Introduction to Materials Characterization*

The macro, micro, and surface composition and structure of materials are determined by their processing and service histories. These conditions, in turn, control material properties and performance. Characterization of a material's composition and structure at these levels provides important information that can be used for several purposes:

- *Quality assurance:* to determine whether processing is done properly
- *Failure analysis:* to determine why properties and performance are different from expected
- Research and product improvement: to develop an understanding of how processing and service history influence properties and performance, and use this understanding to develop improved materials

Two useful ways of classifying materials characterization techniques are by the type of information they obtain and the characteristic sample dimensions from which this information is obtained.

According to the types of information they obtain, techniques are often classified as:

- *Elemental:* What elements are present (qualitative elemental analysis)? In what concentration is each element present (quantitative elemental analysis)?
- *Structural:* How are the atoms crystallographically arranged and spaced? In the case of organic materials, what is the molecular structure?
- Morphological: What are the sizes, shapes, arrangements, and appearances of key features, such as grains, cracks, welds, and interfaces?

According to the dimensions of material sampled, techniques are frequently categorized as:

• *Bulk:* information typically obtained and integrated over surface dimensions on the order of 10^{-2} m (0.39 in.) or more and depths of at least 50×10^{-6} m (1.9×10^{-3} in.), presumably characteristic of the bulk material

- *Micro:* able to obtain information from individual microstructural features; typically able to resolve and characterize features with dimensions of 10^{-6} m (3.93 × 10^{-5} in.) or less
- *Surface:* information obtained only from the first atomic layer or so of the sample, such as sampling depths on the order of 10^{-9} m (3.93 × 10^{-8} in.)

Selection of Materials Characterization Methods

It is very important to keep the previously described categories in mind when selecting appropriate analytical techniques. There is no universal characterization method that provides all information an analyst might want to know about a sample. For each problem, a decision must be made regarding the type of information needed. On the basis of this decision, one or more analytical techniques that will provide this information must be selected.

Selection and use of inappropriate methods can result in data that are analytically correct but inappropriate to the problem at hand. This misuse usually confounds the problem rather than helps solve it. For example, it would be inappropriate to use a bulk analysis technique in an effort to identify a thin layer of surface contamination on a material. The results would reflect the composition of the underlying material, not the contamination on its surface. Conversely, it would be equally inappropriate to use a surface analytical technique to determine the bulk composition of an alloy. The results would reflect whatever contaminants happened to be present on the surface, rather than the composition of the underlying alloy. In selecting analytical techniques, it is critical to think through the current problem, determine what type of information is needed, and select one or more techniques that will provide appropriate types of information.

In addition, in cases where several different types of analyses may be needed to solve a problem, it is important to consider the order in which these analyses are performed, as some types of analysis are destructive or alter the sample, making subsequent types of analysis impossible.

Scope of this Volume

Materials Characterization has been developed with the goal of providing the engineer or scientist who has little background in materials analysis with an easily understood reference book on analytical methods. Although there is an abundance of excellent in-depth texts and manuals on specific characterization methods, they frequently are too detailed or theoretical to serve as useful guides for the average engineer who is primarily concerned with solving a problem rather than becoming an analytical specialist. This Volume describes analytical methods in simplified terms and emphasizes the most common applications and limitations of each method. The intent is to familiarize the reader with the techniques that may be applied to a problem, help identify the most appropriate technique or techniques, and provide sufficient knowledge to interact with the appropriate analytical specialists, thereby enabling materials characterization and troubleshooting to be conducted effectively and efficiently. The intent of this Volume is *not* to make an engineer a materials characterization specialist.

Materials characterization represents many different disciplines depending upon the background of the user. These concepts range from that of the scientist, who thinks of it in atomic terms, to that of the process engineer, who thinks of it in terms of properties, procedures, and quality assurance, to that of the mechanical engineer, who thinks of it in terms of stress distributions and heat transfer. The definition selected for this book states, "Characterization describes those features of composition and structure (including defects) of a material that are significant for a particular preparation, study of properties, or use,

^{*}Adapted from K.H. Eckelmeyer, Introduction and Overview of Materials Characterization, *Metals Handbook Desk Edition*, ASM International, 1998 and R.E. Whan, Introduction to Materials Characterization, *Materials Characterization*, Vol 10, ASM Handbook, ASM International, 1986

and suffice for reproduction of the material." This definition limits the characterization methods included herein to those that provide information about composition, structure, and defects and excludes those methods that yield information primarily related to materials properties, such as thermal, electrical, and mechanical properties.

Most characterization techniques (as defined previously) that are in general use in wellequipped materials analysis laboratories are described in this Volume. These include methods used to characterize materials such as alloys, glasses, ceramics, organics, gases, and inorganics. Techniques used primarily for biological or medical analysis are not included. Some methods that are not widely used but that provide unique or critical information are also described. Several techniques may be applicable for solving a particular problem, providing the engineer, materials scientist, or analyst with a choice or with the possibility of using complementary methods.

Organization

This Volume has been organized for ease of reference by the user. The articles at the beginning of the book include tables, flow charts, and descriptions that can be used to quickly identify techniques applicable to a given problem. In these tables, the most common methods (not necessarily all-inclusive) for analyzing a particular class of materials are listed on the left. The types of information available are listed as column headings. When a particular technique is applicable, an entry appears in the appropriate column. It should be emphasized that lack of an entry for a given technique does not mean that it cannot be adapted to perform the desired analysis; it means simply that that technique is not usually used and others are generally more suitable.

The subdivisions within the Volume address a set of related techniques, for example, spectroscopy. Within each section are several articles, each describing a separate analytical technique. For example, in the Section "Spectroscopy" are the articles "Optical Emission Spectroscopy," "Atomic Absorption Spectros-copy," and "Infrared Spectroscopy," to name a few. Each article begins with a summary of general uses, applications, limitations, sample requirements, and capabilities of related techniques, which is designed to give the reader a quick overview of the technique, and to help him or her decide whether the technique might be applicable to the problem. This summary is followed by text that describes in simplified terms how the technique works, how the analyses are performed, what types of information can be obtained, and what types of materials problems can be addressed. Included are several brief examples that illustrate how the technique has been used to solve typical problems. A list of references at the end of each article directs the reader to more detailed information on the technique.

Introduction to Characterization of Metals

MATERIALS IDENTIFICATION, characterization, and verification are essential for companies to know that their materials or products have been manufactured to correct alloy grade and conform to standards. Metal chemical analysis is also used in reverse engineering to determine the alloys used to produce a component and in failure investigations to establish whether the correct alloy was used.

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- *Morphological:* What are the sizes, shapes, arrangements, and appearances of key features, such as grains, cracks, welds, and interfaces?

When classified by the dimensions of material sampled, techniques are frequently categorized as:

- *Bulk:* Information typically obtained and integrated over surface dimensions on the order of 10^{-2} m or more and depths of at least 50×10^{-6} m, presumably characteristic of the bulk material
- *Micro:* Able to obtain information from individual microstructural features, typically able to resolve and characterize features with dimensions of 10⁻⁶ m or less

• Surface: Information obtained only from the first atomic layer or so of the sample, such as sampling depths on the order of 10^{-9} m

Popular techniques for metals characterization are briefly discussed here, with references to other articles in this Volume. These articles include detailed discussion as well as practical tips for use. An overview of techniques is listed Table 1 and Fig. 1.

Bulk Elemental Analysis

Chemical analysis is often performed by one or more complimentary techniques. The specific technique chosen depends on the type of sample, quantity of material available for analysis, desired result, and cost constraints. In most cases, the applicable analysis techniques can detect parts per million concentrations or better.

Table 1 Analytical methods used for characterization of metals and alloys

	Elemental	Speci		Isotopic or mass	Qualitative analysis (identification of	Semiquantitative analysis (order of	Quantitative analysis (precision of +20% relative standard	Macroanalysis or bulk	Microanalysis	Surface	Major component	Minor component (0.1–10	Trace component (1–1000 ppm, or 0.0001–0.1	Struc-	Morph-
Technique	analysis	-ation	Compound	l analysis	constituents)	magnitude)	deviation)	analysis	(≤10 μm)	analysis	(>10 wt%)	wt%)	wt%)	ture	ology
Atomic force microscopy	Ν		Ν		•	Ν			•	•	•	٠			•
Auger electron spectroscopy	•				•	•			•	•	•	•			
Electron probe x-ray microanalysis	Ν				Ν	Ν	Ν		Ν		Ν	Ν	Ν		
Electron spin resonance	Ν	Ν			Ν	Ν	Ν	Ν				Ν	Ν	Ν	
Elemental and functional group analysis	•		•		•	•	•	•			•	•			
Energy-dispersive x-ray spectroscopy	Ν				Ν	Ν				Ν					
Fourier transform infrared spectroscopy	Ν	D, ●	•		•	Ν	Ν	•	•	•	•	•		•	
Gas chromatography			V		v	V	v	V	V		v	v	v	N,S	
Gas chromatography/ mass spectrometry	Ν	Ν	V	•	V	V	V	V			V	V	V	v	
High-temperature combustion	Ν						Ν	Ν			Ν	Ν	Ν		
						(c	ontinued)								

Key: • = generally usable; N = limited number of elements or functional groups; D = after dissolution; V = volatile liquids; S = under special conditions (i.e., with tandem mass spectrometer detection); C = crystalline solids

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Table 1(Continued)

					Qualitative analysis		Quantitative analysis (precision of +20%					Minor	Trace component (1–1000		
Technique	Elemental analysis	Speci -ation	Compound	or mass analysis	(identification of constituents)	analysis (order of magnitude)	relative standard deviation)	or bulk analysis	Microanalysis (≤10 µm)	Surface analysis	Major component (>10 wt%)	(0.1–10 wt%)	ppm, or 0.0001–0.1 wt%)	Struc- ture	Morph- ology
Image analysis								•	•						•
Inductively coupled plasma mass spectrometry	•			•	•	•	•	•	•	•	•	•	•		
Ion chromatography	D,N		D,N	D,N	D,N	D,N	D,N	D,N		Ν	D,N	D,N	D,N		
Liquid chromatography	· · ·		D		D	D	D	D			D	D	D		
Liquid chromatography mass spectrometry	D, ●	D,N	D,∙	D,●	D	D	D	D			D	D	D		
Low-energy ion-scattering spectroscopy	•				•	•				•	•	•	S		
Molecular fluorescence spectroscopy	D,N	D,N	D,N		D,N	D,N	D,N	D,N			D,N	D,N	D,N		
Neutron activation analysis	Ν			Ν	Ν	Ν	Ν	Ν			Ν	Ν	Ν		
Nuclear magnetic resonance	Ν	D,N	•	D,N,S	Ν	Ν	Ν	Ν			Ν	Ν	S	Ν	S
Optical metallography								•	•						•
Raman spectroscopy	Ν	D, •	D,●		D,•	D,•	D,•	•	•	S	•	•		•	
Scanning electron microscopy							•••		•		Ν	Ν			•
Secondary ion mass spectroscopy	•		S	•	•	Ν			•	•	•	•	•	Ν	N,S
Small-angle x-ray scattering	•		•		•			•						•	
Transmission electron microscopy	S		С		Ν	Ν			•		Ν	Ν		С	•
Ultraviolet/visible absorption spectroscopy	D, ●	D, ●	D,∙		D,●	D,●	D,∙	D,∙			D,●	D,●	D,●		
X-ray diffraction			С		С	С	C.S	С			С	С		С	
X-ray photoelectron spectroscopy	•	Ν	S		•	•	S			•	•	•			
X-ray spectrometry	Ν				Ν	Ν	Ν	Ν			Ν	Ν	Ν		
Key: • = generally usable;	N = limited	number	of elements	or function	nal groups; D = at	fter dissolution; V =	volatile liquids	; S = under speci	al conditions (i.e	., with tan	dem mass spe	ectrometer de	tection); C =	crystalli	ine solids

Bulk/mac	croanalysis I	St	ructure/morphology	Surface analysis		
↓	<u> </u>	Ļ			Ļ	
Elemental qualitative and quantitative	Molecular/compound qualitative and quantitative	Crystal structure	Phase distribution/ morphology	Molecular structure	Elemental	Molecular/ compound
ICP-MS COMB(a) IC(a) ESR(a) MFS(a) NMR(a) UV/VIS XRS(a) EFG NAA(a) EDS	FTIR RS GC(b) LC LC/MS IC(a) NMR(a) MFS(a) UV/VIS XRD(a) EFG	TEM(c) XRD(c)	OM SEM(c) TEM(c) AFM EPMA(c) IA	NMR(a) ESR(a) FTIR RS SAXS	AES SIMS LEISS AFM XPS	FTIR RS SIMS(a) AFM XPS(a)

Fig. 1 Flow charts of common techniques for characterization of metals and alloys. AES: Auger electron spectroscopy; AFM: atomic force microscopy; COMB: high-temperature combustion; EDS: energy-dispersive x-ray spectroscopy; EFG: elemental and functional group analysis; EPMA: electron probe x-ray microanalysis; ESR: electron spin resonance; FTIR: Fourier transform infrared spectroscopy; GC, gas chromatography; GC/MS: gas chromatography/mass spectrometry; IA: image analysis; IC: ion chromatography; ICP-MS, inductively coupled plasma mass spectrometry; LC: liquid chromatography; LC/MS: liquid chromatography; NAA: neutron activation analysis; NMR: nuclear magnetic resonance; OM: optical metallography; RS: Raman spectroscopy; TEM: transmission electron microscopy; UV/VIS: ultraviolet/visible absorption spectroscopy; XPS: x-ray photoelectron spectroscopy; XRD: x-ray diffraction; XRS: x-ray spectrometry. (a) Limited number of elements or groups. (b) Volatile liquids, solids, or components. (c) Under special conditions

The most common techniques for determining chemical composition of metals and alloys include x-ray fluorescence, optical emission spectroscopy, inductively coupled plasma optical emission spectroscopy, and wet chemistry. While these methods work well for most elements, they are not useful for dissolved gases and some nonmetallic elements that can be present in metals as alloying or impurity elements. High-temperature combustion and inert gas fusion methods are typically used to analyze for dissolved gases (oxygen, nitrogen, hydrogen) and, in some cases, carbon and sulfur in metals.

X-Ray Fluorescence

X-ray spectrometry, or x-ray fluorescence (XRF) spectrometry, is an emission spectroscopic technique that has found wide application in elemental identification and determination (see the article "X-Ray Spectroscopy" in this Volume). The technique depends on the emission of characteristic x-radiation, usually in the 1 to 60 keV energy range, following excitation of atomic electron energy levels by an external energy source, such as an electron beam, a charged particle beam, or an x-ray beam. In most sample matrices, laboratory x-ray spectrometry can detect elements at concentrations of less than 1 μ g/g of sample (1 ppm); in a thin-film sample, it can detect total amounts of a few tenths of one microgram.

X-ray spectrometry is one of the few techniques that can be applied to solid samples of various forms. Examples of specialized applications have included the determination of sulfur and wear elements in petroleum products, analysis of forensic samples, and in measurements of electronic and computer-related materials.

Portable XRF instruments are increasingly used for in situ nondestructive characterization, including measurement of lead in painted surfaces in housing. Continuing advances in computer and detector technology have led to further advances in the capabilities and sensitivity of portable XRF instruments for applications such as soil analysis and nondestructive qualitative and quantitative analysis of inorganic elements in archaeological objects. Portable XRF instruments cannot generally provide the low detection limits attained by laboratory methods, but the sensitivity of portable XRF instruments has increased and made possible their use for measurement of lead and other metal in dusts and soils (Ref 1). For example, field XRF can easily provide lead-in-soil detection limits of less than 100 ppm, well below typical regulatory levels of 300 to 1500 ppm.

Optical Emission Spectroscopy

Optical emission spectroscopic (OES) methods originated in experiments performed in the mid-1800s, yet they remain some of the most useful and flexible means of performing elemental analysis. See the article "Optical Emission Spectroscopy" in this Volume for detailed discussion. Free atoms, when placed in an energetic environment, emit light at a series of narrow wavelength intervals. These intervals, termed emission lines, form a pattern the emission spectrum—that is characteristic of the atom generating it. The energetic environment typically is a type of plasma, and the device used to produce such a plasma is commonly termed an emission source.

The presence of an element in a sample is indicated by the presence in light from the source (plasma) of one or more of its characteristic emission lines. The concentration (mass fraction) of that element can be determined by measuring line intensities. Thus, the characteristic emission spectrum forms the basis for qualitative elemental analysis, and the measurement of intensities of the emission lines forms the basis of quantitative elemental analysis.

The spark discharge remains the most commonly used source for bulk analysis of metal alloys. The current trend is mainly toward complete automation. Spark OES systems are increasingly incorporated into automatic laboratories with facilities for sample preparation and sample handling by robots. There also is continued development of more sophisticated electronics to control the waveform of the spark, for increased stability and flexibility.

Inductively Coupled Plasma-Optical Emission Spectroscopy

Inductively coupled plasma optical emission spectrometry (ICP-OES) is a technique for analyzing the concentration of metallic elements in solid and liquid samples. Similar to spark OES, ICP-OES uses the optical emission principles of exited atoms to determine the elemental concentration. However for ICP-OES, solid samples are dissolved (digested) in an appropriate solvent (typically acid) to produce a solution for analysis. The resulting sample solution (or an original liquid solution for analysis) is often diluted in water to obtain a final specimen suitable for analysis (Ref 2).

The ICP-OES technique exhibits the unique properties of providing simultaneous multielement (up to 70) analysis within a few minutes, as well as ensuring over 6 orders of magnitude dynamic range, applicable for most of the elements on the periodic table. This specificity renders ICP-OES the preferred technique to determine both trace, major, and minor elements in a single experiment with minimum chemical interferences.

Development of a similar technique, for isotope and trace analysis—namely inductively coupled plasma mass spectrometry (ICP-MS) began in the 1980s and is currently considered as equally indispensable as ICP-OES (Ref 3).

The ICP-MS technique is recommended for trace analysis, because it provides a significantly lower detection limit (parts per trillion for the majority of the elements). In addition, the technique is not subject to spectral overlap or interferences originated from the optical spectra. In fact, the ICP-MS technique is recommended when elements, such as the rare earth and actinide elements, produce complex optical spectra. Nevertheless, this technique is not suitable for concentrated matrices or high dissolved solid contents, which could saturate the detector. Some minor mass interferences are observed, particularly in the low- to midmass range, due to doubly charged ions, metal oxide ions, and molecular fragments that are originally present in the plasma or formed at the orifice and interface.

Common applications of the ICP-MS technique include isotope ratio analysis and trace impurities for pharmaceutical or biological applications. However, ICP-MS instruments are less robust than ICP-OES, and consumables as well as maintenance can be rather expensive.

High-Temperature Combustion (Ref 2)

High-temperature combustion is used to determine carbon and sulfur content in a variety

of materials. The sample is accurately weighed and placed in a ceramic crucible or combustion boat, often along with combustion accelerators. The crucible is placed in a high-temperature furnace, which is then flooded with oxygen. The furnace is heated to 1370 to 1425 °C (2500 to 2600 °F), causing combustion of the carbon and sulfur in the sample to form CO, CO₂, and SO₂. The gases are separated and analyzed by infrared absorption or thermal conductivity detectors. A heated catalyst is used to convert the CO to CO₂ prior to detection.

The infrared absorption detector measures the absorption of the infrared wavelengths characteristic to CO_2 and SO_2 . The amount of infrared absorption at these wavelengths is correlated to a quantitative content based on standards and the weight of the original specimen.

The thermal conductivity detectors monitor the thermal conductivity of the carrier gas. As the evolved gases pass the detector, changes in the thermal conductivity correspond to a change in the gas (e.g., from the inert carrier gas to hydrogen) and the amount of evolved gas present. These changes correspond to the amount of CO_2 and SO_2 generated and indicate the amount of sulfur or carbon in the original specimen.

Inert Gas Fusion (Ref 2)

Inert gas fusion is a quantitative analytical technique for determining the concentrations of nitrogen, oxygen, and hydrogen in ferrous and nonferrous materials. The sample is accurately weighed and placed in a pure graphite crucible in a fusion furnace with an inert gas atmosphere. The crucible is heated to 2000 to 3000 °C (3630 to 5430 °F), resulting in the sample fusing to a molten state. The hydrogen and nitrogen gases dissociate from the molten material and are carried away from the fusion chamber as H_2 and N_2 . The oxygen released from the material bonds with carbon (from the graphite crucible) to form CO or CO₂ and is carried away.

An inert carrier gas flushes the gases evolved from the sample out of the fusion chamber. The fusion gases are separated and carried to the detector. The individual concentrations for the evolved gases are detected by infrared absorption (for CO and CO₂ only) or thermal conductive techniques (N₂, H₂, CO, and CO₂).

Bulk Structural Analysis

Diffraction techniques are used to gain insight to the atomic structure of the sample surface. Depending on the problem, x-rays, electrons, or neutrons are used, which provide the electron density, electrostatic potential density, and nuclear density (also magnetic spin density) distribution, respectively, in a crystal (Ref 4). Most x-ray diffraction techniques are rapid and nondestructive; some instruments are portable and can be transported to the sample.

The great utility of x-rays for determining the structure and composition of materials is due to the differential absorption of x-rays by materials of different density, composition, and homogeneity. The higher the atomic number of a material, the more x-rays are absorbed.

X-Ray Diffraction

X-ray diffraction (XRD) is the most extensively used method for identifying and characterizing various aspects of metals related to the arrangements and spacings of their atoms. The XRD techniques are equally applicable to other crystalline materials, such as ceramics, geologic materials, and most inorganic chemical compounds. The article "Single-Crystal X-Ray Diffraction" in this Volume explains how single-crystal x-ray diffraction is used to characterize the crystal structure, including determining symmetry, unit cell parameters, atomic coordinates and thermal displacement parameters, bond lengths and angles between the atoms, and structural motive (or topology).

The article "X-Ray Powder Diffraction" (XRPD) in this Volume describes techniques used to characterize samples in the form of loose powders, aggregates of finely divided material, or polycrystalline specimens. The powder method, as it is referred to, is a good phase-characterization tool, partly because it can routinely differentiate between phases having the same chemical composition but different crystal structures (polymorphs). Although chemical analysis can indicate that the empirical formula for a given sample is FeTiO₃, it cannot determine whether the sample is a mixture of two phases (FeO and one of the three polymorphic forms of TiO₂) or whether the sample is the single-phase mineral FeTiO₃ or ilmenite. The ability of XRPD to perform such identifications more simply, conveniently, and routinely than any other analytical method explains its importance in many industrial applications as well as its wide availability and prevalence.

Neutron Diffraction

Neutron diffraction techniques can be used to determine the atomic structure of crystals. Advantages include higher sensitivity to atoms with low atomic numbers (especially hydrogen), ability to distinguish isotopes, deep penetration, and information about magnetic structure. Disadvantages include the requirement for larger crystals (approximately 1 mm³), longer data-collection times, and a nuclear reactor. Despite sharing the scattering mechanism, the interaction of neutrons with matter is fundamentally different than that of x-rays: Photons strongly interact with the electron shell of the atom. Because all electrons interact with radiation, independently of which atoms they are part of, the

scattering for x-rays is related only to the electronic density being proportional to Z^2 , where Z is the atomic number. Nonetheless, both fission and spallation remain quite energy intensive, and thus, usable neutron beams for materials science are only available in large-scale research facilities that house a nuclear reactor or a spallation neutron source. While this requirement has arguably been the biggest hurdle to the growth of neutron sciences, the importance-and uniquenessof neutron diffraction is demonstrated by the construction of high-flux spallation neutron facilities and reactors as well as the technical upgrades and expansions to existing facilities across the world. Improved access has significantly grown the user community and moved the technique from esoteric measurements that once required several cubic centimeter samples measured over days or weeks to time-resolved measurements at subsecond time scales on samples of a few hundred milligrams or less. This technique is described in detail in the article "Neutron Diffraction" in this Volume.

Electron Diffraction

Electron diffraction is similar to x-ray and neutron diffraction and is often used in transmission electron microscopy (see the article "Transmission Electron Microscopy" in this Volume) or scanning electron microscopy (see the article "Scanning Electron Microscopy" in this Volume) as well as electron backscatter diffraction (see the article "Crystallographic Analysis by Electron Backscatter Diffraction in the Scanning Electron Microscope" in this Volume). Electron diffraction is usually used for symmetry determination and raw determination of unit cell parameters and atomic positions; however, recent techniques can determine the structures from these data. Advantages include a nanometer size of single crystals. Disadvantages of this method include the necessity for very careful sample preparation, the requirement for the sample to be electron transparent, and the possibility of damaging the sample by the incident electrons.

Microstructural Analysis

Microstructural analysis is the combined characterization of the morphology, elemental composition, and crystallography of microstructural features through the use of a microscope. Light microscopes have been used to characterize the microstructures of metals for over 100 years. The methods and applications of light microscopy are covered in the article "Light Optical Metallography" in this Volume. While light microscopy is an important metallurgical tool, it has a number of limitations:

• Spatial resolution: Conventional light microscopes cannot resolve features smaller than $\sim 1 \ \mu m$.

- *Depth of field:* Light microscopes cannot image rough surfaces; samples must be flat to be in focus.
- *Type of information provided:* Light microscopes provide images and morphological information, but they do not provide any direct chemical or crystallographic information about the microstructural features observed.

Over the years, several types of electron microscopy have been developed and refined to greatly extend the ability to resolve and characterize the morphologies of much smaller microstructural features, to image rough surfaces, and to obtain direct chemical and crystallographic information about microstructural features.

The following sections briefly review three types of electron microscopies most commonly used in metallurgical studies: scanning electron microscopy, electron probe microanalysis, and transmission electron microscopy.

Scanning Electron Microscopy

The scanning electron microscope (SEM) provides a valuable combination of highresolution imaging, elemental analysis, and, recently, crystallographic analysis. The primary use of an SEM is to produce high-resolution images at magnifications unattainable by optical microscopy, while also providing direct topographic and compositional information. Magnifications up to $100,000 \times$ or more are possible by modern instruments. The SEMs produce nanoscale-resolution imaging and mapping because the electron beam is focused to a ~1 to 10 nm sized probe. Two major advantages of the SEM over the optical microscope as a tool for examining surfaces are improvements in resolution and depth of field.

The components of a typical SEM include an electron-optics column, specimen chamber, support system, and control and imaging system. The electron beam is generated at an electron gun and accelerated toward the sample housed inside a specimen chamber, typically below the electron-optics column. Electromagnetic lenses below the electron gun focus the electron beam to a small probe at the sample surface. Scanning coils deflect the electron probe across the sample surface, and detectors housed either in the specimen chamber or in the electron-optics column collect and report resultant signal intensity as a function of beam position. The SEM operator uses a computer to control the electron optics, detectors, and a motorized stage for sample positioning. During SEM operation, a support system provides cooling water for the electromagnetic lenses and maintains a low pressure within the electron-optics column and the specimen chamber by using vacuum pumps. See the article "Scanning Electron Microscopy" in this Volume for details on the technique and its variations.

Developments in SEM instrumentation during the 1990s and 2000s produced compact SEMs, smaller and more robust instruments as well as some that are portable for remote analysis. More powerful computers, automated stages, and automated SEM control enabled significant advances in high-throughput analysis. Focused ion beams were combined with the SEM to produce dual-beam instruments. Specially designed SEMs, called variable-pressure/environmental SEMs, are equipped with differential pumping so the specimen chamber can operate under higher background pressure environments, a capability that accommodates high-vapor-pressure specimens inside the SEM, such as biological samples, polymers, and liquids.

Electron Probe Microanalysis

Electron-excited x-ray microanalysis is a technique that enables spatially resolved elemental composition measurement at the micrometer to submicrometer lateral and depth resolution. With the exception of hydrogen and helium, which do not produce characteristic x-rays, all elements of the periodic table can be measured. Generally referred to as electron probe microanalysis, the technique is typically performed in an SEM equipped with an energy-dispersive x-ray spectrometer (EDS). The SEM-EDS is capable of quantitative measurements of constituents at the major (concentration C > 10 wt%), minor (1 wt% \leq $C \leq 10$ wt%), and trace (0.05 wt% < C < 1 wt%) levels. When tested on known materials, demonstrated accuracy is generally within ±5% relative in 95% of analyses for major and minor constituents. Low-atomic-number elements, for example, fluorine, oxygen, nitrogen, carbon, and boron, can be measured with useful accuracy as major constituents in fluorides, oxides, nitrides, carbides, and borides. Quantitative compositional mapping can be performed on x-ray spectrum image databases, resulting in elemental images in which the gray or color scale is related to elemental concentration. See the article "Electron Probe X-Ray Microanalysis" in this Volume for detailed explanations and applications.

Transmission Electron Microscopy

A major benefit of the transmission electron microscope (TEM) is its superior resolution over optical microscopy and the SEM. The TEM provides the highest-resolution imaging, elemental analysis, and crystallographic analysis of all the techniques described. It is capable of:

 Imaging of features as small as several tenths of nanometers, down to the scale of individual crystallographic planes and atoms

- Qualitative and semiqualitative elemental analyses with spatial resolution approaching 10 nm, roughly 100 times better than SEMs or electron microprobes
- Identifying crystalline compounds and determining crystallographic orientations of microstructural features as small as 30 nm

The TEM approach is unique among materials characterization techniques in that it enables essentially simultaneous examination of microstructural features through imaging from lower magnifications to atomic resolution and the acquisition of chemical and crystallographic information from small (submicrometer down to the atomic level) regions of the specimen. Specifications and best practices for using the TEM are covered in depth in the article "Transmission Electron Microscopy" in this Volume.

Surface Analysis

A number of methods can be used to obtain information about the chemistry of the first one to several atomic layers of samples of metals, as well as of other materials, such as semiconductors and various types of thin films. A summary of surface analysis techniques is listed in Table 2, showing the topics covered in the Surface Analysis Section of

Table 2 Quick reference summary of surface analysis methods

Analysis method	Analysis probe	Detection signal	Analysis information	Lateral resolution	Depth resolution	Typical applications
Atomic force microscopy	Coated or noncoated cantilever probes made of various materials	Laser light	Images of surface topographical features or other near-field and far-field interactions between probe and sample surface	0.2–10 nm	1080 pm	Biological molecules, biomaterials, cells, crystallography, electrochemistry, polymer chemistry, thin-film studies, nanomaterials, nanotechnology, failure analysis, process development, process control, surface metrology
Auger electron spectroscopy	Electrons	Auger electrons	Elemental composition analysis for all elements except H and He	20 nm	0.5–5 nm	Adhesion, catalysis, corrosion, oxidation, surface chemical reaction, surface contamination, wear, depth profile of each element with ion gun sputtering
Low-energy electron diffraction	Electrons	Diffraction electrons	Surface crystallography and microstructure	10 µm	0.4–2 nm	Adsorption, catalysis, chemical reactions, crystallography, crystal structure in epitaxial growth, film-growth kinetics, grain size and boundary, microstructure, reconstruction, segregation
Scanning probe microscopy	Probes made of various materials	Laser light, electrical current, or other probe- sample interactions	Three-dimensional image with atomic resolution of surface properties such as height, electron tunneling current, electrostatic force, magnetic force, etc.	0.2–10 nm	10–80 pm	Broad usage in research and development of nanomaterials and applications of nanotechnology and micromanufacturing that involves understanding, characterization, and manipulating surfaces at atomic or nanometer scale
Secondary ion mass spectroscopy	Ion beam	Secondary ions	Elemental, isotopic, or molecular composition of the surface through detection of the species with different mass-to-charge ratios	50 nm-10 μm	0.5–10 nm	Concentration depth profiling, identification of inorganic or organic surface layers, isotopic abundances in geological and lunar samples, trace element detection including hydrogen
Thermal desorption spectroscopy	Thermal energy	Desorbed atoms and/ or molecules	Desorption rate of desorbing gases from surfaces as a function of temperature	Not applicable	Not applicable	Adsorption, desorption, and reaction of adsorbed atoms and molecules on surfaces; catalysis; personal exposure to toxic chemicals; indoor air-quality monitoring; identification of volatiles in soil and water; analysis of environmental pollutants; quantification of hydrogen in metals (especially steels); corrosion mechanisms; electrochemistry; tribology
X-ray photoelectron spectroscopy	X-ray	Photoelectrons	Chemical state and composition	20–500 μm for monochromatic x-ray; 10–30 mm (0.4–1.2 in.) for nonmonochromatic x-ray	10 nm	Elemental analysis of all elements with an atomic number of lithium and higher, chemical state identification of surface elements, composition and chemical state depth profiles with ion gun sputtering, determination of oxidation states of metal atoms in metal compounds, identification of surface contaminations, measurement of surface film thicknesses, identification and degradation of polymers

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this Volume. These techniques are capable of providing elemental composition, chemical state, and other important properties of the outermost atomic layers of metals, semiconductors, ceramics, organic materials, and biomaterials in either bulk, thin-film and coating, powder, or particulate format. This Section of the Volume includes articles on recently developed techniques, such as "Introduction to Scanning Probe Microscopy" and "Atomic Force Microscopy," as well as established methods, such as "Auger Electron Spectroscopy," "Low-Energy Electron Diffraction," and "Secondary Ion Mass Spectroscopy."

Metallography

Metallography is the scientific discipline of examining and determining the constitution and the underlying structure of the constituents in metals and alloys. The objective of metallography is to accurately reveal material structure at the surface of a sample and/or from a cross-sectional specimen. Examination may be at the macroscopic, mesoscopic, and/or microscopic levels. For example, cross sections cut from a component or sample may be macroscopically examined by light illumination to reveal various important macrostructural features (on the order of 1 mm to 1 m, or 0.04 in. to 3 ft), such as the ones shown in Fig. 2 and listed here:

- Flow lines in wrought products
- Solidification structures in cast products
- Weld characteristics, including depth of penetration, fusion zone size and number of passes, size of heat-affected zone, and type and density of weld imperfections
- General size and distribution of large inclusions and stringers
- Fabrication imperfections, such as laps, cold welds, folds, and seams, in wrought products
- Gas and shrinkage porosity in cast products
- Depth and uniformity of a hardened layer in a case-hardened product

Macroscopic examination of a component surface is also essential in evaluating the condition of a material or the cause of failure. This may include:

- Characterization of the macrostructural features of a fracture surface to identify the fracture initiation site and changes in the crack-propagation process
- Estimations of surface roughness, grinding patterns, and honing angles
- Evaluation of coating integrity and uniformity
- Determination of extent and location of wear
- Estimation of plastic deformation associated with various mechanical processes
- Determination of the extent and form of corrosive attack; readily distinguishable types of attack include pitting, uniform, crevice, and erosion-corrosion
- Evaluation of tendency for oxidation









- Fig. 2 Examples of uses for metallography. (a) Equiaxed ferrite grain size in plain carbon steel. (b) Ion-carburized gear tooth showing case depth. (c) Microstructure of galvanized coating on steel—thickness and quality. (d) Multipass weld quality in type 304 stainless steel plate. Source: Ref 5–7
- Association of failure with welds, solders, and other processing operations

This listing of macrostructural features in the characterization of metals, although incomplete, represents the wide variety of features that can be evaluated by light macroscopy.

See the articles "Light Optical Metallography" and Quantitative Metallography" in this Volume for further examples and discussion.

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Semiconductor Characterization

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Introduction

This article introduces various techniques commonly used in the characterization of semiconductors and semiconductor devices. Many of the common materials characterization techniques have a variety of applications to semiconductors. Research into semiconductor materials has also led to the development of a large variety of highly specialized characterization approaches that do not possess demonstrated applications outside of the semiconductor field. This article focuses on the first set of techniques, but where possible, references to outside works in the second set are made. Because of space limitations, it is not possible to offer a comprehensive overview of all the various methods and approaches that can be used in characterizing semiconductor materials; consequently, the focus is on the most commonly available techniques and those that are covered in the later sections of this Volume.

As a class of materials, semiconductors are defined not by their elemental composition, position on the periodic table, chemical arrangement, processing history, or microstructure, but instead by a specific property: electrical resistance. Semiconductors are materials with an electrical resistance intermediate between metals and insulators (Ref 1). From a functional perspective, semiconductors form the active material components of structures whose electrical behavior, such as resistance, can be controlled through external stimulation, such as the gate voltage applied to a metaloxide-semiconductor field-effect transistor (MOSFET) or visible light illumination on a photovoltaic. The ability for this coupling to occur arises from interactions between the outer shell electrons and the potential energy landscape created by the atomic cores within semiconducting materials.

This class of materials is characterized by an energy gap between an electronic conduction band and valence band, both of which are partially occupied at room temperature with electronic carriers. These carriers are electrons in the valence band and holes in the conduction band. The population of these carriers can be

manipulated, most frequently through addition or removal of specific atomic constituents called dopants, through application of an external electric field, and by exposure to radiation such as visible light. The carriers generated by these various stimuli move either in an electric field via drift or due to concentration gradients via diffusion. This fundamental relationship between the density of electronic carriers, the currents and voltages generated by their motion, and these external stimuli form the basis for a variety of solid-state transducers that can convert information or energy from one form to another. The modern world contains many examples of these devices, including transistors, integrated circuits, diodes, photovoltaics, digital cameras, and displays.

The large family of semiconducting materials that has been identified and applied to problems in science and technology spans a wide range of material classes. To guide the interested reader most quickly to the relevant material, this article is divided into sections based on classes of semiconductors that share a common set of analytic techniques. A number of techniques have uses across these categories, such as scanning electron microscopy for imaging surfaces at high spatial resolution, while other techniques may have a more specific and specialized application, such as Raman spectroscopy for assessing the material quality of graphene sheets.

Single-crystal semiconductors include some of the most common semiconducting materials, particularly single-crystal silicon, which is the basis for the majority of the microelectronics industry. This section also considers germanium, gallium arsenide (GaAs), and the various epitaxial thin film semiconductors that can be grown on single-crystal wafer substrates. These materials are characterized first by their single-crystal nature and lack of transverse phase domains or grain boundaries, and often are fabricated at very high purity levels. Despite their high purity, the behavior of devices fabricated from these materials can still be quite sensitive to trace elemental constituents. These trace elements may be added intentionally, such as in the case of dopants, which are added to manipulate the relative concentration of positive to negative charge carriers in the material. Trace elements may also be unintentional contaminants. In either case, techniques with extremely low detection limits are often required for effective analysis in these systems. In many cases, it may not be practical to directly detect these trace constituents, but it may be simpler and more cost-effective to indirectly measure them through electrical testing.

Polycrystalline and amorphous semiconductors have wide application in technologies that require large-area devices such as electronic displays and photovoltaics. These materials by definition contain structural defects. In the case of polycrystalline materials, these consist of grain or phase boundaries, dislocations, and various point crystal defects. One way to conceive of amorphous materials is that they lie at the end of a continuum, where the density of defects becomes so high the material no longer exhibits the long-range structural order required to produce discrete features in x-ray, electron, or neutron diffraction. Organic semiconductors essentially lie between the amorphous and polycrystalline regimes, and are discussed in a separate section in this article.

The most common element in industrial application for amorphous and polycrystalline materials is also silicon, and amorphous silicon and polycrystalline silicon each have many applications where some electronic performance can be sacrificed in order to reduce cost. However, a number of other materials are also used in thin film form for various applications including silicon-germanium alloy and chalcogenides such as copper indium gallium selenide (Cu[In,Ga]Se2) and cadmium telluride (CdTe). As a class, these materials tend to lack the extremely high purity characteristic of single-crystal semiconductors; therefore, a larger variety of chemical analysis techniques can be used to adequately determine their composition. A wider variety of microstructural questions are also relevant to polycrystalline materials, whose properties are often strongly dependent on the density and distribution of crystalline defects.

While many oxides are insulating, a subset of oxide materials exhibit resistances and band

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gaps within the semiconducting range. These semiconductors are commonly transition metal oxides that are typically polycrystalline or polyphasic. Some oxides form naturally on metallic surfaces, but fabrication by other methods is typically utilized for commercial quality and processing requirements. Given the diverse nature of the oxides that fall into the category of semiconductors, it may not be surprising that the routes to fabricating these materials are equally diverse. Techniques related to the confirmation of fabrication processing parameters varies depending on the route employed. Independent of the route, both the grain structure and composition can dominate the final oxide material properties. Consequently, techniques that are sensitive to these properties can be necessary for analysis of these systems.

Organic semiconductors are small molecules or polymers possessing a backbone of alternating single and double bonds between carbon atoms. Primary applications of organic semiconductors are in displays and photovoltaics. Organic semiconductors are synthesized via wet chemistry techniques; thus, structural and optoelectronic properties can be easily tuned. Thin films of semiconducting polymers are fabricated using coating or printing techniques, and vacuum-based thermal evaporation is typically utilized for high-performance small-molecule-based thin films. Organic semiconductor thin films typically consist of a mix of amorphous and polycrystalline domains; properties of these thin films are commonly characterized using electrical, optical, and surface scanning probe-based techniques.

Low-dimensional semiconductors are materials and structures with at least one critical dimension that is within the nanoscale. This can include monolayers, quantum wells, nanowires/nanoribbons/nanorods, and quantum dots. While some of these nanoscale materials are composed of materials that are also semiconductors in their bulk form, others are composed of materials whose bulk and nanoscale properties greatly differ. In these cases, sufficiently reducing the size of the material's volume in one or more dimensions can lead to quantum confinement and opening of a band gap. To create these low-dimensional materials, two general fabrication schemes are commonly used: a top-down approach, which generally involves lithographic patterning and etching of a bulk or thin film material; and a bottom-up approach, which generally entails building nanostructures from atomic or molecular precursors. These length scales, usually less than optical wavelengths, can limit the usefulness of diffraction-limited characterization techniques (e.g., optical microscopy), because they may not be able to achieve the necessary spatial resolution. That being the case, techniques that are commonly utilized to characterize low-dimensional materials are usually real-space electron- or probe-based microscopy techniques.

As an overview, Figure 1 and Table 1 list some of the most common tools used for the characterization of the various classes of semiconducting materials considered in this article.

Single-Crystal Semiconductors

The starting point for many microelectronic devices is a single-crystal wafer of an elemental or compound semiconductor, most frequently silicon or GaAs, although a limited number of other materials are also available in wafer form. Insulating or metal substrates may also be used in some applications; however, their characterization is not the focus here. In some cases the wafer itself is the basis for a device, such for single-crystal silicon photovoltaics, but in many other cases devices are patterned onto the outer surface of the wafer by means of lithographic patterning and a variety of growth, deposition, etching, diffusion, and implantation processes. Several semiconductor materials, particularly silicon, are routinely prepared with specialized processing that generates material of very high purity with virtually no incorporated crystalline defects or other inhomogeneities. Material of this high quality is often required for the repeatable fabrication of dense integrated circuitry. Nonetheless, a number of materials questions may arise regarding the compositional purity, crystallographic structure, surface morphology, and chemistry of these materials during research and development, prototyping, manufacturing, and end use of these materials.

There is an even larger set of semiconducting materials that are available only in the form of thin films grown on the surface of single-crystal wafers. For a few specific classes of materials and deposition techniques, these thin films can be grown epitaxially on the surface of a single-crystal substrate, meaning that the atoms align in a second single crystal of the new material with a well-defined crystallographic



Fig. 1 Flow charts of common techniques for characterization of semiconductors. ICP-MS: inductively coupled mass spectrometry; ESR: electron spin resonance; NMR: nanomagnetic resonance; UV-vis: ultraviolet-visible spectroscopy; XRS: x-ray Raman spectroscopy; NAA: neutron activation analysis; FTIR: Fourier-transform infrared spectrometry; RS: Raman spectroscopy; GC: gas chromatography; GC-MS: gas chromatography-mass spectrometry; LC: liquid chromatography; LC-MS: liquid chromatography-mass spectrometry; XRD: x-ray diffraction; TEM: transmission electron microscopy; OM: optical microscopy; SAKS: x-ray solution scattering; AES: Auger electron spectroscopy; SIMS: secondary ion mass spectroscopy; LEISS: low-energy ion scattering spectroscopy

Table 1 Selected techniques

	Bulk/elemental	Microstructural	Surface analysis
Single crystal	EPMA, IR/FTIR, PL/tr:PL	XRD, XRF, TEM, EELS, RBS, EBIC, CL	SIMS, RBS, XPS, AFM, LEED, RHEED, SEM
Polycrystalline/ amorphous	EPMA, IR/FTIR, PL/tr:PL	ND, TEM, EELS, EBIC/ LBIC, SEM, SKPM	SIMS, XPS, AFM, SEM, RBS
Oxides	EPMA, IR/FTIR, PL/tr:PL	XRD, EBSD, TEM, SAED, AES, RS	SEM, XPS, LEED, RHEED, OM, EDS, STM, AFM, NIM, RS
Organic	UV-vis, PL/tr:PL	X-ray (GIWAXS)	AFM
Low-dimensional	(See surface analysis)	SAED, TEM	LEED, RHEED, SEM, SPM, AFM, STM, SCM, EFM, SKPM, EDS,

EELS, XPS, SIMS, LEAP, ARPES

EPMA: electron microprobe analysis; IR/FTIR: infrared spectrometry, Fourier-transform infrared spectrometry; PL/tr:PL: photoluminescence/ time-resolved photoluminescence; XRD: x-ray diffraction; XRF: x-ray fluorescence; TEM: transmission electron microscopy; EELS: electronenergy loss spectroscopy; EBIC/LBIC: electron-beam-induced current/light-beam-induced current; CL: cathodoluminescence; SEM: scanning electron microscopy; SKPM: scanning Kelvin probe microscopy; SIMS: secondary ion mass spectroscopy; RBS: Rutherford backscattering spectrometry; XPS: x-ray photoelectron spectroscopy; AFM: atomic force microscopy; EFM: electrostatic force microscopy; SCM: scanning capacitance microscopy; NIM: nanoimpedance microscopy; LEED: low-energy electron diffraction; RHEED: reflection high-energy electron diffraction; ND: neutron diffraction; LEAP: local electron atom probe; ARPES: angle-resolved photoemission spectroscopy; U-vis: ultraviolet-visible spectroscopy; SAED: selected area electron diffraction; AES: Auger electron spectroscopy; GWAXS: grazing-incidence wide angle x-ray spectrometry; STM: scanning tunneling microscopy; SPM: scanning probe microscopy; RSR Amann spectroscopy relationship to the substrate. These materials have many of the same characteristics as the single-crystal substrates themselves: they typically have very high purities and low densities of crystallographic defects. For this reason, there is a large degree of overlap in the characterization tools and strategies used for epitaxial films.

Single-crystal wafer substrates also play a role in a variety of devices that may use other classes of semiconductor for their active layers. Other examples of thin films utilizing these single-crystal wafer substrates span several classes of materials discussed in this article, including amorphous and polycrystalline semiconductors, and oxide semiconductors. There are also many examples of devices featuring organic semiconductors and low-dimensional materials that are built on single-crystal wafers, especially silicon. For this reason, an understanding of the behavior of single-crystal semiconductors in the various common characterization tools and techniques is an important place to begin a discussion of semiconductor characterization in general.

Material Classification

The main characteristic that defines a single crystal is a lack of internal crystallographic boundaries, such as grain boundaries or phase boundaries. Of course, every object in the world has an external surface, so in this sense every single crystal has one continuous grain boundary that defines its external surface. This definition captures both single-crystal wafers as well as epitaxial thin films, which can be viewed as a separate single crystal stacked on top of a single-crystal wafer substrate, or a series of such crystals for a multilayer structure. Such multilayer structures may contain a high spatial density of planar interfaces perpendicular to the stacking direction, but in order to fall in the single crystal category, they must lack internal grain boundaries.

Another level of classification that is frequently used is the division of these materials into elemental semiconductors and compound semiconductors. Elemental semiconductors are single crystals of a single element, primarily the group IV elements carbon, silicon, germanium, and tin, of which silicon and germanium are by far the most common in application. Compound semiconductors may be binary combinations of rows 3 and 5 of the periodic table (e.g., GaAs), rows 2 and 6 of the periodic table (e.g., CdTe), or more complex compounds arising from three or more elements, such as aluminum gallium arsenide and Cu(In,Ga)Se₂ (Ref 1, 2).

Fabrication Methods

Bulk single crystals suitable for creating wafers can be fabricated by a variety of meltsolidification techniques. The most common technique is the Czochralski (CZ) process, in which a single-crystal boule is drawn out of a molten pool of the source material. This is accomplished by placing a single-crystal seed in contact with the liquid surface. At the interface of the colder solid in contact with the molten liquid, epitaxial solidification occurs, and the growing crystal is slowly drawn away from the liquid surface where additional solidification occurs. The orientation of the growing crystal is then determined by the orientation of the single-crystal seed. Modifications to the process are required to grow compound semiconductors, in particular the addition of a background pressure of the more volatile component or the use of a boron oxide liquid encapsulant on the surface of the liquid melt (Ref 1, 2).

Compositional purity for intrinsic materials, as well as accurate homogeneous control of dopant atoms, is accomplished through a number of steps in the process. Raw materials are extracted from mineral sources via a large variety of processing steps. For the most common semiconductor, silicon, the raw material is SiO₂ sand. A lower-grade metallurgical silicon is separated from the oxygen through high-temperature reaction with a carbon source, such as coal. Metallurgical-grade silicon contains a number of undesirable atomic constituents, particularly iron. A secondary purification step is performed in a chemical reaction producing trichlorosilane or silane gas, which is subsequently purified by fractional distillation and converted back to silicon through chemical decomposition (Ref 1, 2).

The crystal growth process itself provides another degree of refinement due to segregation of minor constituents preferentially into the solid phase rather than the liquid phase. Table 2, adapted from Ref 1, shows that this segregation can provide a large degree of additional purification for some elements such as iron, which is an undesirable contaminant in silicon. Other elements, such as boron, do not segregate as strongly, which provides an advantage when those elements can be used to provide a background doping level, if the goal is to produce an electron majority or hole majority conducting material of uniform composition. Other techniques exist for additional

Table 2Segregation ratios of impurities in
silicon. A smaller ratio indicates that a solid
solidifying from a melt will contain less of
the indicated species; a higher ratio
indicates that it will contain more. Adapted
from Ref 1

Impurity	C _{solid} /C _{liqu}			
В	0.8			
Al	0.002			
Р	0.35			
As	0.3			
С	0.07			
Fe	8×10^{-6}			
0	1.25			

purification of semiconductor materials, such as zone refinement (Ref 1).

The CZ process is capable of producing high-purity single-crystal samples of silicon that are nearly defect free. Dislocations may be generated during the initial stages of growth due to thermal shock in the single-crystal seed when it touches the molten silicon pool, but their propagation into the bulk of the boule can be prevented by inclusion of a thin neck region between the seed and the primary bulk of the boule. However, the CZ process is not capable of producing defect-free materials for all semiconductors. Twin defects are difficult to suppress in indium phosphide (InP), and GaAs wafers cut from CZ boules may have a dislocation density of several thousands per squared centimeter. Other processes including the Bridgeman technique and the vertical gradient freeze method, are employed to produce GaAs materials with lower crystal defect density (Ref 2).

Thin film epitaxy can be conducted by a variety of strategies in which precursors of the desired elements are transported to the surface of a single-crystal wafer substrate. Conditions at the sample surface are controlled to encourage condensation of the desired solid via several mechanisms, including precipitation from a supersaturated solution during liquid phase epitaxy, and high-temperature chemical reaction between a metal chloride gas or a metal organic liquid precursor vapor and group V hydride gases in the case of vapor phase epitaxy and metal organic chemical vapor deposition.

A discussion of semiconductor processing would be incomplete without reference to how these materials are used to form electronic devices. The first requirement for many electronic devices is the formation of electronic junctions between volumes of material that have either electrons or holes as the majority electronic charge carriers. Elemental semiconductors can be fabricated as intrinsic semiconductors, where the shorthand is *i*, meaning the number of electrons and holes is equal at room temperature. These materials can also be doped by adding small concentrations of other elements to produce either an electron majority, called an *n*-type material, or a hole majority, called a *p*-type material. Doping is accomplished through the addition of dilute concentrations of other elements, such as boron and phosphorous in silicon.

Doping is one of the key features facilitating standard silicon electronics, because a silicon wafer can be doped in some locations as n-type, and in other locations as p-type via ion implantation or diffusion of appropriate dopant atoms. This allows the formation of a variety of lateral combinations of p and n regions, forming the basic structure required for diodes, transistors, and other electronic elements which are the constituents of integrated circuits. A number of compound materials can also be doped; however, many of them can