the kinetic energy distribution of the ejected electrons is known as Ultraviolet Photoelectron Spectroscopy (UPS). The physics of the technique is the same as XPS, the only differences being that much lower photon energies are used and the primary emphasis is on examining the valence electron levels, rather than core levels. Owing to this emphasis, the primary use, when investigating solid surfaces, is for electronic structure studies in surface physics rather than for materials analysis. There are, however, a number of situations where UPS offers advantages over XPS for materials surface analysis.

Elemental analysis	Not usually, sometimes from available core levels
Destructive	No, some beam damage to radiation-sensitive material
Chemical state information	Yes, but complicated using valence levels; for core levels as for XPS
Depth probed	2–100 Å
Depth profiling	Yes, over the depth probed; deeper profiling requires sputter profiling
Lateral resolution	Generally none (mm size), but photoelectron microscopes with capabilities down to the 1-μm range exist
Sample requirements	Vacuum-compatible material; flat samples best; size accepted depends on instrumentation
Main use	Electronic structure studies of free molecules (gas phase), well-defined solid surfaces, and adsorbates on solid surfaces
Instrument cost	No commercial instruments specifically for UPS; usually an add-on to XPS (incremental cost ~$30,000) or done using a synchrotron facility as the photon source
Size	10 ft. × 10 ft. for a stand-alone system

Auger Electron Spectroscopy (AES)   1.5.3

Auger Electron Spectroscopy (AES) uses a focused electron beam to create secondary electrons near the surface of a solid sample. Some of these (the Auger electrons) have energies characteristic of the elements and, in many cases, of the chemical bonding of the atoms from which they are released. Because of their characteristic energies and the shallow depth from which they escape without energy loss, Auger electrons are able to characterize the elemental composition and, at times, the chemistry of the surfaces of samples. When used in combination with ion sputtering to gradually remove the surface, Auger spectroscopy can similarly characterize the sample in depth. The high spacial resolution of the electron beam and the process allows microanalysis of three-dimensional regions of solid samples. AES has the attributes of high lateral resolution, relatively high sensitivity, standardless semi-quantitative analysis, and chemical bonding information in some cases.

Range of elements	All except H and He
Destructive	No, except to electron beam-sensitive materials and during depth profiling
Elemental Analysis	Yes, semiquantitative without standards; quantitative with standards
Absolute sensitivity	100 ppm for most elements, depending on the matrix
Chemical state information?	Yes, in many materials
Depth probed	5–100 Å
Depth profiling	Yes, in combination with ion-beam sputtering
Lateral resolution	300 Å for Auger analysis, even less for imaging
Imaging/mapping	Yes, called Scanning Auger Microscopy, SAM
Sample requirements	Vacuum-compatible materials
Main use	Elemental composition of inorganic materials
Instrument cost	$100,000–$800,000
Size	10 ft. × 15 ft.

Reflected Electron Energy-Loss Spectroscopy (REELS)   1.5.4

In Reflected Electron Energy-Loss Spectroscopy (REELS) a solid specimen, placed in a vacuum, is irradiated with a narrow beam of electrons that are sufficiently energetic to induce electron excitations with atoms or clusters of atoms. Some of the incident electrons reemerge from the sample having lost a specific amount of energy relative to the well-defined energy E_0 of the incident electron. The number, direction k, and energy of the emitted electrons can be measured by an electron energy analyzer. Composition, crystal structure, and chemical bonding information can be obtained about the sample's surface from the intensity and line shape of the emitted electron energy-loss spectra by comparison to standards.

Range of elements	Hydrogen to uranium; no isotopes
Destructive	No
Chemical bond information	Yes; energetics and orientation
Depth profiling	Yes; tilting or ion sputtering
Quantification	Standards required
Accuracy	Few percent to tens of percent
Detection limits	Few tenths of a percent
Probing depth	0.07–3.0 nm
Lateral resolution	100 nm–50 μm; sample independent; not limited by rediffused primaries
Imaging/mapping	Yes, called REELM
Sample requirements	Solids; liquids; vacuum compatible; typically < 2.5 cm-diameter, < 1.5 cm-thickness
Main use	Few-monolayer thin-film analysis, e.g., adsorbate and very thin-film reactions; submicron detection of metal hydrides
Instrument cost	$0–$700,000, free on any type of electron-excited Auger spectrometer
Size	None extra over Auger spectrometer

X-Ray Fluorescence (XRF) 1.6.1

In X-Ray Fluorescence (XRF), an X-ray beam is used to irradiate a specimen, and the emitted fluorescent X rays are analyzed with a crystal spectrometer and scintillation or proportional counter. The fluorescent radiation normally is diffracted by a crystal at different angles to separate the X-ray wavelengths and therefore to identify the elements; concentrations are determined from the peak intensities. For thin films XRF intensity–composition–thickness equations derived from first principles are used for the precision determination of composition and thickness. This can be done also for each individual layer of multiple-layer films.

Range of elements	All but low-Z elements: H, He, and Li
Accuracy	±1% for composition, ±3% for thickness
Destructive	No
Depth sampled	Normally in the 10-μm range, but can be a few tens of Å in the total-reflection range
Depth profiling	Normally no, but possible using variable-incidence X rays
Detection limits	Normally 0.1% in concentration.
Sensitivity	$10–10^5$ Å in thickness can be examined
Lateral resolution	Normally none, but down to 10 μm using a microbeam
Chemical bond information	Normally no, but can be obtained from soft X-ray spectra
Sample requirements	≤5.0 cm in diameter
Main use	Identification of elements; determination of composition and thickness
Instrument cost	$50,000–$300,000
Size	5 ft. × 8 ft.

Total Reflection X-Ray Fluorescence Analysis (TXRF)

1.6.2

In Total Reflection X-Ray Fluorescence Analysis (TXRF), the surface of a solid specimen is exposed to an X-ray beam in grazing geometry. The angle of incidence is kept below the critical angle for total reflection, which is determined by the electron density in the specimen surface layer, and is on the order of mrad. With total reflection, only a few nm of the surface layer are penetrated by the X rays, and the surface is excited to emit characteristic X-ray fluorescence radiation. The energy spectrum recorded by the detector contains quantitative information about the elemental composition and, especially, the trace impurity content of the surface, e.g., semiconductor wafers. TXRF requires a specular surface of the specimen with regard to the primary X-ray light.

Range of elements	Sodium to uranium
Destructive	No
Chemical bonding information	Not usually
Depth probed	Typically 1–5 nm
Depth profiling capability	Limited (variation of angle of incidence)
Quantification	Yes
Accuracy	1–20%
Detection limits	10^{10}–10^{14} at/cm^2
Lateral resolution	Limited, typically 10 mm
Sample requirements	Specular surface, typically $\geq$ 2.5-cm diameter
Main use	Multielement analysis, excellent detection limits for heavy metals; quantitative measurement of heavy-metal trace contamination on silicon wafers
Instrument cost	$300,000–$600,000

Particle-Induced X-Ray Emission (PIXE)   1.6.3

Particle-Induced X-Ray Emission (PIXE) is a quantitative, nondestructive analysis technique that relies on the spectrometry of characteristic X rays emitted during irradiation of a specimen with high-energy ionic particles (~0.3–10 MeV). The process is analogous to the emission of characteristic X rays under electron and photon bombardment of a specimen (see the articles on EDS, EMPA, and XRF). With appropriate corrections, X-ray yields (X rays per particle) can be converted to elemental concentrations. The background X-ray radiation for PIXE is much less than that for electron excitation; thus, the detection limits for trace elements using PIXE is orders of magnitude better. PIXE is best for the analysis of thin samples, surface layers, and samples with limited amounts of materials, while photon bombardment (XRF) is better for bulk analysis and thick specimens. Using wavelength-dispersive detectors, PIXE, EMPA, and XRF can provide identification of the chemical bonding of elements. Although EMPA and EDS require that the specimen be in vacuum, PIXE and XRF can be performed with the specimen in vacuum or at atmospheric pressure.

Range of elements	Lithium to uranium
Chemical bonding information	Yes, when spectral resolution is high
Depth probed	$\leq 10\ \mu m$
Depth profiling	Yes, by varying angle of incidence or particle energy.
Detection limits	Thin, freestanding foil, 0.1–10 ppm; surface layers on thick specimens, 10^{13}–5×10^{15} at/cm^2; Bulk specimens, 1–100 ppm
Accuracy	~2–10%, with standards
Lateral resolution	~5 μm–2 mm
Imaging/mapping	Yes
Sample requirements	Solids, liquids, and gases
Main use	Fast analysis for many elements, in all materials, simultaneously
System cost	~$1,000,000, including small ion accelerator (2-MeV H$^+$)
System size	~100 sq. ft. floor space

Photoluminescence (PL)

In photoluminescence one measures physical and chemical properties of materials by using photons to induce excited electronic states in the material system and analyzing the optical emission as these states relax. Typically, light is directed onto the sample for excitation, and the emitted luminescence is collected by a lens and passed through an optical spectrometer onto a photodetector. The spectral distribution and time dependence of the emission are related to electronic transition probabilities within the sample, and can be used to provide qualitative and, sometimes, quantitative information about chemical composition, structure (bonding, disorder, interfaces, quantum wells), impurities, kinetic processes, and energy transfer.

Destructiveness	Nondestructive
Depth probed	0.1–3 μm; limited by light penetration depth and carrier diffusion length
Lateral resolution	Down to 1–2 μm
Quantitative abilities	Intensity-based impurity quantification to several percent possible; energy quantification very precise
Sensitivity	Down to parts-per-trillion level, depending on impurity species and host
Imaging/mapping	Yes
Sample requirements	Liquid or solid having optical transitions; probe size 2 μm to a few cm
Main uses	Band gaps of semiconductors; carrier lifetimes; shallow impurity or defect detection; sample quality and structure
Instrument cost	Less than $10,000 to over $200,000
Size	Table top to small room

Modulation Spectroscopy 1.7.2

Modulation spectroscopy is a powerful experimental method for measuring the energy of transitions between the filled and empty electronic states in the bulk (band gaps) or at surfaces of semiconductor materials over a wide range of experimental conditions (temperature, ambients, etc.). By taking the derivative of the reflectance (or transmittance) of a material in an analog manner, it produces a series of sharp, derivative-like spectral features corresponding to the photon energy of the transitions. These energies are sensitive to a number of internal and external parameters such as chemical composition, temperature, strain, and electric and magnetic fields. The line widths of these spectral features are a function of the quality of the material.

Destructiveness	Some methods are nondestructive
Depth probed	For bulk applications 0.1–1 μm; for surface applications one monolayer is possible
Lateral resolution	Down to 100 μm
Image/mapping	Yes
Sensitivity	Alloy composition (e.g., $Ga_{1-x}Al_xAs$) $\Delta x = 0.005$; carrier concentration 10^{15}–10^{19} cm^{-3}
Main uses	Contactless, nondestructive monitoring of band gaps in semiconductors; Wide range of temperatures and ambients (air, ultrahigh vacuum); *in-situ* monitoring of semiconductor growth
Instrument cost	$30,000–$100,000
Size	For most methods about 2 × 3 ft.

Variable-Angle Spectroscopic Ellipsometry (VASE)

In Variable-Angle Spectroscopic Ellipsometry (VASE), polarized light strikes a surface and the polarization of the reflected light is analyzed using a second polarizer. The light beam is highly collimated and monochromatic, and is incident on the material at an oblique angle. For each angle of incidence and wavelength, the reflected light intensity is measured as a function of polarization angle, allowing the important ellipsometric parameter to be determined. An optimum set of angle of incidence and wavelength combinations is used to maximize measurement sensitivity and information obtained. Physical quantities derivable from the measured parameter include the optical constants of bulk or filmed media, the thicknesses of films (from 1 to a few hundred nm), and the microstructural composition of a multiconstituent thin film. In general only materials with parallel interfaces, and with structural or chemical inhomogeneities on a scale less than about 1/10 the wavelength of the incident light, can be studied by ellipsometry.

Main use	Film thicknesses, microstructure, and optical properties
Optical range	Near ultraviolet to mid infrared
Sample requirements	Planar materials and interfaces
Destructive	No, operation in any transparent ambient, including vacuum, gases, liquids, and air
Depth probed	Light penetration of the material (tens of nm to μm)
Lateral resolution	mm normally, 100 μm under special conditions
Image/mapping	No
Instrument cost	\$50,000–\$150,000
Size	0.5 m × 1 m

Fourier Transform Infrared Spectroscopy (FTIR)   1.8.1

The vibrational motions of the chemically bound constituents of matter have frequencies in the infrared regime. The oscillations induced by certain vibrational modes provide a means for matter to couple with an impinging beam of infrared electromagnetic radiation and to exchange energy with it when the frequencies are in resonance. In the infrared experiment, the intensity of a beam of infrared radiation is measured before (I_0) and after (I) it interacts with the sample as a function of light frequency, $\{w_i\}$. A plot of I/I_0 versus frequency is the "infrared spectrum." The identities, surrounding environments, and concentrations of the chemical bonds that are present can be determined.

Information	Vibrational frequencies of chemical bonds
Element Range	All, but not element specific
Destructive	No
Chemical bonding information	Yes, identification of functional groups
Depth profiling	No, not under standard conditions
Depth Probed	Sample dependent, from μm's to 10 nm
Detection limits	Ranges from undetectable to $< 10^{13}$ bonds/cc. Sub-monolayer sometimes
Quantification	Standards usually needed
Reproducibility	0.1% variation over months
Lateral resolution	0.5 cm to 20 μm
Imaging/mapping	Available, but not routinely used
Sample requirements	Solid, liquid, or gas in all forms; vacuum not required
Main use	Qualitative and quantitative determination of chemical species, both trace and bulk, for solids and thin films. Stress, structural inhomogeneity
Instrument cost	$50,000–$150,000 for FTIR; $20,000 or more for non-FT spectrophotometers
Instrument size	Ranges from desktop to (2 × 2 m)

Raman Spectroscopy 1.8.2

Raman spectroscopy is the measurement, as a function of wavenumber, of the inelastic light scattering that results from the excitation of vibrations in molecular and crystalline materials. The excitation source is a single line of a continuous gas laser, which permits optical microscope optics to be used for measurement of samples down to a few μm. Raman spectroscopy is sensitive to molecular and crystal structure; applications include chemical fingerprinting, examination of single grains in ceramics and rocks, single-crystal measurements, speciation of aqueous solutions, identification of compounds in bubbles and fluid inclusions, investigations of structure and strain states in polycrystalline ceramics, glasses, fibers, gels, and thin and thick films.

Information	Vibrational Frequencies of chemical bonds
Element range	All, but not element specific
Destructive	No, unless sample is susceptible to laser damage
Lateral resolution	1 μm with microfocus instruments
Depth profiling	Limited to transparent materials
Depth probed	Few μm to mm, depending on material
Detection limits	1000 Å normally, submonolayer in special cases
Quantitative	With difficulty; usually qualitative only
Imaging	Usually no, although imaging instruments have been built
Sample requirements	Very flexible: liquids, gases, crystals, polycrystalline solids, powders, and thin films
Main use	Identification of unknown compounds in solutions, liquids, and crystalline materials; characterization of structural order, and phase transitions
Instrument cost	$150,000–$250,000
Size	1.5 m × 2.5 m

High-Resolution Electron Energy Loss Spectroscopy (HREELS) 1.8.3

In High-Resolution Electron Energy Loss Spectroscopy (HREELS), a highly monoenergetic beam of low energy (1–10 eV) electrons is focused onto a sample's surface, and the scattered electrons are analyzed with high resolution of the scattering energy and angle. Some of the scattered electrons suffer small characteristic energy losses due to vibrational excitation of surface atoms and molecules. A vibrational spectrum can be obtained by counting the number of electrons versus the electron energy loss relative to the elastically scattered (no energy loss) electron beam. This spectrum is used mainly to identify chemical species (functional groups) in the first layer of the surface. Often this layer contains adsorbed species on a solid.

Information	Molecular vibrational frequencies
Main use	Nondestructive identification of the molecular functional groups present at surfaces
Range of elements	Not element specific
Bonding	Any chemical bonds that have vibrations in the range 50–4000 cm^{-1}
Detection limits	0.1% monolayer for strong vibrational bands
Quantification	Difficult, possible with standards
Depth probed	2 nm
Lateral resolution	1 mm^2
Sample requirements	Single-crystal samples of conductors best; other solid samples are suitable, including polycrystalline metals, polymeric materials, semiconductors, and insulators, ultrahigh vacuum compatible; typically $\geq$ 5 mm diameter, 1–3 mm thick
Instrument cost	$100,000 plus associated techniques and vacuum system
Size	Attaches to vacuum chamber by 8–14 inch diameter flange.

Solid State Nuclear Magnetic Resonance (NMR)   1.8.4

Solid state Nuclear Magnetic Resonance (NMR) exploits the interaction of nuclear magnetic moments with electromagnetic waves in the radio frequency region. In the experiment, a solid specimen (crystalline or amorphous, aligned or randomly oriented) is placed in a strong external magnetic field (typically 1–14 Tesla) and irradiated with intense radio frequency pulses over a frequency range required to excite a specific atomic nucleus from the ground magnetic (spin) state to another higher state. As the nucleus releases back to its ground state the sample re-emits a radio signal at the excitation frequency, which is detected by electromagnetic induction and Fourier transformed to yield a plot of intensity versus frequency. The spectrum thus obtained identifies the presence of the atom and its relative concentration (with standards) and is a sensitive indicator of structural and chemical bonding properties. It can serve for phase identification as well as for the characterization of local bonding environments in disordered materials.

Elements detected	All elements possessing an isotope with a suitable magnetic dipole moment (about half the elements in the periodic table)
Detection limit	On the order of 10^{18} atoms of the nuclear isotope studied
Surface sensitivity	Not intrinsically surface sensitive: Surface areas > 10 m^2/g required or desirable for surface studies
Typical sample size	10–500 mg, varies greatly with the nucleus studied; sample length, 0.5–5 cm; width, 0.5–2 cm
Measurement conditions	Usually at ambient temperature and pressure
Sample form	Powder, single crystal, randomly oriented, or aligned film
Main use	Element-selective phase identification and quantification, structural characterization of disordered states
Instrument cost	\$200,000–\$1,200,000, depending mostly on the field strength desired
Space requirement	300 ft.^{2}

Rutherford Backscattering Spectrometry (RBS) 1.9.1

Rutherford Backscattering Spectrometry (RBS) analysis is performed by bombarding a sample target with a monoenergetic beam of high-energy particles, typically helium, with an energy of a few MeV. A fraction of the incident atoms scatter backwards from heavier atoms in the near-surface region of the target material, and usually are detected with a solid state detector that measures their energy. The energy of a backscattered particle is related to the depth and mass of the target atom, while the number of backscattered particles detected from any given element is proportional to concentration. This relationship is used to generate a quantitative depth profile of the upper 1–2 μm of the sample. Alignment of the ion beam with the crystallographic axes of a sample permits crystal damage and lattice locations of impurities to be quantitatively measured and depth profiled. The primary applications of RBS are the quantitative depth profiling of thin-film structures, crystallinity, dopants, and impurities.

Range of elements	Lithium to uranium
Destructive	$\sim 10^{13}$ He atoms implanted; radiation damage.
Chemical bonding information	No
Quantification	Yes, standardless; accuracy 5-20%
Detection limits	10^{12}–10^{16} atoms/cm^2; 1–10 at.% for low-Z elements; 0–100 ppm for high-Z elements
Lateral resolution	1–4 mm, 1 μm in specialized equipment
Depth profiling	Yes and nondestructive
Depth resolution	2–30 nm
Maximum depth	~ 2 μm, 20 μm with H$^+$
Imaging/mapping	Under development
Sample requirements	Solid, vacuum compatible
Main use	Nondestructive depth profiling of thin films, crystal damage information
Instrument cost	$450,000–$1,000,000
Size	2 m × 7 m

Elastic Recoil Spectrometry (ERS) 1.9.2

Energetic recoil ions, $^1H^+$ and $^2H^+$, are produced when $^4He^+$ ions having energies in the MeV range undergo elastic nucleus–nucleus collisions within a hydrogen- or deuterium-containing solid sample. Energy spectrometry of the recoiling ions identifies their mass and depth of origin. The total hydrogen content of a thin layer may be determined directly from the recoil fluence. In combination with Rutherford Backscattering (RBS) analysis of the same sample, elastic recoil spectra provide concentration profiles and complete compositional analysis of near-surface regions of the sample material. ERS requires equipment common to RBS analysis. It is the simplest ion beam technique for hydrogen profiling, since ion backscattering (RBS) from hydrogen is not possible.

Range of elements	Unique selection of ^1H, ^2H
Destructive	Radiation damage may release H in polymers
Chemical bonding information	None
Quantitation	Absolute atoms/cm^2 ± 2% typically
Sensitivity	5×10^{13} atom/cm^2 or 0.01 at.% (typically)
Depth probed	≤ 1 μm typically
Depth profiles	Yes; concentration profile to ± 1% relative
Depth resolution	Varies with depth; 300–600 Å at depth 1000 Å in Si
Lateral resolution	1–4 mm typically
Sample requirements	Solid, vacuum compatible, dimensions ≥ 5 mm
Main use	Determination of H concentrations in thin films; rapid; matrix-independent
Instrument cost	As for RBS; MeV accelerator ($1,000,000–$1,500,000); services available
Size	Requires laboratory ≥ 20 ft. × 50 ft., depending on instrument

Medium-Energy Ion Scattering with Channeling and Blocking (MEIS)   1.9.3

Medium-Energy Ion Scattering (MEIS) with channeling and blocking is a quantitative, real space, nondestructive technique for studying the composition and structure of surfaces and interfaces buried up to a few atomic layers below the surface. Single-crystal or epitaxial samples are required for the structural determinations. The basic quantities measured are the energy and angular distribution of backscattered ions in the 50–400 keV range. The technique has elemental and depth sensitivity. The ion angular distributions are characterized by minima (dips) in intensity, the positions of which are closely connected to the relative positions of atoms in the surface layer. MEIS is more surface sensitive, and more complex instrumentally than other surface ion spectroscopies, though interpretation is straightforward. The technique is useful for the analysis of all ultrahigh vacuum compatible solids, and in particular metals, semiconductors, and overlayers on such surfaces (submonolayer adsorbate concentrations, thin films of silicides, etc.).

Elements detected	all elements
Elemental sensitivity	Scales as the square of nuclear charge; best for heavy elements (< 10^{-4} monolayer); poor for hydrogen
Chemical sensitivity	None
Depth probed	Typically 4–5 atomic layers, but up to 200 Å in special cases
Depth resolution	Optimally on a monolayer level
Quantification	Absolute technique for elemental concentrations
Lateral resolution	None
Destructive	Not inherently
Sample requirements	Ultrahigh vacuum compatibility; practical size ~1 cm in diameter
Main uses	Determination of structural parameters of surfaces and interfaces; very high resolution depth profiling
Accuracy	> 1% (structural parameters); element dependent (composition)
Cost	$1,000,000–$2,000,000
Size	~ 7 m × 3 m

Ion Scattering Spectroscopy (ISS) 1.9.4

In Ion Scattering Spectroscopy (ISS) a low-energy monoenergetic beam of ions is focused onto a solid surface and the energy of the scattered ions is measured at some fixed angle. The collision of the inert ion beam, usually $^3He^+$, $^4He^+$, or $^{20}Ne^+$, follows the simple laws of conservation of momentum for a binary elastic collision with an atom in the outer surface of the solid. The energy loss thus identifies the atom struck. Inelastic collisions and ions that penetrate deeper than the first atomic layer normally do not yield a sharp, discrete peak. Neighboring atoms do not affect the signal because the kinetics of the collision are much shorter than bond vibrations. A spectrum is obtained by measuring the number of ions scattered from the surface as a function of their energy by passing the scattered ions through an energy analyzer. The spectrum is normally plotted as a ratio of the number of ions of energy E versus the energy of the primary beam E_0. This can be directly converted to a plot of relative concentration versus atomic number, Z. Extremely detailed information regarding the changes in elemental composition from the outer monolayer to depths of 50 Å or more are routinely obtained by continuously monitoring the spectrum while slowly sputtering away the surface.

Range of elements	All but helium; hydrogen indirectly
Sample requirements	Any solid vacuum-compatible material
Sensitivity	< 0.01 monolayer, 0.5% for C to 50 ppm for heavy metals
Quantitation	Relative; 0.5–20%
Speed	Single spectrum, 0.1 s; nominal 100-Å profile, 30 min
Depth of analysis	Outermost monatomic layer to any sputtered depth
Lateral resolution	150 µm
Imaging	Yes, limited
Sample damage	Only if done with sputter profiling
Main uses	Exclusive detection of outer most monatomic layer and very detailed depth profiles of the top 100 Å
Instrument cost	$25,000–$150,000
Size	10 ft. × 10 ft.

Dynamic Secondary Ion Mass Spectrometry (Dynamic SIMS) 1.10.1

In Secondary Ion Mass Spectrometry (SIMS), a solid specimen, placed in a vacuum, is bombarded with a narrow beam of ions, called primary ions, that are sufficiently energetic to cause ejection (sputtering) of atoms and small clusters of atoms from the bombarded region. Some of the atoms and atomic clusters are ejected as ions, called secondary ions. The secondary ions are subsequently accelerated into a mass spectrometer, where they are separated according to their mass-to-charge ratio and counted. The relative quantities of the measured secondary ions are converted to concentrations, by comparison with standards, to reveal the composition and trace impurity content of the specimen as a function of sputtering time (depth).

Range of elements	H to U; all isotopes
Destructive	Yes, material removed during sputtering
Chemical bonding information	In rare cases, from molecular clusters, but see Static SIMS
Quantification	Standards usually needed
Accuracy	2% to factor of 2 for concentrations
Detection limits	10^{12}–10^{16} atoms/cm^3 (ppb–ppm)
Depth probed	2 nm–100 μm (depends on sputter rate and data collection time)
Depth profiling	Yes, by the sputtering process; resolution 2–30 nm
Lateral resolution	50 nm–2 μm; 10 nm in special cases
Imaging/mapping	Yes
Sample requirements	Solid conductors and insulators, typically ≤ 2.5 cm in diameter, ≤ 6 mm thick, vacuum compatible
Main use	Measurement of composition and of trace-level impurities in solid materials a function of depth, excellent detection limits, good depth resolution
Instrument cost	$500,000–$1,500,000
Size	10 ft. × 15 ft.

Static Secondary Ion Mass Spectrometry (Static SIMS) 1.10.2

Static Secondary Ion Mass Spectrometry (SIMS) involves the bombardment of a sample with an energetic (typically 1–10 keV) beam of particles, which may be either ions or neutrals. As a result of the interaction of these primary particles with the sample, species are ejected that have become ionized. These ejected species, known as secondary ions, are the analytical signal in SIMS.

In static SIMS, the use of a low dose of incident particles (typically less than 5×10^{12} atoms/cm^2) is critical to maintain the chemical integrity of the sample surface during analysis. A mass spectrometer sorts the secondary ions with respect to their specific charge-to-mass ratio, thereby providing a mass spectrum composed of fragment ions of the various functional groups or compounds on the sample surface. The interpretation of these characteristic fragmentation patterns results in a chemical analysis of the outer few monolayers. The ability to obtain surface chemical information is the key feature distinguishing static SIMS from dynamic SIMS, which profiles rapidly into the sample, destroying the chemical integrity of the sample.

Range of elements	H to U; all isotopes
Destructive	Yes, if sputtered long enough
Chemical bonding information	Yes
Depth probed	Outer 1 or 2 monolayers
Lateral resolution	Down to ~100 μm
Imaging/mapping	Yes
Quantification	Possible with appropriate standards
Mass range	Typically, up to 1000 amu (quadrupole), or up to 10,000 amu (time of flight)
Sample requirements	Solids, liquids (dispersed or evaporated on a substrate), or powders; must be vacuum compatible
Main use	Surface chemical analysis, particularly organics, polymers
Instrument cost	$500,000–$750,000
Size	4 ft. × 8 ft.

Surface Analysis by Laser Ionization (SALI)   1.10.3

In Surface Analysis by Laser Ionization (SALI), a probe beam such as an ion beam, electron beam, or laser is directed onto a surface to remove a sample of material. An untuned, high-intensity laser beam passes parallel and close to but above the surface. The laser has sufficient intensity to induce a high degree of nonresonant, and hence nonselective, photoionization of the vaporized sample of material within the laser beam. The nonselectively ionized sample is then subjected to mass spectral analysis to determine the nature of the unknown species. SALI spectra accurately reflect the surface composition, and the use of time-of-flight mass spectrometers provides fast, efficient and extremely sensitive analysis.

Range of elements	Hydrogen to Uranium
Destructive	Yes, surface layers removed during analysis
Post ionization approaches	Multiphoton ionization (MPI), single-photon ionization (SPI)
Information	Elemental surface analysis (MPI); molecular surface analysis (SPI)
Detection limit	ppm to ppb
Quantification	~10% using standards
Dynamic range	Depth profile mode ~10^4
Probing depth	2–5 Å (to several µm in profiling mode)
Lateral resolution	down to 60 nm
Mass range	1–10,000 amu or greater
Sample requirements	Solid, vacuum compatible, any shape
Main uses	Quantitative depth profiling, molecular analysis using SPI mode; imaging
Instrument cost	$600,000–$1,000,000
Size	Approximately 45 sq. ft.

Sputtered Neutral Mass Spectrometry (SNMS)   1.10.4

Sputtered Neutral Mass Spectrometry (SNMS) is the mass spectrometric analysis of sputtered atoms ejected from a solid surface by energetic ion bombardment. The sputtered atoms are ionized for mass spectrometric analysis by a mechanism separate from the sputtering atomization. As such, SNMS is complementary to Secondary Ion Mass Spectrometry (SIMS), which is the mass spectrometric analysis of sputtered ions, as distinct from sputtered atoms. The forte of SNMS analysis, compared to SIMS, is the accurate measurement of concentration depth profiles through chemically complex thin-film structures, including interfaces, with excellent depth resolution and to trace concentration levels. Generically both SALI and GDMS are specific examples of SNMS. In this article we concentrate on post ionization only by electron impact.

Range of elements	Li to U
Destructive	Yes, surface material sputtered
Chemical bonding information	None
Quantification	Yes, accuracy × 3 without standards; 5–10% with analogous standard; 30% with dissimilar standard
Detection limits	10–100 ppm
Depth probed	15 Å (to many μm when profiling)
Depth profiling	Yes, by sputtering
Lateral resolution	A few mm in direct plasma sputtering; 0.1–10 μm using separate, focused primary ion-beam sputtering
Imaging/mapping	Yes, with separate, focused primary ion-beam
Sample requirements	Solid conducting material, vacuum compatible; flat wafer up to 5-mm diameter; insulator analysis possible
Main use	Complete elemental analysis of complex thin-film structures to several μm depth, with excellent depth resolution
Cost	$200,000–$450,000
Size	2.5 ft. × 5 ft.

Laser Ionization Mass Spectrometry (LIMS)   1.10.5

In Laser Ionization Mass Spectrometry (LIMS, also LAMMA, LAMMS, and LIMA), a vacuum-compatible solid sample is irradiated with short pulses (~10 ns) of ultraviolet laser light. The laser pulse vaporizes a microvolume of material, and a fraction of the vaporized species are ionized and accelerated into a time-of-flight mass spectrometer which measures the signal intensity of the mass-separated ions. The instrument acquires a complete mass spectrum, typically covering the range 0–250 atomic mass units (amu), with each laser pulse. A survey analysis of the material is performed in this way. The relative intensities of the signals can be converted to concentrations with the use of appropriate standards, and quantitative or semi-quantitative analyses are possible with the use of such standards.

Range of elements	Hydrogen to uranium; all isotopes
Destructive	Yes, on a scale of few micrometers depth
Chemical bonding information	Yes, depending on the laser irradiance
Quantification	Standards needed
Detection limits	10^{16}–10^{18} at/cm^3 (ppm to 100 ppm)
Depth probed	variable with material and laser power
Depth profiling	Yes, repeated laser shots sample progressively deeper layers; depth resolution 50–100 nm
Lateral resolution	3–5 µm
Mapping capabilities	No
Sample requirements	Vacuum-compatible solids; must be able to absorb ultraviolet radiation
Main use	Survey capability with ppm detection limits, not affected by surface charging effects; complete elemental coverage; survey microanalysis of contaminated areas, chemical failure analysis
Instrument cost	$400,000
Size	9 ft. × 5 ft.

Spark Source Mass Spectrometry (SSMS) 1.10.6

Spark Source Mass Spectrometry (SSMS) is a method of trace level analysis—less than 1 part per million atomic (ppma)—in which a solid material, in the form of two conducting electrodes, is vaporized and ionized by a high-voltage radio frequency spark in vacuum. The ions produced from the sample electrodes are accelerated into a mass spectrometer, separated according to their mass-to-charge ratio, and collected for qualitative identification and quantitative analysis.

SSMS provides complete elemental surveys for a wide range of sample types and allows the determination of elemental concentrations with detection limits in the range 10–50 parts per billion atomic (ppba).

Range of elements	All elements simultaneously
Destructive	Yes, material is removed from surface
Chemical bonding information	No
Sensitivity	Sub-ppma; 0.01–0.05 ppma typical
Accuracy	Factor of 3, without standards, or factor of 1.2, with standards
Bulk analysis	Yes
Depth probed	1 –5-μm depth
Depth profiling	Yes, but only 1–5 μm resolution
Lateral resolution	None
Sample requirements	Bulk solid: 1/16 in × 1/16 in × 1/2 in; powder: 10–100 mg; thin film: 1 cm^2 × ~5 μm
Sample conductivity	Conductors and semiconductors: direct analysis; insulators (>10^7 (ohm-cm)$^{-1}$): pulverize and mix with a conductor
Main use	Complete trace elemental survey of solid materials with accuracy to within a factor of 3 without standards
Cost	Used instrumentation only: $10,000–$100,000
Size	9 ft. × 10 ft.

Glow-Discharge Mass Spectrometry (GDMS)   1.10.7

Glow-Discharge Mass Spectrometry is the mass spectrometric analysis of material sputtered into a glow-discharge plasma from a cathode. Atoms sputtered from the sample surface are ionized in the plasma by Penning and electron impact processes, giving ion yields that are matrix-independent and very similar for all elements. Sputtering is rapid (about 1 μm/min) and ion currents are high, yielding sub-ppbw detection limits. Thus GDMS provides accurate concentration measurements, as a function of depth, from major to ultratrace levels over the full periodic table.

Range of elements	Lithium to uranium
Destructive	Yes, surface material sputtered
Chemical bonding information	No
Quantitation	Yes, with standards, 20% accuracy, 5% precision
Detection limits	pptw (GDMS), 10 ppbw (GDQMS)
Depth probed	100 nm to many μm, depending on sputter time
Depth profiling	Yes, by sputtering
Lateral resolution	A few mm
Imaging/mapping	No
Sample requirements	Solid conducting material, vacuum compatible; pin sample ($2 \times 2 \times 20$ mm^3) or flat wafer sample (10–20 mm diameter); insulator analysis possible
Main use	Complete qualitative and quantitative bulk elemental analysis of conducting solids to ultratrace levels
Instrument cost	$200,000–$600,000
Size	6.5 ft. × 6.4 ft. (GDMS) 2.3 ft. × 5.7 ft. (GDQMS)

Inductively Coupled Plasma Mass Spectrometry (ICPMS)   1.10.8

Inductively Coupled Plasma Mass Spectrometry (ICPMS) uses an inductively coupled plasma to generate ions that are subsequently analyzed by a mass spectrometer. The plasma is a highly efficient ion source that gives detection limits below 1 ppb for most elements. The technique allows both fully quantitative and semiquantitative analyses. Samples usually are introduced as liquids but recent developments allow the direct sampling of solids by laser ablation-ICPMS, and gases and vapors using a special torch design. Solids or thin films are, however, more usually digested into solution prior to analysis.

Range of elements	Lithium to uranium, all isotopes; some elements excluded
Destructive	Yes
Chemical bonding information	No
Quantification	Yes, both semiquantitative and quantitative
Accuracy	0.2% isotopic; 5% or better quantitative; and 20% or better semiquantitative
Detection limits	Sub-ppb for most elements
Depth probed	1–10 µm per laser pulse, for solids
Depth profiling	Yes, with, laser ablation
Lateral resolution	20–50 µm for laser ablation
Imaging/mapping capabilities	No, but possible for laser ablation
Sample requirements	Solutions, digestible solids, solids, gases, and vapors
Main use	High-sensitivity elemental and isotopic analysis of high-purity chemicals and water
Instrument cost	$150,000–$750,000
Size	8 ft. × 8 ft.

Inductively Coupled Plasma-Optical Emission Spectroscopy (ICP-OES)   1.10.9

In Inductively Coupled Plasma-Optical Emission Spectroscopy (ICP-OES), a gaseous, solid (as fine particles), or liquid (as an aerosol) sample is directed into the center of a gaseous plasma. The sample is vaporized, atomized, and partially ionized in the plasma. Atoms and ions are excited and emit light at characteristic wavelengths in the ultraviolet or visible region of the spectrum. The emission line intensities are proportional to the concentration of each element in the sample. A grating spectrometer is used for either simultaneous or sequential multielement analysis. The concentration of each element is determined from measured intensities via calibration with standards.

Range of elements	At least 70 elements can be determined
Destructive	Yes
Quantification	Standards (often pure aqueous solutions)
Accuracy	10% or better with simple standards; as good as 0.5% with appropriate techniques
Precision	Typically 0.2–0.5% for solutions or dissolved solids; 3–10% for direct solid analysis
Detection limits	Typically sub-ppb to 100 ppb; tens of pg to ng
Sample requirements	Liquids, directly; solids, following dissolution; solids, surfaces, and thin films with special methods (e.g., laser ablation)
Depth probed	µm scale for solids
Sample size	2–5 mL of solution; µL of solution with special techniques; µg to mg of solid
Main uses	Rapid, quantitative measurement of trace to minor elemental composition of solids and solutions; excellent detection limits, with linear calibration over ~5 orders of magnitude
Instrument cost	$40,000–$200,000
Size	4–8 ft. × 4 ft.

Neutron Diffraction

Diffraction is a technique that uses interference of short wavelength particles (such as neutrons or electrons) or photons (X or γ rays) reflected from planes of atoms in crystalline materials to yield three-dimensional structural information at the atomic level. Neutron diffraction, like X-ray diffraction is a nondestructive technique that can be used for atomically resolved structure determination and refinement, phase identification and quantification, residual stress measurements, and average particle-size determination of crystalline materials. The major advantages of neutron diffraction compared to other diffraction techniques, namely the extraordinarily greater penetrating nature of the neutron and its direct interaction with nuclei, lead to its use in measurements under special environments, experiments on materials requiring a depth of penetration greater than about 50 μm, or structure refinements of phases containing atoms of widely varying atomic numbers.

Range of elements	All elements detected approximately equally, except vanadium
Destructive	No
Bonding information	No
Depth probed	Yields bulk information of macro-sized samples (thin films for determining magnetic ordering)
Lateral resolution	None
Quantitation	Can be used to quantify crystalline phases
Structural accuracy	Atomic positions to 10^{-13} m, accuracy of phase quantitation ~1% molar
Imaging capabilities	None to date
Sample requirements	Material must be crystalline at data collection temperatures
Main uses	Atomic structure refinements or determinations and residual stress measurements, all in bulk materials
Instrument cost	Instruments are at government-funded facilities; cost for proprietary experiments $1000–$9000 per day

Neutron Reflectivity 1.11.2

In neutron reflectivity, neutrons strike the surface of a specimen at small angles and the percentage of neutrons reflected at the corresponding angle are measured. The angular dependence of the reflectivity is related to the variation in concentration of a labeled component as a function of distance from the surface. Typically the component of interest is labeled with deuterium to provide mass contrast against hydrogen. Use of polarized neutrons permits the determination of the variation in the magnetic moment as a function of depth. In all cases the optical transform of the concentration profiles is obtained experimentally.

Range of elements	All elements and their isotopes
Destructive	No
Quantification	Requires model calculations
Detection limits	Not suited for trace element analysis
Depth profiling	Yes
Penetration depth	mm
Depth resolution	1 nm
Lateral resolution	No
Imaging/mapping	No
Sample requirements	Solids or liquids, typically 5–10 cm in diameter, usually deuterium labeled
Main use	Concentration profiles in organic materials and between interfaces of organic materials
Instrument cost	$300,000, requires access to neutrons

Neutron Activation Analysis (NAA) 1.11.3

In Neutron Activation Analysis (NAA), samples are placed in a neutron field typically available in a research nuclear reactor. Following neutron capture, trace impurities present in the sample become radioactive. Samples are removed from the reactor and analyzed using γ-ray spectroscopy. Gamma rays or high-energy photons (~1 MeV) are given off as a result of the radioactive decay process. The spectrometer measures the energies of the γ rays and "counts" the number of γ rays of each energy emitted from the sample. Each radioisotope of an impurity emits a signature, or characteristic, γ ray. Therefore, the energy of the γ ray identifies the element, while the number of counts provides the concentration. Since neutrons and γ rays are penetrating radiations, only a bulk composition is obtained. Surface analysis can be accomplished by combining NAA with chemical etching techniques.

Elements measured	Two-thirds of the periodic table: transition metals, halogens, lanthanides, and platinum-group metals
Destructive	No, sample rendered radioactive
Chemical bonding	No, nuclear process
Quantification	Yes, with or without standard
Accuracy	5–20%
Detection limits	10^8–10^{14} atoms/cc (ppb-ppt)
Depth probed	Bulk technique
Depth resolution	Few μm (using chemical etching, otherwise none)
Lateral resolution	None
Imaging/mapping	No, limited autoradiography
Sample requirements	Conductors, insulators, or plastics; flexible sample size, down to 0.5 gms material
Main use	Simultaneous quantitative trace impurities analysis; particularly sensitive to gold
Instrument cost	$50,000
Size	Specialized radiation laboratories needed

Nuclear Reaction Analysis (NRA)   1.11.4

In Nuclear Reaction Analysis (NRA), a beam of charged particles with energy from a few hundred keV to several MeV is produced in an accelerator and bombards a sample. Nuclear reactions with low-Z nuclei in the sample are induced by the ion beam. Products of these reactions (typically protons, deuterons, tritons, He, α particles, and γ rays) are detected, producing a spectrum of particle yield versus energy. Depth information is obtained from the spectrum using energy loss rates for incident and product ions traveling through the sample. Particle yields are converted to concentrations with the use of experimental parameters and nuclear reaction cross sections.

Range of elements	Hydrogen to calcium; specific isotopes
Destructive	No, but some materials may be damaged by ion beams
Chemical bonding information	No
Depth profiling	Yes
Quantification	Yes, standards usually unnecessary
Accuracy	A few percent to tens of percent
Detection limits	Varies with specific reaction; typically 10–100 ppm
Depth probed	Several μm
Depth resolution	Varies with specific reaction; typically a few nm to hundreds of nm
Lateral resolution	Down to a few μm with microbeams
Imaging/mapping	Yes, with microbeams
Sample requirements	Solid conductors and insulators
Main use	Quantitative measurement of light elements (particularly hydrogen) in solid materials, without standards; has isotope selectivity
Instrument Cost	Several million dollars for high-energy ion accelerator
Size	Large laboratory for accelerator

Surface Roughness: Measurement, Formation by Sputtering, Impact on Depth Profiling 1.12.1

Surface roughness is commonly measured using mechanical and optical profilers, scanning electron microscopes, and atomic force and scanning tunneling microscopes. Angle-resolved scatterometers can also be applied to this measurement. The analysis surface can be roughened by ion bombardment, and roughness will degrade depth resolution in a depth profile. Rotation of the sample during sputtering can reduce this roughening.

Mechanical Profiler

Depth resolution	0.5 nm
Minimum step	2.5–5 nm
Maximum step	~150 μm
Lateral resolution	0.1–25 μm, depending on stylus radius
Maximum sample size	15-mm thickness, 200-mm diameter
Instrument cost	$30,000–$70,000

Optical Profiler

Depth resolution	0.1 nm
Minimum step	0.3 nm
Maximum step	15 μm
Lateral resolution	0.35–9 μm, depending on optical system
Maximum sample size	125-mm thickness, 100-mm diameter
Instrument cost	$80,000–$100,000

SEM (see SEM article)

Scanning Force Microscope (see STM/SFM article)

Depth resolution	0.01 nm
Lateral resolution	0.1 nm
Instrument cost	$75,000–$150,000

Scanning Tunneling Microscope (see STM/SFM article)

Depth resolution	0.001 μm
Lateral resolution	0.1 nm
Instrument cost	$75,000–$150,000

Optical Scatterometer (see next article)

Depth resolution	0.1 nm (root mean square)
Instrument cost	$50,000–$150,000

Optical Scatterometry 1.12.2

Optical scatterometry involves illuminating a sample with light and measuring the angular distribution of light which is scattered. The technique is useful for characterizing the topology of two general categories of surfaces. First, surfaces that are nominally smooth can be examined to yield the root-mean-squared (rms) roughness and other surface statistics. Second, the shapes of structure (lines) of periodically patterned surfaces can be characterized. The intensity of light diffracted into the various diffraction orders from the periodic structure is indicative of the shape of the lines. If the line shape is influenced by steps involved in processing the sample, the scattering technique can be used to monitor the process. This has been applied to several steps involved in microelectronics processing. Scatterometry is noncontact, nondestructive, fast, and often yields quantitative results. For some applications it can be used *in-situ*.

Parameters measured	Surface topography (rms roughness, rms slope, and power spectrum of structure); scattered light; line shape of periodic structure (width, side wall angle, height, and period)
Destructive	No
Vertical resolution	≥ 0.1 nm
Lateral resolution	$\geq \lambda/2$ for topography characterization; much smaller for periodic structure characterization (λ is the laser wavelength used to illuminate the sample)
Main uses	Topography characterization of nominally smooth surfaces; process control when characterizing periodic structure; can be applied *in situ* in some cases; rapid; amenable to automation
Quantitative	Yes
Mapping capabilities	Yes
Instrument cost	$10,000–$200,000 or more
Size	1 ft. × 1 ft. to 4 ft. × 8 ft.

Magneto-optic Kerr Effect (MOKE) 1.12.3

The Magneto-Optic Kerr Effect (MOKE) is an optical technique to determine the orientation and relative magnitude of the net magnetic moment near the surface of a magnetic sample. It is based on the proportionality between the net magnetization M of a material and a small, but measurable, change in the polarization of visible light that has been reflected from the surface of a magnetic sample. The orientation of the magnetization is determined from the sign of the rotation and the geometry of the setup. MOKE measurements can be made as a function of external magnetic field. This gives a determination of the magnetic hysteresis loop of the material. MOKE measurements can be done at MHz frequencies, as well as under dc conditions, making it suitable for examining magnetic domain dynamics or static domain imaging.

Range of elements	Magnetic materials only; not element specific
Destructive	No
Quantification	Standards are needed to find M
Sensitivity	~1 monolayer of magnetic material
Depth probed	20–40 nm
Lateral resolution	Limited by spatial focus of light, greater than about 0.3 μm
Imaging/mapping capabilities	Yes
Sample requirements	Magnetic material of interest must be within optical penetration depth of the probing light
Main use	Hysteresis loops and magnetic anisotropies of ultrathin ferromagnetic films; dynamic magnetic domain imaging (MHz rates) magneto-optic data recording
Instrument cost	$20,000–$150,000
Size	~ 1 m × ~1 m

Physical and Chemical Adsorption for the Measurement of Solid Surface Areas 1.12.4

Physical adsorption isotherms are measured near the boiling point of a gas (e.g., nitrogen, at 77 K). From these isotherms the amount of gas needed to form a monolayer can be determined. If the area occupied by each adsorbed gas molecule is known, then the surface area can be determined for all finely divided solids, regardless of their chemical composition. In the case of metal surfaces, the area can be measured by the chemisorption of simple molecules like H_2 and CO. Chemisorption isotherms will measure selectively only the metal area. This is especially useful when the metal is dispersed on high area oxide supports. Usually H_2 is adsorbed at 25° C; no adsorption of H_2 occurs on the support under these conditions. At finite pressures (~10 cm Hg), each surface metal atom adsorbs one hydrogen atom, giving an adsorbed monolayer. The spacing of metal atoms is usually known, so that the number of hydrogen atoms gives directly the area of metal at the surface, or the dispersion.

Range of elements	Not element specific
Sample requirements	Vacuum compatible solids, stable to 200°C, any shape
Destructive	No
Chemical bonding information	None
Depth examined	Surface adsorbed layers only
Detection limits	Above about 1 m^2/g
Precision	1% or better
Quantification	Standards are available
Main uses	*Physical adsorption*—surface areas of any stable solids, e.g., oxides used as catalyst supports and carbon black: *Chemisorption*—measurements of particle sizes of metal powders, and of supported metals in catalysts
Instrument cost	Homemade, or up to $25,000
Size	2 ft. × 3 ft.