Throughout this chapter, this logo indicates an opportunity for online self-study at www.tinyurl.com/skoogpia7, linking you to interactive tutorials, simulations, and exercises.

The surface of a solid in contact with a liquid or gaseous phase usually differs substantially from the interior both in chemical composition and physical properties. Characterization of these surface properties is often of vital importance in a number of fields, including heterogeneous catalysis, sensor development and uses, biotechnology, and semiconductor thin-film technology. Such characterization also aids in understanding corrosion and adhesion mechanisms, activity of metal surfaces, embrittlement properties, and behavior and functions of biological membranes. This chapter deals with the investigation of solid surfaces by spectroscopic and microscopic methods. Although the emphasis is on solid surfaces, some of the techniques are also applicable to other interfaces, such as liquid-liquid and liquid-gas interfaces.

21A INTRODUCTION TO THE STUDY OF SURFACES

Before considering how surfaces are characterized, we first need to define what constitutes the surface of a solid or a liquid in contact with a gaseous or liquid second phase.

21A-1 Definition of a Surface

A surface is defined here as the boundary layer between a solid, or sometimes a liquid, and a vacuum, a gas, or a liquid. Generally, we think of a surface as a part of the material that differs in composition from the average composition of the bulk material. By this definition, the surface comprises not only the top layer of atoms or molecules of a solid but also a transition layer with a nonuniform composition that varies continuously from that of the outer layer to that of the bulk. Thus, a surface may be several or even several tens of atomic layers deep. Ordinarily, however, the difference in composition of the surface layer does not significantly affect the measured overall average composition of the bulk because the surface layer is generally only a tiny fraction of the total solid. From a practical standpoint, it appears best to adopt as an operational definition of a surface that volume of the solid that is sampled by a specific measurement technique. This definition recognizes that if we use several surface techniques, we may in fact be sampling different surfaces and may obtain different, albeit useful, results.

21A-2 Types of Surface Measurements

During the last century, many different methods have been developed for characterizing surfaces. The classical methods, which are still important, provide much useful information about the physical nature of surfaces but less about their chemical nature. These methods use optical and electron microscopic images of surfaces as well as measurements of adsorption isotherms, surface areas, surface roughness, pore sizes, and reflectivity. Beginning in the 1950s, spectroscopic surface methods began to appear that provided information about the chemical nature of surfaces.

This chapter is divided into several major parts. After an introduction to surface methods in Section 21B, we then discuss...
electron spectroscopic techniques, ion spectroscopic techniques, and photon spectroscopic techniques to identify the chemical species making up surfaces and to determine their concentrations. Sections 21F and 21G describe modern microscopic methods for imaging surfaces and determining their morphology and their physical features.

**21B SPECTROSCOPIC SURFACE METHODS**

Generally, the chemical composition of the surface of a solid or a biological sample differs, often significantly, from the interior or bulk of the material. Thus far in this text, we have focused on analytical methods that provide information about bulk composition only. In certain areas of science and engineering, however, the chemical composition of a surface layer is much more important than is the bulk composition of the material.

Spectroscopic surface methods provide both qualitative and quantitative chemical information about the composition of a surface layer that is a few tenths of nanometers (a few angstroms) to a few nanometers (tens of angstroms) thick. In this section we describe some of the most widely used of these spectroscopic techniques.1

**21B-1 Spectroscopic Surface Experiments**

Figure 21-1 illustrates the general way spectroscopic examinations of surfaces are performed. In this example, a solid sample is irradiated with a primary beam made up of photons, electrons, ions, or neutral molecules. Impact of this beam on a surface results in formation of a secondary beam also consisting of photons, electrons, molecules, or ions from the solid surface. The secondary beam is detected by the spectrometer. Note that the type of particle making up the primary beam is not necessarily the same as that making up the secondary beam. The secondary beam, which results from scattering, sputtering, or emission, is then studied by a variety of spectroscopic methods.

The most effective surface methods are those in which the primary beam, the secondary beam, or both are made up of either electrons, ions, or molecules and not photons because this limitation assures that the measurements are restricted to the surface of a sample and not to its bulk. For example, the maximum penetration depth of a beam of 1-keV electrons or ions is approximately 2.5 nm (25 Å), whereas the penetration depth of a photon beam of the same energy is about 1000 nm ($10^4$ Å). Thus, for many methods that include two beams of photons, such as X-ray fluorescence (see Chapter 12), infrared (IR) reflection spectroscopy (see Chapter 17), ellipsometry, or resonance Raman spectroscopy (see Chapter 18), precautions must be taken to limit the measurements to a surface layer. The techniques involving primary and detected (secondary) beams of photons discussed in this section are surface plasmon resonance, nonlinear optical spectroscopy, and ellipsometry.

There are several ways to classify surface techniques. Many of these are based on the nature of the primary and detected beams. Table 21-1 lists the most widely used spectroscopic techniques. These will be discussed further in this section.

**21B-2 Sampling Surfaces**

Regardless of the type of spectroscopic surface method being used, three types of sampling methods are available. The first involves focusing the primary beam on a single small area of the sample and observing the secondary beam. Often, the spot is chosen visually with an optical microscope. The second method involves mapping the surface, in which a region of the surface is scanned by moving the primary beam across the surface in a raster pattern of measured increments and observing changes in the secondary beam that result. The mapping may be linear or two dimensional. The third technique is known as depth profiling. Here, a beam of ions from an ion gun etches a hole in the surface by sputtering. During this process a finer primary beam produces a secondary beam from the center of the hole, which provides the analytical data on the surface composition as a function of depth.

**21B-3 Surface Environment**

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

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A problem frequently encountered in surface analyses is contamination of the surface by adsorption of components of the atmosphere, such as oxygen, water, or carbon dioxide. Even in a vacuum, this type of contamination occurs in a relatively short time. For example, at a pressure of $1.3 \times 10^{-4}$ Pa (1 torr), a monolayer of gas molecules will cover a clean surface in just 3 s. At $10^{-6}$ Pa, coverage occurs in about 1 h. At $10^{-8}$ Pa, 10 h is required. Because of adsorption problems, provisions must often be made to clean the sample surface, usually in the chamber used for irradiating the sample. Cleaning may involve baking the sample at a high temperature, sputtering the sample with a beam of inert gas ions from an electron gun, mechanical scraping or polishing of the sample surface with an abrasive, ultrasonic washing of the sample in various solvents, and bathing the sample in a reducing atmosphere to remove oxides.

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

**21C ELECTRON SPECTROSCOPY**

The first three methods listed in Table 21-1 are based on detection of emitted electrons produced by incident beams. In these methods, the signal from the analyte is encoded in a beam of electrons rather than photons. The spectrometric measurements then consist of the determination of the power of this beam as a function of the energy $h\nu$ or frequency $\nu$ of the electrons. This type of spectroscopy is termed *electron spectroscopy*.

Although the basic principles of electron spectroscopy were well understood a century ago, the widespread application of this technique to chemical problems did not occur until relatively recently. Studies in the field were inhibited by the lack of technology necessary for performing high-resolution spectral measurements of electrons having energies varying from a few tenths to several thousand electron volts. By the late 1960s, this technology had developed, and commercial electron spectrometers began to appear in the marketplace. With their appearance,
an explosive growth in the number of publications devoted to electron spectroscopy occurred.\textsuperscript{3}

There are three types of electron spectroscopy for the study of surfaces. The most common type, which is based on irradiation of the sample surface with monochromatic X-radiation, is called X-ray photoelectron spectroscopy (XPS). It is also termed electron spectroscopy for chemical analysis. Much of the material in this chapter is devoted to XPS. The primary beam for photoelectron spectroscopy can also consist of ultraviolet photons, in which case the technique is called ultraviolet photoelectron spectroscopy (UPS). Here, a monochromatic beam of ultraviolet radiation causes ejection of electrons from the analyte. This type of electron spectroscopy is not as common as the other two, and we shall not discuss it further. The second type of electron spectroscopy is called Auger (pronounced oh-ZHAY) electron spectroscopy (AES). Most commonly, Auger spectra are excited by a beam of electrons, although X-rays are also used. Auger spectroscopy is discussed in Section 21C-2. The third type of electron spectroscopy is electron energy-loss spectroscopy (EELS), in which a low-energy beam of electrons strikes and interacts with the surface, exciting surface vibrational transitions. The resultant energy loss is then detected and related to the vibrations excited. We briefly describe EELS in Section 21C-3. Several other electron spectroscopic techniques are useful including low-energy electron diffraction (LEED) and reflection high-energy electron diffraction (RHEED). These techniques are beyond the scope of this book.

Electron spectroscopy is a powerful tool for the identification of all the elements in the periodic table with the exception of hydrogen and helium. More important, the method permits determination of the oxidation state of an element and the type of species to which it is bonded. Finally, the technique provides useful information about the electronic structure of molecules.

Electron spectroscopy has been successfully applied to gases and solids and more recently to solutions and liquids. Because of the poor penetrating power of electrons, however, these methods provide information about solids that is restricted largely to a surface layer a few atomic layers thick (2 to 5 nm). Usually, the composition of such surface layers is significantly different from the average composition of the entire sample. Indeed, the most important and valuable current applications of electron spectroscopy are to the qualitative analysis of the surfaces of solids and more recently to solutions and liquids. Because of the poor penetrating power of electrons, however, these methods provide information about solids that is restricted largely to a surface layer a few atomic layers thick. Typically, the composition of such surface layers is significantly different from the average composition of the entire sample.

Principles of XPS

The use of XPS was pioneered by the Swedish physicist K. Siegbahn, who subsequently received the 1981 Nobel Prize in Physics for his work.\textsuperscript{4} Siegbahn chose to call the technique electron spectroscopy for chemical analysis (ESCA) because, in contrast to the other two electron spectroscopies, XPS provides information about not only the atomic composition of a sample but also the structure and oxidation state of the compounds being examined. Figure 21-3 is a schematic representation of the physical process involved in XPS. The three lower lines labeled $E_{b1}$, $E_{b2}$, and $E_{b3}$ represent energies of the inner-shell K and L electrons of an atom. The upper three lines represent some of the energy levels of the outer shell, or valence, electrons. As shown in the illustration, one of the photons of a monochromatic X-ray beam of known energy $h\nu$ displaces an electron $e^-$ from a K orbital of energy $E_{b1}$. The process can be represented as

\begin{equation}
A + h\nu \rightarrow A^{++} + e^- \quad (21-1)
\end{equation}

where A can be an atom, a molecule, or an ion and $A^{++}$ is an electronically excited ion with a positive charge one greater than that of A.

The kinetic energy of the emitted electron $E_b$ is measured in an electron spectrometer. The binding energy of the electron $E_b$ can then be calculated by means of the equation

\begin{equation}
E_b = h\nu - E_{b1} - w \quad (21-2)
\end{equation}

In this equation, $w$ is the work function of the spectrometer, a factor that corrects for the electrostatic environment in which the electron is formed and measured. Various methods are available to determine the value of $w$. The binding energy of an electron is characteristic of the atom and orbital that emit the electron.

Figure 21-2 shows a low-resolution, or survey, XPS spectrum consisting of a plot of electron-counting rate as a function of binding energy $E_b$. The analyte consisted of an organic compound made up of six elements. With the exception of hydrogen, well-separated peaks for each of the elements can be observed. In addition, a peak for oxygen is present, suggesting that some surface oxidation of the compound had occurred. Note that, as expected, the binding energies for 1s electrons increase with

\begin{footnotesize}
\begin{enumerate}
\end{enumerate}
\end{footnotesize}
thus appear at lower kinetic energies or higher binding energies (Equation 21-2). It is evident from Figure 21-2 that XPS provides a means of qualitative identification of the elements present on the surface of solids.

**Instrumentation**

Instruments for electron spectroscopy are offered by several instrument manufacturers. These products differ considerably in types of components, configurations, and costs. Some are designed for a single type of application, such as XPS, and others can be adapted to AES and UPS by purchase of suitable accessories. All are expensive ($300,000 to $106).

Electron spectrometers are made up of components whose functions are analogous to those encountered in optical spectroscopic instruments. These components include (1) a source; (2) a sample holder; (3) an analyzer, which has the same function as a monochromator; (4) a detector; and (5) a data analysis system. Figure 21-4 shows a typical arrangement of these components. Electron spectrometers generally require elaborate vacuum systems to reduce the pressure in all of the components to as low as 10⁻⁶ to 10⁻¹⁰ Pa (10⁻⁸ to 10⁻¹⁰ torr).²

**Sources.** The simplest X-ray sources for XPS spectrometers are X-ray tubes equipped with magnesium or aluminum targets and suitable filters. The Kα lines for these two elements

tron experiments. A synchrotron can provide a tunable source of X-rays for photoelectric excitation with high flux and at low cost. Such sources are widely used in combination with a monochromator to obtain a monochromatic X-ray source and a hemispherical field spectrometer. A synchrotron produces broadband radiation that is highly collimated and polarized. Such sources are also useful for obtaining high-flux beams of X-rays.

A synchrotron is a ring-shaped accelerator that produces a continuous stream of electrons. These electrons are then retarded to produce X-rays. The X-rays are then collimated and polarized to provide a highly monochromatic beam. This beam can be used to excite photoelectrons from a sample and then analyzed with a spectrometer. The result is a high-resolution spectrum of the sample.

Solid samples are usually introduced into the analytical chamber of an XPS instrument using a sample manipulator and holder. Solid samples positioned as closely as possible to the X-ray source and the entrance slit of the spectrometer (see Figure 21-4). To avoid attenuation of the electron beam, the sample compartment must be evacuated to a pressure of $10^{-3}$ Pa or less. Often, however, much better vacuums ($10^{-7}$ to $10^{-8}$ Pa) are required to avoid contamination of the sample surface by substances such as oxygen or water that react with or are adsorbed on the surface.

Gas samples are leaked into the sample area through a slit of such a size as to provide a pressure of perhaps 1 Pa. Higher pressures lead to excessive attenuation of the electron beam, which is due to inelastic collisions; on the other hand, if the sample pressure is too low, weakened signals are obtained.

**Analyzers.** The analyzer consists of the collection lens or lenses and the electron energy analyzer, which disperses the emitted electrons according to their kinetic energy. The lens system usually allows a wide collection angle (~30°) for high efficiency. In some angle-resolved experiments, an aperture reduces the angles collected. Such experiments are used in depth-profiling studies.

Typically, photoelectron experiments are carried out in constant analyzer energy mode, in which electrons are accelerated or retarded by the lens system to some user-defined energy as they pass through the analyzer (the pass energy, $E$ in Figure 21-4). Often, pass energies of 5–25 eV will yield high-resolution spectra. Survey scans use pass energies of 100–200 eV. The signal intensity decreases as the pass energy decreases.

Most energy analyzers are of the type illustrated in Figure 21-4, in which the electron beam is deflected by the electrostatic field of a hemispherical capacitor. The electrons thus travel in a curved path from the lens to the multichannel transducer. The radius of curvature depends on the kinetic energy of the electrons and the magnitude of the electrostatic field. An entire spectrum is obtained by varying the field so as to focus the resolution elements of an electron spectrum are monitored simultaneously and the data stored in a computer for subsequent display. The advantages of such a system are similar to those realized with multichannel photon detectors.

**Transducers.** Most modern electron spectrometers are based on solid-state, channel electron multipliers, which consist of tubes of glass that have been doped with lead or vanadium. When a potential difference of several kilovolts is applied across the materials, a cascade of 10^{6} to 10^{8} electrons is produced for each incident electron. The pulses are then counted electronically (see Section 4C). Several manufacturers are now offering two-dimensional multichannel electron detectors that are analogous in construction and application to the multichannel photon detectors described in Section 7E-3. Here, all of the resolution elements of an electron spectrum are monitored simultaneously and the data stored in a computer for subsequent display. The advantages of such a system are similar to those realized with multichannel photon detectors.

**Sample Holders.** Solid samples are usually introduced into the analytical chamber by means of a preparation chamber. This chamber can be isolated from the analytical chamber and allowed to reach atmospheric pressure for sample loading. The preparation chamber is then evacuated to the high vacuum of the analytical chamber.

After the samples are transferred to the analytical chamber, they are then positioned with a sample manipulator and holder. Solid samples positioned as closely as possible to the X-ray source and the entrance slit of the spectrometer.
TABLE 21-2 Chemical Shifts as a Function of Oxidation State

<table>
<thead>
<tr>
<th>Element</th>
<th>Oxidation State</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nitrogen (1s)</td>
<td>−2</td>
</tr>
<tr>
<td>Sulfur (1s)</td>
<td>−2</td>
</tr>
<tr>
<td>Chlorine (2p)</td>
<td>−2</td>
</tr>
<tr>
<td>Copper (1s)</td>
<td>−2</td>
</tr>
<tr>
<td>Iodine (4s)</td>
<td>−2</td>
</tr>
<tr>
<td>Europium (3d)</td>
<td>−2</td>
</tr>
</tbody>
</table>

*All shifts are in electron volts measured relative to the oxidation states indicated by (*). (Reprinted with permission from D. M. Hercules, Anal. Chem., 1970, 42, 20A, DOI: 10.1021/ac60283a717. Copyright 1970 American Chemical Society.)

1Type of electrons given in parentheses.
2Arbitrary zero for measurement, end nitrogen in NaN₃.
3Middle nitrogen in NaN₃.

Instruments allows many data-analysis options, including peak finding, peak identification, and peak intensity measurement. Many packages also include chemometric data analysis such as multivariate statistical processing and pattern recognition.

Applications of XPS

XPS provides qualitative and quantitative information about the elemental composition of matter, particularly of solid surfaces. It also often provides useful structural information.

Qualitative Analysis. Figure 21-2 shows a low-resolution, wide-scan XPS spectrum, called a survey spectrum, which serves as the basis for the determination of the elemental composition of samples. With a magnesium or aluminum Kα source, all elements except hydrogen and helium emit core electrons having characteristic binding energies. Typically, a survey spectrum encompasses a kinetic energy range of 250 to 1500 eV, which corresponds to binding energies of about 0 to 1250 eV. Every element in the periodic table has one or more energy levels that will result in the appearance of peaks in this region. In most instances, the peaks are well resolved and lead to unambiguous identification provided the element is present in concentrations greater than about 0.1%. Occasionally, peak overlap is encountered, such as O(1s) with Sb(3d) or Al(2s, 2p) with Cu(3s, 3p). Usually, problems due to spectral overlap can be resolved by investigating other spectral regions for additional peaks. Often, peaks resulting from Auger electrons are found in XPS spectra (see, for example, the peak at about 610 eV in Figure 21-2). Auger lines are readily identified by comparing spectra produced by two X-ray sources (usually magnesium and aluminum Kα). Auger lines remain unchanged on the kinetic energy scale but photoelectron peaks are displaced. The reason for the behavior of Auger electrons will become apparent in the next section.

Chemical Shifts and Oxidation States. When one of the peaks of a survey spectrum is examined under conditions of higher energy resolution, the position of the maximum depends to a small degree on the chemical environment of the atom responsible for the peak. That is, variations in the number of valence electrons, and the type of bonds they form, influence the binding energies of core electrons. The effect of the number of valence electrons and thus the oxidation state is demonstrated by the data for several elements shown in Table 21-2. Note that in each case, binding energies increase as the oxidation state becomes more positive. This chemical shift can be explained by assuming that the attraction of the nucleus for a core electron is diminished by the presence of outer electrons. When one of these electrons is removed, the effective charge sensed for the core electron is increased, and an increase in binding energy results.

One of the most important applications of XPS has been the identification of oxidation states of elements in inorganic compounds.

Chemical Shifts and Structure. Figure 21-5 illustrates the effect of structure on the position of peaks for an element. Each peak corresponds to the 1s electron of the carbon atom indicated by dashes above it in the structural formula. The shift in binding energies can be rationalized by taking into account the influence of the various functional groups on the effective nuclear charge experienced by the 1s core electron. For example, of all of the attached groups, fluorine atoms have the greatest ability to withdraw electron density from the carbon atom. The effective nuclear charge felt by the carbon 1s electron is therefore a maximum, as is the binding energy.
Chapter 21 Surface Characterization by Spectroscopy and Microscopy

Figure 21-6 indicates the position of peaks for sulfur in its several oxidation states and in various types of organic compounds. The data in the top row demonstrate the effect of oxidation state. Note also in the last four rows of the chart that XPS discriminates between two sulfur atoms contained in a single ion or molecule. Thus, two peaks are observed for thiosulfate ion (S\(_{2}\)O\(_{3}\)\(^{2-}\)), suggesting different oxidation states for the two sulfur atoms.

XPS spectra provide not only qualitative information about types of atoms present in a compound but also the relative number of each type. Thus, the nitrogen 1s spectrum for sodium azide (Na\(_{4}\)N\(_{3}\)) is made up of two peaks having relative areas in the ratio of 2:1 corresponding to the two end nitrogens and the center nitrogen, respectively.

It is worthwhile pointing out again that the photoelectrons produced in XPS are incapable of passing through more than perhaps 5–10 nm of a solid. Thus, the most important applications of electron spectroscopy, like X-ray microprobe spectroscopy, are for the accumulation of information about surfaces. Depth profiling is, however, possible by using deconvolution methods. Examples of some of the uses of XPS include identification of active sites and poisons on catalytic surfaces, determination of surface contaminants on semiconductors, analysis of the composition of human skin, and study of oxide surface layers on metals and alloys. Spatial mapping and imaging are also possible with microprobe methods.

It is also evident that the method has a substantial potential in the elucidation of chemical structure (see Figures 21-5 and 21-6). Information from XPS spectra is comparable to that from nuclear magnetic resonance (NMR) or IR spectroscopy. The ability of XPS to distinguish among oxidation states of an element is noteworthy.

Note that the information obtained by XPS must also be present in the absorption edge of an X-ray absorption spectrum for a compound. Most X-ray spectrometers, however, do not have sufficient resolution to permit ready extraction of this structural information.

**Quantitative Applications.** Once, XPS was not considered to be a very useful quantitative technique. However, there has been increasing use of XPS for determining the chemical composition of the surface region of solids.\(^7\) If the solid is homogeneous to a depth of several electron mean free paths, we can express the number of photoelectrons detected each second \(I\) as

\[
I = n\phi\sigma\epsilon ATI
\]

where \(n\) is the number density of atoms (atoms cm\(^{-3}\)) of the sample, \(\phi\) is the flux of the incident X-ray beam (photons cm\(^{-2}\) s\(^{-1}\)), \(\sigma\) is the photoelectric cross section for the transition (cm\(^2\)/atom), \(\epsilon\) is the angular efficiency factor for the instrument,

For a given transition, the six last terms are constant, and we can write the atomic sensitivity factor $S$ as

$$ S = \sigma \varepsilon \eta \lambda T I $$  \hspace{1cm} (21-4)

For a given spectrometer, a set of relative values of $S$ can be developed for the elements of interest. Note that the ratio $I/S$ is directly proportional to the concentration $n$ on the surface. The quantity $I$ is usually taken as the peak area, although peak heights are also used. Often, for quantitative work, internal standards are used. Relative precisions of about 5% are typical. For the analysis of solids and liquids, it is necessary to assume that the surface composition of the sample is the same as its bulk composition. For many applications this assumption can lead to significant errors. Detection of an element by XPS requires that it be present at a level of at least 0.1%. Quantitative analysis can usually be performed if 5% of the element is present.

### 21C-2 Auger Electron Spectroscopy

In contrast to XPS, AES is based on a two-step process in which the first step involves formation of an electronically excited ion $A^{++}$ by exposing the analyte to a beam of electrons or sometimes X-rays. With X-rays, the process shown in Equation 21-1 occurs. For an electron beam, the excitation process can be written

$$ A + e^- \rightarrow A^{++} + e^{+} + e^{-} $$  \hspace{1cm} (21-5)

where $e^{-}$ represents an incident electron from the source, $e^{+}$ represents the same electron after it has interacted with $A$ and has thus lost some of its energy, and $e^{-}$ represents an electron ejected from one of the inner orbitals of $A$.

As shown in Figure 21-7a and b, relaxation of the excited ion $A^{++}$ can occur in two ways:

$$ A^{++} \rightarrow A^{+} + e^{-} $$  \hspace{1cm} (21-6)

or

$$ A^{++} \rightarrow A^{+} + h\nu_I $$  \hspace{1cm} (21-7)

In this instance, $e^{-}$ corresponds to an Auger electron and $h\nu_I$ represents a fluorescence photon.

The relaxation process described by Equation 21-7 is X-ray fluorescence, which was described in Chapter 12. Note that the energy of the fluorescence radiation $h\nu_I$ is independent of the excitation energy. Thus, polychromatic radiation can be used for the excitation step. In Auger emission, shown by Equation 21-6, the energy given up in relaxation results in the ejection of an Auger electron $e^{-}$ with kinetic energy $E_{A}$. Note that the energy of the Auger electron is independent of the energy of the photon or electron that originally created the vacancy in energy level $E_{b}$. Thus, as is true in fluorescence spectroscopy, a monoenergetic source is not required for excitation. Because the Auger lines are independent of the input energy, it is possible to differentiate between Auger lines in a spectrum and the XPS peaks.

The kinetic energy of the Auger electron is the difference between the energy released in relaxation of the excited ion ($E_{b} - E_{A}$) and the energy required to remove the second electron from its orbital ($E_{b}$). Thus,

$$ E_{A} = (E_{b} - E_{A}) - E_{b} = E_{b} - 2E_{b} $$  \hspace{1cm} (21-8)

Auger emissions are described in terms of the type of orbital transitions involved in the production of the electron. For example, a KLL Auger transition involves an initial removal of a K electron followed by a transition of an L electron to the K orbital with the simultaneous ejection of a second L electron. Other common transitions are LMM and MNN.

Like XPS spectra, Auger spectra consist of a few characteristic peaks lying in the region of 20 to 1000 eV. Figure 21-8 shows typical Auger spectra obtained for two samples of a 70:30 copper-nickel alloy. Note that the derivative of the counting rate as a function of the kinetic energy of the electron $dN(E)/dE$ is the ordinate. Derivative spectra are standard for Auger spectroscopy to enhance the small peaks and to repress the effect of the large, but slowly changing, scattered electron background.
radiation. Also note that the peaks are well separated, making qualitative identification fairly straightforward.

Auger electron emission and X-ray fluorescence (Figure 21-7) are competitive processes, and their relative rates depend on the atomic number of the element involved. High atomic numbers favor fluorescence, and Auger emission predominates with atoms of low atomic numbers. As a result, X-ray fluorescence is not very sensitive for detecting elements with atomic numbers smaller than about 10.

Auger and XPS provide similar information about the composition of matter. The methods tend to be complementary rather than competitive, however, with Auger spectroscopy being more reliable and efficient for certain applications and XPS for others. As mentioned earlier, most instrument manufacturers recognize the complementary nature of Auger and XPS by making provisions for both kinds of measurements with a single instrument.

The particular strengths of Auger spectroscopy are its sensitivity for atoms of low atomic number, its minimal matrix effects, and above all its high spatial resolution, which permits detailed examination of solid surfaces. The high spatial resolution arises because the primary beam is made up of electrons, which can be more tightly focused on a surface than can X-rays. To date, Auger spectroscopy has not been used extensively to provide the kind of structural and oxidation state information that was described for XPS. Quantitative analysis with AES is not as straightforward as with XPS because of derivative mode data presentation and the presence of fine structure peaks. Often, the integrated area is the preferred parameter for quantitative work. Semiquantitative methods are available and widely used.

**Instrumentation**

The instrumentation for AES is similar to that for XPS except that the source is usually an electron gun rather than an X-ray tube. A schematic of a common type of electron gun is given in Figure 21-9. This source consists of a heated tungsten filament, which is usually about 0.1 mm in diameter and bent into the shape of a hairpin with a V-shape tip. The cathodic filament is maintained at a potential of 1 to 50 kV with respect to the anode contained in the gun. Surrounding the filament is a grid cap, or Weynelt cylinder, which is biased negatively with respect to the filament. The effect of the electric field in the gun is to cause the emitted electrons to converge on a tiny spot called the crossover that has a diameter $d_0$.

Cathodes constructed in the form of lanthanum hexaboride ($\text{LaB}_6$) rods are also used in electron guns when a source of greater brightness is desired. This type of source is expensive and requires a better vacuum system to prevent oxide formation, which causes the efficiency of the source to deteriorate rapidly. The most significant type of source that has been introduced in recent years is based on field emission. Here, the source is a sharp-tip (100 nm or less) tungsten or carbon cathode. When this type of cathode is held at a high voltage, the electric field at the tip is so intense ($>10^7$ V/cm) that electrons are produced by a quantum mechanical tunneling process in which no thermal energy is required to free the electrons from the potential barrier that normally prevents their emission. Field emission sources provide a beam of electrons that have a crossover diameter of only 10 nm compared with 10 μm for LaB$_6$ rods and 50 μm for tungsten hairpins. The disadvantages of this type of source are its fragility and the fact that it also requires a better vacuum than does an ordinary filament source.

Electron guns produce a beam of electrons with energies of 1 to 10 keV, which can be focused on the surface of a sample for Auger electron studies. One of the special advantages of Auger spectroscopy is its capability for very high spatial-resolution scanning of solid surfaces. Normally, electron beams with

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2. In quantum mechanics, there is a finite probability that a particle can pass through a potential energy barrier and appear in a region forbidden by classical mechanics. This process is called tunneling. It can be an important process for light particles, such as protons and electrons.
The microprobes and are used for scanning solid surfaces to detect the spectrum is obtained by bombarding a small area (5 to 500 μm) diameter) of the surface with a beam of electrons from a gun. A derivative electron spectrum, such as that shown in Figure 21-8, is then obtained with an analyzer. An advantage of Auger spectroscopy for surface studies is that the low-energy Auger electrons (20 to 1000 eV) are able to penetrate only a few atomic layers, 0.3 to 2 nm (3 to 20 Å) of solid. Thus, whereas the electrons from the electron guns penetrate to a considerably greater depth below the sample surface, only those Auger electrons from the first four or five atomic layers escape to reach the analyzer. Consequently, an Auger spectrum is likely to reflect the true surface composition of solids.

The two Auger spectra in Figure 21-8 are for samples of a 70% Cu to 30% Ni alloy, which is often used for structures where saltwater corrosion resistance is required. Corrosion resistance of this alloy is markedly enhanced by preliminary anodic oxidation in a strong solution of chloride. Figure 21-8A is the spectrum of an alloy surface that has been passivated in this way. Spectrum B is for another sample of the alloy in which the anodic oxidation potential was not great enough to cause significant passivation. The two spectra reveal the chemical differences between the two samples that account for the greater corrosion resistance of the former. First, the copper-to-nickel ratio in the surface layer of the nonpassivated sample is approximately that for the bulk, whereas in the passivated material the nickel peaks completely overshadow the copper peak. Furthermore, the oxygen-to-nickel ratio in the passivated sample approaches that for pure anodized nickel, which also has a high corrosion resistance. Thus, the resistance toward corrosion of the alloy appears to result from the creation of a surface that is largely nickel oxide. The advantage of the alloy over pure nickel is its significantly lower cost.

**Depth Profiling of Surfaces.** Depth profiling involves the determination of the elemental composition of a surface as it is being etched away (sputtered) by a beam of argon ions. Either XPS or Auger spectroscopy can be used for elemental detection, although the latter is the more common. Figure 21-10 shows schematically how the process is carried out with a highly focused Auger microprobe with a beam diameter of about 5 μm. The microprobe and etching beams are operated simultaneously, with the intensity of one or more of the resulting Auger peaks being recorded as a function of time. Because the etching rate is related to time, a depth profile of elemental composition is obtained. Such information is of vital importance in a variety of studies such as corrosion chemistry, catalyst behavior, and properties of semiconductor junctions.

Figure 21-11 gives a depth profile for the copper-nickel alloy described in the previous section (Figure 21-8). The ratios of the peak intensities for copper versus nickel are recorded as a function of sputtering time. Curve A is the profile for the sample that had been passivated by anodic oxidation. With this sample, the copper-to-nickel ratio is essentially zero for the first 10 minutes of sputtering, which corresponds to a depth of about 50 nm. The ratio then rises and approaches that for a sample of alloy that had been chemically etched so that its surface is approximately that of the bulk sample (curve C). The profile for the nonpassivated sample (curve B) resembles that of the chemically etched sample, although some evidence is seen for a thin nickel oxide coating.

**Line Scanning.** Line scans are used to characterize the surface composition of solids as a function of distance along a straight line of 100 μm or more. For this purpose, an Auger microprobe is used that produces a beam that can be moved across a surface in a reproducible way. Figure 21-12 shows Auger line scans along the surface of a semiconductor device. In the upper figure,
the relative peak amplitude of an oxygen peak is recorded as a function of distance along a line; the lower figure is the same scan produced when the analyzer was set to a peak for gold.

21C-3 Electron Energy-Loss Spectrometry

In EELS, a low-energy (1 to 10 eV) beam of electrons is focused on the surface of a sample and the scattered electrons are analyzed according to scattering energy and scattering angle. Some of the scattered electrons will suffer losses in energy because of vibrational excitation of surface molecules. With high-resolution EELS, a vibrational spectrum can be obtained by counting the number of electrons with a given energy loss relative to the elastically scattered electrons and reporting this count as a function of energy. Such spectra have been used to identify functional groups in the first layer of a surface including adsorbates and provide information on chemical bonding, such as oxidation states and coordination numbers.

In many cases EELS spectra are obtained in conjunction with electron microscopy experiments (see Section 21G). However, dedicated instruments and instruments combined with other electron spectroscopy techniques (XPS, AES) are available commercially. Typically, the resolution of EELS instruments is >10 cm\(^{-1}\), which is low compared to IR and Raman instruments but quite suitable for identifying and characterizing surface species.

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21D ION SPECTROSCOPIC TECHNIQUES

The techniques named in rows 5–7 of Table 21-1 detect a secondary beam of ions and are classified as ion spectroscopic techniques. These include secondary-ion mass spectrometry, ion-scattering spectroscopy, Rutherford backscattering spectroscopy, and laser-microprobe mass spectrometry.

21D-1 Secondary-Ion Mass Spectrometry

Secondary-ion mass spectrometry (SIMS) is the most highly developed of the mass spectrometric surface methods, with several manufacturers offering instruments for this technique. SIMS has proven useful for determining both the atomic and the molecular composition of solid surfaces.12

There are basically three variations of the SIMS experiment. Static SIMS is used for elemental analysis of sub-monolayers on surfaces. Although SIMS is basically a destructive technique, static conditions maintain the surface integrity during the time scale of the experiment. Dynamic SIMS is used to obtain compositional information as a function of depth below the surface. The dynamic SIMS experiment takes advantage of the destructive nature of SIMS to obtain information on various layers of materials. Imaging SIMS, also called scanning SIMS, is used to provide spatial images of surfaces.

There are two types of SIMS instruments: secondary-ion mass analyzers are used for static and dynamic SIMS, and microprobe analyzers are used for imaging SIMS. Both are based on bombarding the surface of the sample with a beam of 5- to 20-keV ions. Usually, Ar+ ions are used, although Cs+, N2+, or O2+ are also common. The ion beam is formed in an ion gun in which the gaseous atoms or molecules are ionized by an electron-ionization source. The positive ions are then accelerated by applying a high dc voltage. The impact of these primary ions causes the surface layer of atoms of the sample to be stripped (sputtered) off, largely as neutral atoms. A small fraction, however, forms as positive (or negative) secondary ions that are drawn into a spectrometer for mass analysis. In static SIMS, the sputtering is so slow that consumption of the sample is essentially negligible.

In secondary-ion mass analyzers, which serve for general surface analysis and for depth profiling, the primary ion-beam diameter ranges from 0.3 to 5 mm. Double-focusing, single-focusing, time-of-flight, and quadrupole spectrometers are used for mass determination. Typical transducers for SIMS are electron multipliers, Faraday cups, and imaging detectors. These spectrometers yield qualitative and quantitative information about all of the isotopes (hydrogen through uranium) present on a surface. Relative sensitivity factors vary considerably from ion to ion. Detection limits for most trace elements vary from $1 \times 10^{-12}$ atoms/cm$^2$ to $1 \times 10^{-16}$ atoms/cm$^2$. By monitoring peaks for one or a few isotopes, as a function of time, concentration profiles can be obtained with a depth resolution of 5 nm to 10 nm (50 to 100 Å).

Ion microprobe analyzers are more sophisticated (and more expensive) instruments based on a beam of primary ions focused to a diameter of 200 nm to 1 μm. This beam can be moved across a surface (rastered) for about 300 μm in both the x and y directions. A microscope is provided to permit visual adjustment of the beam position. Mass analysis is performed with a double-focusing spectrometer. In some instruments, the primary ion beam passes through an additional low-resolution mass spectrometer so that only a single type of primary ion bombards the sample. The ion microprobe version of SIMS permits detailed studies of solid surfaces.

21D-2 Ion-Scattering and Rutherford Backscattering Spectroscopy

Ion-scattering spectroscopy (ISS) and Rutherford backscattering spectroscopy (RBS) are similar techniques in that a primary ion beam is used to probe a surface.13 In both techniques, the energy distribution of ions backscattered from the sample is measured. Ions striking a solid surface can give rise to a variety of collisional processes as well as electronic excitations. Analysis of the energy spectra of the scattered ions can give information about the atomic masses, their concentrations, and their geometric arrangement on the surface.

The major difference between the two techniques lies in the energies of the incoming ion beam. In ISS, also called low-energy ion scattering, the primary ion energies are in the range of 0.5–5 keV. Noble gas ions, such as He+, Ar+, and Ne+, and alkali ions, such as Li+, Na+, or K+, are used. An electron ionization source is most often used with an electrostatic or time-of-flight analyzer. In the ISS technique, information is obtained from the upper atomic layer or, in some cases, from one or two layers directly below.

In Rutherford backscattering, the primary ion beam ranges in energy from 100 keV for H+ to several MeV for He+, He++ (alpha particles), and heavier ions. Van de Graaff generators are often used to produce beams of energetic ions. As shown in Figure 21-13, RBS instruments often use solid-state particle detectors and multichannel analyzers for energy resolution. Magnetic and electrostatic analyzers are also used for high-resolution studies. Information in RBS arises from a thickness of about 100 nm, although with special techniques surface analysis is also

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possible. With RBS, it is possible to determine atomic masses and elemental concentrations as a function of depth below the surface.

Because of its sensitivity to the top layer of the surface, ISS has proven very useful in providing surface compositional analysis of materials such as catalysts and alloys. ISS can also provide structural information on metal, semiconductor, metal oxide, and adsorbate surfaces. The major limitations of ISS are associated with difficulties in providing quantitative results, because of neutralization reactions and other interactions. Collisional processes and inelastic energy losses also make absolute mass determinations difficult. In compositional analysis, ISS is complementary to AES although not as generally applicable.

RBS can provide absolute quantitative analysis of elemental composition with an accuracy of about 5%. It can provide depth-profile information from surface layers and thin films to a thickness of about 1 µm. In some cases, however, the high-energy beam can damage the surface. This is particularly a problem with insulating materials, such as polymers, alkali halides, and oxides. The Mars Pathfinder mission in 1997 contained an alpha proton X-ray spectrometer (APXS). In its RBS mode, the spectrometer bombarded samples with alpha particles and determined elemental composition via energy analysis of the backscattered particles. In addition to RBS, the APXS instrument was designed to carry out proton emission and particle-induced X-ray emission (PIXE) experiments. Soil and rock compositions were measured and compared to those from the earlier Viking mission. Subsequent Mars missions, including the 2012 Mars Science Laboratory aboard the rover Curiosity also contained APXS instruments.

**21D-3 Laser-Microprobe Mass Spectrometry**

Laser-microprobe mass spectrometers are used for the study of solid surfaces. Ablation of the surface is accomplished with a high-power, pulsed laser, usually a Nd-YAG laser. After frequency quadrupling, the Nd-YAG laser can produce 266-nm radiation focused to a spot as small as 0.5 µm. The power density of the radiation within this spot can be as high as $10^{10}$ to $10^{11}$ W/cm$^2$. On ablation of the surface a small fraction of the atoms are ionized. The ions produced are accelerated and then analyzed, usually by time-of-flight mass spectrometry. In some cases laser microprobes have been combined with quadrupole ion traps and with Fourier transform mass spectrometers. Laser-microprobe tandem mass spectrometry is also receiving current research attention. In addition, laser ablation has been used to vaporize samples prior to introduction into inductively coupled plasmas for either emission or mass spectral analysis.\(^{14}\)

Laser-microprobe mass spectrometry has an unusually high sensitivity (down to $10^{-20}$ g), is applicable to both inorganic and organic (including biological) samples, has a spatial resolution of about 1 µm, and produces data at a rapid rate. Some typical applications of laser ablation mass spectrometry include determination of the calcium distribution in retinas, determination of fluorine distributions in dental hard tissue, bioimaging of cells and tissues, 3D mapping of surface layers, and analysis of forensic evidence.\(^{15}\)

**21E SURFACE PHOTON SPECTROSCOPIC METHODS**

In this section we discuss methods in which photons provide both the primary beam and the detected beam. The techniques discussed are listed in Table 21-1; namely, **surface plasmon resonance**, **sum frequency generation**, and **ellipsometry**. The electron and ion spectroscopic surface techniques described previously all suffer from one disadvantage: they require an ultra-high vacuum environment and provide no access to buried interfaces. The photon spectroscopic methods described here can all deal with surfaces in contact with liquids and, in some cases, surfaces that are buried under transparent layers.

**21E-1 Surface Plasmon Resonance**

Surface plasmon waves are surface electromagnetic waves that propagate in the xy plane of a metal film when the free electrons interact with photons. An easy way to obtain the resonance


condition is to arrange for total internal reflection at an interface, as shown in Figure 21-14. Here, a monochromatic light beam from a laser propagates in a medium of higher refractive index, such as glass. If the radiation strikes an interface to a medium of lower refractive index, such as air or water, total internal reflection can occur if the angle of incidence is greater than the critical angle. The radiation is focused and coupled into the interface by a prism coupler or a diffraction grating. With total internal reflection, an evanescent wave (see Section 17B-3) is generated in the medium of lower refractive index that decays exponentially with distance from the interface. As we have seen in Chapter 17, the evanescent wave can be absorbed in the less dense medium and the beam attenuated by attenuated total reflection.

If the internally reflecting interface is coated with a conducting material, such as a thin metal film, the \( p \)-polarized component of the evanescent wave may penetrate the metallic layer and excite surface plasmon waves. If the metal is nonmagnetic, such as gold, the surface plasmon wave is also \( p \)-polarized, which creates an enhanced evanescent wave. Because of the penetration of the electric field into the lower-refractive-index medium, the interaction is quite sensitive to the refractive index at the metal film surface. When the angle is suitable for surface plasmon resonance (SPR), a sharp decrease in the reflected intensity is observed, as can be seen in Figure 21-14. The resonance condition can be related to the refractive index of the metal film and can be used to measure this quantity and other properties of the surface.

The most interesting aspect of SPR is its sensitivity to materials adsorbed onto the metal film and the interactions of these materials, particularly biomolecules. A linear relationship is often found between the resonant energy and the concentration of biologically relevant materials such as sugars, DNA molecules, and proteins. Because of this sensitivity, SPR has become an important technique for biosensors. Biomolecular interactions, such as antibody-antigen binding or enzyme-substrate binding, occur at the sensor surface. Such interactions alter the refractive index and change the SPR angle needed to achieve resonance. The SPR angle, \( \theta_{\text{SPR}} \), can be monitored as a function of time to give information on the kinetics of binding reactions at the surface.

Many other potential applications of surface plasmon waves have been envisioned, including miniaturized devices, such as filters, polarizers, and light sources. The field has been termed molecular plasmonics.

### 21E-2 Sum-Frequency Generation

Sum-frequency generation (SFG) is a nonlinear optical technique based on the interaction of two photons at a surface. The result of the wave-mixing interaction is the production of a single photon whose frequency is the sum of the incident frequencies. If the two incident photons are of the same frequency, the technique is called second-harmonic generation because the exiting photon has a frequency twice that of the incident photons. Because this is a weak second-order process, intense lasers must be used.

SFG can be applied to solid-liquid, solid-gas, liquid-gas, or liquid-liquid interfaces. The process becomes most efficient when either the incident frequency or the outgoing frequency correspond to an allowed electronic or vibrational transition. Usually, one of the sources is a tunable laser to allow the incident frequency to be varied.

One of the most useful of the possible sum-frequency techniques is vibrational sum-frequency (SF) spectroscopy in which one of the incident beams is in the infrared (IR) spectral region and the other is in the visible region. Figure 21-15 shows two configurations that can be used. In Figure 21-15a, the arrangement for studying the interface between two immiscible liquids such as water and \( \text{CCl}_4 \) is shown. Here, a total internal reflection geometry is used. In Figure 21-15b, an external reflection geometry is shown for studying an air-water interface. The sum frequency could also be collected in transmission mode rather than in the reflection modes shown. In both cases, pulsed, high-intensity lasers are used. The most common lasers for vibrational SFG have been Nd-YAG and Ti-sapphire. Various combinations have been used to provide tunable IR radiation and fixed-frequency visible radiation. The pulses must overlap

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**Note:**


to the analysis of very thin films on surfaces. In ellipsometry, a polarized incident beam, often from a laser, is reflected from the film, and the reflected light is analyzed to determine a change in the state of polarization. The change in the amplitude and the phase of the reflected light are then related to properties such as film refractive index, absorptivity, optical anisotropy, and thickness.

The basic measurements in ellipsometry involve measuring the reflection coefficients for parallel \( R_{||} \) and perpendicularly polarized light \( R_{\perp} \) (sometimes called \( s \)- and \( p \)-polarized light, respectively). The ratio of these values, which is a complex number, gives the elliptical angle \( \Psi \) and the phase shift \( \Delta \) according to

\[
\frac{R_{||}}{R_{\perp}} = \tan(\Psi)e^{i\Delta}
\]  

(21-9)

The parameters \( \Psi \) and \( \Delta \) can reveal the thickness of the reflecting layer and its optical properties.

Several different types of ellipsometers are available commercially. The earliest type was the null-type ellipsometer in which a circularly polarized incident beam was reflected off the sample surface onto an analyzer. The incident-beam polarization state was chosen by a polarizer and compensator so that linearly polarized light was obtained after reflection. The analyzer was then rotated until it was perpendicular to the polarization axis of the light coming from the sample as indicated by a minimum in the light intensity. Some instruments today still use the null principle, but they are computer controlled and have solid-state cameras as detectors.

Another type of ellipsometer uses a phase modulation technique. In this technique, a rotating quarter-wave plate or acoustooptic modulator rapidly changes the state of polarization of the incident beam. Characteristics of the reflected light are obtained from an analysis of the modulated detector signal and used to calculate film thickness and other quantities.

Spectroscopic ellipsometry acquires the ellipsometric parameters as a function of wavelength and often angle of incidence. Modern spectroscopic ellipsometers use solid-state cameras to collect variable-wavelength data. Many of the more recent instruments also use Fourier transform techniques because of high signal-to-noise ratios and other inherent advantages.

### 21E-3 Ellipsometry

Ellipsometry is a technique that uses polarized light to probe the dielectric properties of samples.\(^{22}\) It is most commonly applied

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The resulting X-ray emission is detected and analyzed with either a wavelength- or an energy-dispersive spectrometer.\(^{22}\)

**Instruments**

Figure 21-16 is a schematic of an electron microprobe system. The instrument uses three integrated sources of radiation: an electron beam, a visible light beam, and an X-ray beam. A vacuum system is required that provides a pressure of less than \(10^{-3}\) Pa as is a wavelength- or an energy-dispersive X-ray spectrometer (a wavelength-dispersive system is shown in Figure 21-16). The electron beam is produced by a heated tungsten cathode and an accelerating anode (not shown). Several electromagnetic lenses focus the beam on the specimen; the diameter of the beam is between 0.1 and 1 \(\mu\)m. An associated optical microscope is used to locate the area to be bombarded. Finally, the X-ray fluorescence photons produced by the electron beam are collimated, dispersed by a single crystal, and detected by a gas-filled transducer. Considerable design effort is required to arrange the three systems spatially so that they do not interfere with one another.

The specimen stage usually has a mechanism to move the sample in two mutually perpendicular directions and rotate it as well, which permits the surface to be scanned.

**Applications**

The electron microprobe provides a wealth of information about the physical and chemical nature of surfaces. Applications have included phase studies in metallurgy and ceramics, the investigation of grain boundaries in alloys, the measurement of diffusion rates of impurities in semiconductors, the determination of occluded species in crystals, and the study of the active sites of heterogeneous catalysts. In all of these applications, both qualitative and quantitative information about surfaces is obtained.

Figure 21-17 illustrates the use of the electron microprobe for the analysis of an \(\alpha\)-cohenite (Fe\(_3\)C) particle in a lunar rock. The data were obtained by a linear scan of the particle observed visually on the surface and by measurement of the intensity of the characteristic emission line for each of four elements.

**21F-2 Scanning Electron Microscopy**

The classical method for obtaining detailed information about the physical nature of surfaces was optical microscopy, which is still an important technique. The resolution of optical microscopy is limited by diffraction effects, however, to about the wavelength of light. Much higher-resolution information is obtained by using one of the electron microscopic methods. The two most important methods are *scanning electron microscopy* and *transmission electron microscopy*.\(^{23}\) The so-called *scanning probe*

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microscopy methods, featuring scanning tunneling microscopy and atomic force microscopy, have also become important surface characterization methods and are discussed in Section 21G.

Although scanning and transmission electron microscopy methods have many similarities, scanning electron microscopy can be thought of as providing images of external morphology, similar to those accessed by the human eye. In contrast, transmission electron microscopy probes the internal structure of solids and gives us information about microstructural detail that is not familiar to the eye. We will restrict our discussion here to scanning electron microscope (SEM) methods.

In obtaining an SEM image, a finely focused beam of electrons impinges on the surface of the solid sample. In analog instruments, the beam of electrons is scanned across the sample in a raster scan by scan coils. The resulting raster scanning pattern is similar to that used in television or computer displays (liquid crystal displays [LCDs] or cathode ray tubes [CRTs]) in which the electron beam is (1) swept across the surface linearly in the x direction, (2) returned to its starting position, and (3) shifted downward in the y direction by a standard increment. This process is repeated until a desired area of the surface has been scanned. In more recent instruments, the same effect is achieved by digital control over the beam position on the sample. In either the analog scanning case or in digital systems, a signal is received above the surface (the z direction) and stored in a computer where it is ultimately converted to an image. Several types of signals are produced from a surface in this process, including backscattered, secondary, and Auger electrons; X-ray fluorescence photons; and other photons of various energies. All of these processes have been used for surface studies. In SEM instruments, backscattered and secondary electrons are detected and used to construct the image. For chemical analysis purposes, many modern SEMs also have X-ray detectors that allow qualitative and quantitative determinations to be made by means of X-ray fluorescence. As discussed in the preceding section, electron microprobe analyzers are instruments specifically made for X-ray analysis.

**Instrumentation**

Figure 21-18 shows a schematic diagram of an SEM with a microprobe attachment. Both an electron detector and an X-ray detector are present. For simplicity, an analog scanning system is illustrated.

**Electron Gun and Optics.** The electron source is usually a tungsten filament source, although field emission guns are also used for high-resolution work. The electrons are accelerated to an energy between 1 and 30 keV. The magnetic condenser and objective lens systems reduce the spot size to a diameter of 2–10 nm when it reaches the specimen. The condenser lens system, which consists of one or more lenses, is responsible for the throughput of the electron beam reaching the objective lens; the objective lens determines the size of the beam hitting the sample surface.

Scanning with an SEM is accomplished by the two pairs of electromagnetic coils located within the objective lens (see Figure 21-18); one pair deflects the beam in the x direction across the sample, and the other pair deflects it in the y direction. Scanning is controlled by applying an electrical signal to one pair of scan coils, such that the electron beam strikes the sample to one side of the center axis of the lens system. By varying the electrical signal to this pair of coils (that is, the x coils) as a function of time, the electron beam is moved in a straight line across the sample and then returned to its original position. After completion of the line scan, the other set of coils (y coils in this case) is used to deflect the beam slightly, and the scanning of the beam using the x coils is repeated. Thus, by rapidly moving the beam, the entire sample surface can be irradiated with the electron beam. The signals to the scan coils can be either analog or digital. Digital scanning has the advantage of very reproducible movement and location of the electron beam. The signal from the sample can be encoded and stored in digital form along with digital representations of the x and y positions of the beam.

In analog SEMs, the signals that drive the electron beam in the x and y directions also drive the horizontal and vertical scans of a CRT. The image of the sample is produced by using the output of a detector to control the intensity of the spot on the CRT. Thus, this method of scanning produces a map of the sample in which there is a one-to-one correlation between the signal produced at a particular location on the sample surface and a corresponding point on the CRT display. The magnification (M) achievable in the SEM image is given by

\[
M = \frac{W}{w}
\]  

where W is the width of the CRT display and w is the width of a single line scan across the sample. Because W is a constant, increased magnification is achieved by decreasing w. For example, if the electron beam is made to scan a raster 10 µm × 10 µm on the sample and the image is displayed on a CRT screen 100 mm × 100 mm, the linear magnification will be 10,000×. The inverse relationship between magnification and the width of the scan across the sample implies that a beam of electrons focused to an infinitely small point could provide infinite magnification. A variety of other factors, however, limit the magnification achievable to a range from about 10× to 100,000×.

**Samples and Sample Holders.** Sample chambers are designed for rapid changing of samples. Large-capacity vacuum pumps are used to hasten the switch from ambient pressure to \( \sim 10^{-4} \) Pa or less for conventional SEMs. The sample holder, or stage, in most instruments is capable of holding samples many centimeters on an edge. Furthermore, the stage can be moved in the x, y, and z directions, and it can be rotated about each axis.

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As a result, the surfaces of most samples can be viewed from various perspectives. Environmental SEMs, discussed later, use much higher pressures in the sample chamber and allow for variations in temperature and gas composition.

Samples that conduct electricity are easiest to study, because the unimpeded flow of electrons to ground minimizes artifacts associated with the buildup of charge. In addition, samples that are good conductors of electricity are usually also good conductors of heat, which minimizes the likelihood of their thermal degradation. Unfortunately, most biological specimens and most mineral samples do not conduct. A variety of techniques have been developed for obtaining SEM images of nonconducting samples, but the most common approaches involve coating the surface of the sample with a thin (~10 nm) metallic film produced by sputtering or by vacuum evaporation. Regardless of the method of producing a conductive coating, a delicate balance must be struck between the thinnest uniform coating achievable and an excessively thick coating that obscures surface details. Coating the sample may also interfere with other detection modes (e.g., X-ray emission). The environmental SEM discussed later can be directly used with nonconducting specimens.

Examining nonconductive materials, particularly polymers and biological materials, may present other difficulties, such as thermal degradation, radiation damage, and sample volatility in the high vacuum.

**Electron-Beam Interactions.** The versatility of the SEM and electron microprobe for the study of solids arises from the wide variety of signals generated when the electron beam interacts with the solid. Figure 21–19 illustrates the signals that can result. We consider just three of these signals: backscattered electrons, secondary electrons, and X-ray emission. The interactions of a solid with an electron beam can be divided into two categories: *elastic* interactions that affect the trajectories of the electrons...
in the beam without altering their energies significantly and inelastic interactions, which result in transfer of part or all of the energy of the electrons to the solid. The excited solid then emits secondary electrons, Auger electrons, X-rays, and sometimes longer-wavelength photons.

When an electron collides elastically with an atom, the direction of the electron changes, but the speed of the electron is virtually unaffected, so that the kinetic energy remains essentially constant. The angle of deflection for any given collision is random and can vary from 0° to 180°. Figure 21-20 is a computer simulation of the random behavior of 5 electrons and 100 electrons when they enter a solid normal to the surface. The energy of the beam is assumed to be 20 keV, which is typical. Note that such a beam penetrates to a depth of 1.5 µm or more. Some of the electrons eventually lose energy by inelastic collisions and remain in the solid; the majority, however, undergo numerous collisions and, as a result, eventually exit from the surface as backscattered electrons. It is important to note that the beam of backscattered electrons has a much larger diameter than the incident beam—that is, for a 5-nm incident beam, the backscattered beam may have a diameter of several micrometers. The diameter of the backscattered beam is one of the factors limiting the resolution of an electron microscope. Backscattered electrons have a broad energy spread, ranging from 50 eV up to the energy of the incident beam.

When the surface of a solid is bombarded with an electron beam having an energy of several keV, electrons having energies of 50 eV or less are emitted from the surface along with the backscattered electrons. The number of these secondary electrons is generally one half to one fifth or less the number of backscattered electrons. Secondary electrons are produced as a result of interactions between the energetic beam electrons and weakly bound conduction electrons in the solid, which leads to ejection of the conduction band electrons with a few electron volts of energy. Secondary electrons are produced from a depth of only 50 to 500 Å and exit in a beam that is slightly larger in diameter than the incident beam. Secondary electrons can be prevented from reaching the detector by applying a small negative bias to the transducer housing.

X-ray photons are yet a third product of electron bombardment of a solid. Both characteristic line spectra and an X-ray continuum are produced. This radiation serves as the basis for the electron microprobe for X-ray fluorescence analysis of SEM images.

The region the electrons penetrate is known as the interaction volume. Even though radiation is generated within this volume, it will not be detected unless it escapes from the specimen. X-rays are not easily absorbed and so most escape. For X-rays, the sampling volume, which is the volume of material contributing to the X-ray signal, is on the order of the interaction volume as shown in Figure 21-21. The backscattered electrons will not escape if they have penetrated more than a fraction of a micrometer. Thus, the backscattered signal originates from
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a much smaller volume. The secondary electron signal arises from a region that is on the order of the diameter of the incident electron beam. For this reason, secondary electron signals are capable of giving much higher spatial resolution than the other signals, and they are the most widely used signals in the SEM system.

Transducers. Secondary electrons are most often detected by a scintillator-photomultiplier system, called the Everhart-Thornley detector and illustrated in Figure 21-22. The secondary electrons strike a scintillator that then emits light. The emitted radiation is carried by a light pipe to a photomultiplier tube where it is converted into pulses of electrons. These pulses are then used to control the brightness of the electron beam in a CRT.

Because the energy of the secondary electrons is too low (<50 eV) to excite the scintillator directly, the electrons are first accelerated. Acceleration is accomplished by applying a bias voltage of approximately +10 keV to a thin film of aluminum covering the scintillator. A positively biased metal collector grid surrounds the scintillator and prevents the high voltage from affecting the incident electron beam. The grid also improves the collection efficiency by attracting secondary electrons, including those not initially moving toward the detector.

A large-area modification of the scintillation detector is used to detect backscattered electrons. This design maximizes the solid angle of collection. No biased grid is needed because of the high energies of the backscattered electrons. Semiconductor detectors are also widely used for backscattered electrons. When a high-energy electron strikes the detector, electron-hole pairs are produced that create a photocurrent. A semiconductor detector is small enough to be placed adjacent to the sample, which leads to high collection efficiency. The main disadvantage compared to scintillators is the relatively slow response time.

The X-ray analysis in most SEMs is the energy-dispersive analyzer using a semiconductor detector, such as a lithium-drifted silicon, Si(Li); lithium-drifted germanium, Ge(Li); silicon pin photodiode, or the silicon drift detector, SDD; as discussed in Section 12B-4. Wavelength-dispersive systems have also been used in electron microprobe analyses.

Data Handling and Processing. Data handling and processing depend on whether the SEM is an analog type or a newer digital microscope. With an analog microscope, two image monitors are used. With the first, the operator views the scanned image to identify features of interest and to focus and optimize the system. Observation is usually done at scan rates of fifty frames per second so that the image appears as a television image. The second monitor is a high-resolution CRT for photographic recording. The scan rate is usually slowed to obtain a high-quality image. One frame may take as long as 50 to 100 s. Hence, the requirements for viewing the image and obtaining a photographic record often conflict.

With digital SEMs, the beam stays on each point on the specimen for a predetermined period instead of the raster scanning of the analog system. The image is then constructed by recording each pixel on a framestore element. The framestore image is persistent, in contrast to a CRT image. Hence, the operator can view the image without using TV scan rates. With a framestore system, it is possible to use frame averaging, in some CCD cameras are subdivided into two areas, one to capture the image and one to store frames of the image. The framestore region is protected against photons and only stores information transferred from the image region. Alternatively, separate storage devices can be used as framestore systems.
which the data from successive scans are averaged for each pixel. A permanent record of the image is obtained by saving the frames as a bitmap image. Images can be treated in a variety of ways to provide contrast enhancement, inversion, mixing, subtraction, and color coding.

The Environmental SEM

The conventional SEM operates with a vacuum of $10^{-4}$ Pa or less. Samples must be clean, dry, and electrically conductive. Samples that have volatile components must be pretreated. In the mid-1980s, the so-called environmental SEM (ESEM) was developed. The ESEM maintains a high vacuum in the electron gun and microscope column but allows the sample to be placed in a higher-pressure region (1–50 torr). The sample environment can be varied by varying the pressure, temperature, and gas composition. The ESEM typically has three chambers: the gun, the microscope column, and the sample chamber. These regions are separated by small apertures, often corresponding to the electron beam apertures. Each region has its own pumping system.

Both secondary and backscattered electrons may be detected with an ESEM. The Everhart-Thorley detector shown in Figure 21-22 cannot be used because the high bias voltage of the scintillator would cause electrical breakdown at high pressures. Instead, gas-phase secondary electron detectors, which make use of cascade amplification, are used. These not only enhance the secondary electron signal but also produce positive ions, which are attracted to the insulated specimen surface and suppress charging artifacts. Large-area scintillation detectors can be used to detect backscattered electrons as with conventional SEM systems.

The ESEM allows samples to be observed in their natural states without the extensive modifications or preparations associated with a conventional SEM. Wet, dirty, oily, and nonconductive samples can be examined. Conductive coatings that mask valuable information are not needed. The environmental sample chamber becomes an additional tool that allows interactions between the sample and the environment to be studied by electron microscopy.

The only drawback to ESEM systems compared to conventional SEM instruments is a small loss of resolution due to elastic collisions between the electrons and gas molecules at the higher pressures. However, these collisions help to dissipate any accumulated electrical charges, which aids in the examination of nonconductive samples.

Applications

Scanning electron microscopy provides morphological and topographic information about a wide variety of solid surfaces. Several representative examples shown in Figure 21-23 illustrate the kind of information obtained by this technique.

21G SCANNING PROBE MICROSCOPES

Scanning probe microscopes (SPMs) are capable of resolving details of surfaces down to the atomic level. The first example of this type of microscope, the scanning tunneling microscope, was described in 1982. Only four years later, in 1986, its inventors, G. Binnig and H. Roher, were awarded the Nobel Prize in Physics for their work. Currently, the primary use of SPMs is for measuring surface topography of samples.

Unlike optical and electron microscopes, SPMs reveal details not only on the lateral $x$- and $y$-axes of a sample but also on the $z$-axis, which is perpendicular to the surface. Typically, the resolution of SPMs is about 2 nm (20 Å) in the $x$ and $y$ directions, but with ideal samples and the best instruments it can be as low as 0.1 nm (1 Å). Resolution in the $z$ dimension is generally better than 0.1 nm. For comparison, the resolution of a typical electron microscope is about 5 nm.

We shall discuss here two types of SPMs that are the most widely used and available from several commercial sources: the scanning tunneling microscope (STM) and the atomic force microscope (AFM). Both are based on scanning the surface of the sample in an $xy$ raster pattern with a very sharp tip that moves up and down along the $z$-axis as the surface topography changes. This movement is measured and translated by a computer into an image of the surface topography. This image often shows details on an atomic-size scale. A third type of SPM, the scanning electrochemical microscope, is described in Chapter 25 in our discussion of electrochemistry.

21G-1 The Scanning Tunneling Microscope

The Binnig-Roher microscope, which earned its inventors the Nobel Prize, was a STM. This device was found to be capable of resolving features on an atomic scale on the surface of a conducting solid surface. These instruments are now available from several instrument manufacturers and are used on a routine basis in hundreds of laboratories throughout the world. Their main disadvantage is the requirement that the surface being examined conduct electricity. The AFM, discussed in the next section, does not suffer from this limitation.

Simulation: Learn more about scanning probe techniques at www.tinyurl.com/skoogpia7

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Principle of the STM

In a STM, the surface of a sample is scanned in a raster pattern by a very fine metallic tip. The STM is based on the principle of quantum mechanical tunneling, which occurs when a small bias voltage (mV to 3 V) is applied between a sharp tip and a conducting sample and the tip is within a few nanometers of the surface. The magnitude of the tunneling current $I_t$ is given by

$$I_t = Ve^{-Cd}$$  \hspace{1cm} (21-11)

where $V$ is the bias voltage, $C$ is a constant, and $d$ is the distance between the probe and the surface. The basic STM is illustrated in Figure 21-24a. The STM can, in principle, be operated in two modes. In the constant-height mode, the tip position is kept constant in the $z$ direction while the tunneling current $I_t$ is monitored. In the constant-current mode, the tunneling current $I_t$ is kept constant while the $z$ position of the tip changes to keep $d$ constant, as shown in Figure 21-24a. In this case the $z$ position of the tip is monitored. Most modern STMs operate in the constant-current mode. The up-and-down motion of the
Chapter 21 Surface Characterization by Spectroscopy and Microscopy

tip then reflects the topography of the surface. The round balls in the figure represent individual carbon atoms in a sample of pyrolytic graphite. For clarity, the tip is shown as a rounded cone, and the path of the tip during a scan in the $x$ direction is shown by the blue line.

Equation 21-11 reveals that the tunneling current decreases exponentially with the separation between the tip and the sample. This rapid decrease in current with distance causes the tunneling current to be significant only for very small tip-sample separation and is responsible for the high resolution achieved in the $z$ direction.

Sample Scanners
In early STMs, three piezoelectric transducers arranged orthogonally controlled the three-dimensional motion of the tip, as shown in Figure 21-24a. Application of a dc voltage along its length varies the length of each transducer, thus making it possible to move the tip in a three-dimensional pattern (see Section 1C-4 for a discussion of the composition and properties of piezoelectric transducers). Depending on the composition of the piezoelectric ceramic material and the dimensions of the transducer, the degree of expansion or contraction can be made as small as 1 nm for every volt applied, which provides remarkably sensitive control of the tip position.

Modern scanning microscopes no longer use the tripod design shown in Figure 21-24a but instead are based on a hollow-tube piezoelectric device, shown in Figure 21-25. The outer surface of the tube, which is typically between 12 and 24 mm long and 6 and 12 mm in diameter, is coated with a thin layer of metal. This conducting layer is divided into four equal segments by vertical strips containing no metal coating. Application of voltages to opposite strips of metal bends the tube in the $x$ and $y$ directions as indicated. Likewise, application of a voltage along the interior axis of the cylinder lengthens or shortens the tube in the $z$ direction. A tip in the center of one end of the cylinder can then be made to move in three dimensions by application of suitable voltages.

Scanning microscopes typically use scanners with lateral scan ranges of a few nanometers to more than 100 µm. Height differences from less than 0.1 nm to perhaps 10 µm are encountered. The maximum scan size is determined by the length, diameter, and wall thickness of the cylinder as well as the strain coefficient of its ceramic material.

**Computer Interface**

Computer control is an essential part of all scanning tunneling microscopes. Most commercial STMs use software and digital-to-analog converters to generate the $xy$ raster scan. The computer processes the voltages applied to the $x$, $y$, and $z$ piezoelectric elements and converts them into contour maps such as that shown in Figure 21-24b. With more sophisticated instruments the images may take the form of gray-level images or pseudocolored elevation maps.

The blue line in Figure 21-24a shows the tip path as it scans in the $x$ direction over the surface of a sample of highly oriented pyrolytic graphite. After a scan in the $x$ direction is completed, the tip is returned to its original position and then moved down one line by application of an appropriate voltage to the $y$ piezoelectric transducer. This process is repeated until a plot of the entire sample is obtained as shown in Figure 21-24b. A series of contour lines show the position of the electron cloud of each carbon atom on the surface of the sample.

Because the output signal from the detector is so sensitive to the distance between the sample and the tip, differences in distances along a given contour in the figure are revealed to 1/100 of an atomic dimension. The lateral resolution along a given contour depends on the radius of curvature of the tip. When this radius is that of a single atom, as it usually is, atomic resolution is observed.

**Tips**

The tunneling tip is a crucial component of the STM. The best images are obtained when tunneling is limited to a single metal atom at the tip end. Fortunately, with a little care, it is possible to construct this type of tip by cutting platinum-iridium wires or by electrochemical etching of tungsten metal. The reason a single-atom tip is not as difficult to prepare as might be expected is because of the exponential increase in tunneling current with decreasing gap (Equation 21-11). Thus, typically, the tunneling current increases by a factor of 10 when the gap distance decreases by 0.1 nm (1 Å). That is, if there is one atom at the tip apex closer to the sample surface by 0.1 nm than any other, nearly all of the current will flow through that atom to the sample, and atomic resolution is achieved.

**21G-2 The Atomic Force Microscope**

The AFM, which was invented in 1986, permits resolution of individual atoms on both conducting and insulating surfaces. In this procedure, a flexible force-sensing cantilever stylus is scanned in a raster pattern over the surface of the sample. The force acting between the cantilever and the sample surface causes minute deflections of the cantilever, which are detected by optical means. As in the STM, the motion of the tip, or sometimes the sample, is achieved with a piezoelectric tube. During a scan, the force on the tip is held constant by the up-and-down motion of the tip, which then provides the topographic information. The advantage of the AFM is that it is applicable to nonconducting samples.

![Piezoelectric scanner of the segmented tube design.](image-url)

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Figure 21-26 shows schematically the most common method of detecting the deflection of the cantilever holding the tip. A laser beam is reflected off a spot on the cantilever to a segmented photodiode that detects the motion of the probe. The output from the photodiode then controls the force applied to the tip so that it remains constant. The optical control system is analogous to the tunneling-current control system in the STM.

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Figure 21-27 shows a common design of an AFM. The movement system is a tubular piezoelectric device that moves the sample in x, y, and z directions under the tip. The signal from the laser beam detector is then fed back into the sample piezoelectric transducer, which causes the sample to move up and down, maintaining a constant force between the tip and the sample.

**The Tip and Cantilever**

The performance of an AFM critically depends on the physical characteristics of the cantilever and tip. In early AFMs, cantilevers were cut from metal foil and tips were made from crushed diamond particles. The tips were painstakingly manually glued to the cantilevers. Currently, this crude method has been replaced by semiconductor mass production methods in which integral cantilever-tip assemblies are produced by etching single chips of silicon, silicon oxide, or silicon nitride. The most common cantilever-tip assemblies in use today are micromachined from monolithic silicon as shown in Figure 21-28. As can be seen, the cantilevers and tips are remarkably small (ideally, a single atom at the tip apex).

**AFM Modes**

Three modes are commonly used in AFMs: contact mode, noncontact mode, and tapping mode. Contact mode is the most common. In this mode, the tip is in constant contact with the surface of the sample. The majority of AFM measurements are made under ambient pressure conditions or in liquids, and surface tension forces from adsorbed gases or from the liquid layer may pull the tip downward. These forces, although quite small, may be large enough to damage the sample surface and distort the image. This problem is particularly bothersome with softer materials, such as biological samples, polymers, and even some seemingly hard materials, such as silicon wafers. In addition, many samples can trap electrostatic charges, which can contribute to an attractive force between the probe and the sample. This can lead to additional frictional forces as the tip moves over the sample, which dull the tip and damage the sample.

The problem of surface damage can be largely overcome by a process in which the tip periodically contacts the surface for only a brief time and then is removed from the surface. In this tapping-mode operation, the cantilever oscillates at a frequency of a few hundred kilohertz. The oscillation is driven by a constant driving force and the amplitude is monitored continuously. The cantilever is positioned so that the tip touches the surface at only the bottom of each oscillation cycle. This technique has been used successfully to image a wide variety of materials that have been difficult or impossible to image by the ordinary contact mode.

The least common mode of operation is the noncontact mode, in which the tip hovers a few nanometers above the sample surface. Attractive van der Waals forces between the tip and the sample are detected as the tip scans over the surface. These forces are substantially weaker than those detected in contact-mode AFMs. Hence, the tip is oscillated and ac detection techniques are used to recover the small signals.

**Multimode Scanning Probe Microscopes**

Many commercial SPMs are capable of multimode operation. They can be used as AFMs in contact, tapping, and noncontact modes and as STMs. Other operational modes, such as lateral force mode, torsional mode, and magnetic force mode may also be possible, depending on the manufacturer and model.

**Some Typical Applications of Scanning Probe Microscopes**

SPMs have allowed scientists and engineers to see surface structures with unprecedented resolution. As a consequence, SPMs have been used in a number of fields. For example, in the semiconductor field they have been used for the characterization of silicon surfaces and defects on these surfaces, as well as imaging...
of magnetic domains on magnetic materials; in biotechnology, imaging of such materials as DNA, chromatin, protein-enzyme interactions, membrane viruses, and so on. An advantage of AFM is that it permits underwater imaging of biological samples under conditions that cause less distortion of the image. For softer samples, distortion often arises because a microdrop of water forms at the tip-surface interface. Capillary forces from this drop exceed the normal force between the tip and sample and obscure surface details. If the sample is in water, water is above the tip as well as below and capillary forces in the up and down directions cancel.

An interesting example of the potential of STM measurements is illustrated in Figure 21-29. The image was produced from the surface of a sample of iodine atoms absorbed on platinum. The hexagonal pattern of absorbed iodine atoms is interrupted by a defect where an iodine atom is absent, which appears as a divot in the bottom center of the image. The scan that is shown represents a 3 nm × 3 nm area of the platinum surface. This example shows how an STM may be used to reveal structures of solid surfaces at the atomic level.

Figure 21-30 is an image of two intertwined DNA molecules on a mica surface obtained by a tapping-mode AFM scan. Such measurements allow biochemists to study the structure of DNA and other biomolecules with relative ease.

In recent years it has become possible to chemically modify probes to increase selectivity and applicability to chemical problems. Figure 21-31 shows an interesting application of an
FIGURE 21-30 Two double-stranded DNA molecules imaged on mica, showing the ability of an AFM to resolve overlapping molecules. (Courtesy of W. B. Stine, University of California, San Diego. With permission.)

FIGURE 21-31 Detection of a functional group by atomic force microscopy. (a) Carboxylic acid groups are chemically attached to a gold-coated AFM tip. (b) Schematic views of the experiment. (Inset) Interaction between the gold tip coated with —COOH groups and the sample coated with both —CH₃ and —COOH groups. (Adapted from C. D. Frisbie, L. F. Rozsnyai, A. Noy, M. S. Wrighton, and C. M. Lieber, Science, 1994, 265, 2071, DOI: 10.1126/science.265.5181.2071. With permission.)
AFM. In this experiment, a gold-coated Si$_3$N$_4$ tip is immersed for a time in a solution containing an organosulfur compound such as 11-thioundecanoic acid. The result is that the ends of the acid molecules opposite the carboxylic acid group become covalently attached to the probe tip, so that the tip is then effectively coated with carboxylic acid groups as shown in Figure 21-31a. When the probe tip is then scanned across a surface having various attached organic functional groups, as shown in Figure 21-31b, the differences in frictional forces between the acid groups on the tip and other functional groups on the surface of the sample result in an image that is a map of the positions of surface functional groups. This technique is termed chemical force microscopy (Figure 21-32). Studies such as these illustrate that scanning probe microscopy provides quite specific qualitative analytical information as well as information on the spatial arrangement of analytes on surfaces. Because of this, atomic force microscopy and its various modifications, including the inverted design where the sample is placed on the end of the cantilever, have recently been proposed as general analytical instruments for solving a variety of problems.\textsuperscript{32}

QUESTIONS AND PROBLEMS

*Answers are provided at the end of the book for problems marked with an asterisk.

Problems with this icon are best solved using spreadsheets.

21-1 Describe the mechanism of the production of an LMM Auger electron.

21-2 Describe how it is possible to distinguish between XPS peaks and Auger electron peaks.

21-3 Explain why the information from an XPS chemical shift must also be contained in an X-ray absorption edge.

21-4 An XPS electron was found to have a kinetic energy of 1076.8 eV when a Mg Kα source was used (λ = 0.98900 nm). The electron spectrometer had a work function of 14.7 eV.

   (a) Calculate the binding energy for the emitted electron.
   (b) If the signal was from a S(2s) electron, was the analyte S^2-, S^6, SO_2^2-, or SO_2^2-?
   (c) What would the kinetic energy have been if an Al Kα source had been used (λ = 0.83393 nm)?
   (d) If the ejected electron with the Mg Kα source had been an Auger electron, what would its kinetic energy be with the Al Kα source?

21-5 An XPS electron was found to have a kinetic energy of 1055.3 eV when ejected with an Al Kα source (λ = 0.83393 nm) and measured in a spectrometer with a work function of 25.1 eV. The electron is believed to be a N(1s) electron in NaNO_3.

   (a) What was the binding energy for the electron?
   (b) What would be the kinetic energy of the electron if a Mg Kα (λ = 0.98900 nm) source were used?
   (c) How could one be sure that a peak was an XPS and not an Auger electron peak?
   (d) At what binding and kinetic energies would a peak for NaNO_2 be expected when the Al Kα source was used with the same spectrometer?

21-6 Compare EELS to conventional IR and Raman spectroscopy. Focus on what is used to excite and detect vibrations. What are the advantages and limitations of EELS?

21-7 Compare ISS to RBS. For both cases, draw diagrams of the instrumental setup. Describe any differences in the information obtained by the two techniques.

21-8 How does static SIMS instrumentally differ from dynamic SIMS? How does the information obtained from static SIMS differ from that obtained from dynamic SIMS? What is imaging SIMS? What type of information is obtained with imaging SIMS?

21-9 What are the main advantages of surface photon techniques when compared with electron and ion spectroscopic methods? What are the major disadvantages?

21-10 What is a buried interface and what techniques are available to study buried interfacial phenomena?

21-11 Name three possible sources of signals with the SEM. Differentiate between elastic and inelastic scattering of electrons.

21-12 Name the two most common types of SPMs.

   (a) How do they differ?
   (b) What are the advantages of each type?
   (c) What are the major limitations of each type?

21-13 If the tunneling current is 8.7 pA when an STM probe is 0.40 nm from a surface and 17.0 pA when the probe is 0.50 nm from the surface, calculate the current on moving the tip in 0.10-nm steps from 0.40 nm to 1.50 nm.
Challenge Problem

21-14 Quantitative X-ray photoelectron spectrometry has become more popular in recent years. The factors relating the intensity of emission to atomic concentration (density) are given in Equation 21-3.

(a) Of the factors influencing the emission intensity, identify those related to the analyte.

(b) Identify the factors influencing the emission intensity related to the spectrometer.

(c) The measured quantity in quantitative XPS is usually \( I/S \), where \( I \) is the peak area and \( S \) is the sensitivity factor for the element of interest. If this quantity is measured for the analyte \( (I/S)_a \) and the corresponding value measured for an internal standard with a different transition \( (I/S)_i \), show by means of an equation how the ratio \( (I/S)_a / (I/S)_i \) is related to the atomic concentration ratio of the analyte to the internal standard.

(d) If all the elements on a surface are measured by XPS, show that the fractional atomic concentration \( f_A \) of element A is given by

\[
 f_A = \frac{I_A/S_A}{\sum (I_n/S_n)}
\]

where \( I_n \) is the measured peak area for element \( n \), \( S_n \) is the atomic sensitivity factor for that peak, and the summation is carried out over all \( n \).

(e) For a polyurethane sample in which carbon, nitrogen, and oxygen were detected by XPS, the sensitivity factor for C was 0.25 on the spectrometer used. The sensitivity factor for N was 0.42 and that for O was 0.66 on the same spectrometer. If the peak areas were \( C(1s) = 26,550 \), \( N(1s) = 4475 \), and \( O(1s) = 13,222 \), what were the atomic concentrations of the three elements?

(f) What are the limitations of quantitative analysis with XPS? Why might the atomic concentrations measured not correspond to the bulk composition?

(g) For polyurethane, the stoichiometric atomic concentrations are C = 76.0%, N = 8.0%, and O = 16.0%. Calculate the percentage error in the values obtained in part (e) for each element.
Instrumental Analysis in Action

Assessing the Authenticity of the Vinland Map: Surface Analysis in the Service of History, Art, and Forensics

The Vinland Map

The controversial Vinland map came to light in the 1950s when it was put up for sale by a private library in Europe and eventually purchased by a rare-books dealer in New Haven, Connecticut. It was donated to Yale University in 1965 and is now owned by the Yale University Library. As can be seen in Figure IA3-1, the Vinland map is a medieval-style map of the New World showing a large island in the Western Atlantic called Vinlandia Insula, which generally resembles the northeastern part of North America (Vinland). The map was first revealed to the world in 1965 together with an unknown document dating to the 1440s titled “Tartar Relation.” If genuine, it would imply that a large portion of North America was known to western Europeans prior to Columbus.

The case for the authenticity of the map was enhanced when it was discovered that wormholes in the map lined up exactly with wormholes in the “Tartar Relation” and in another authentic medieval document, the “Speculum Historiale.” The map was thought to have been bound with these two documents at one time.

The map was largely believed to be authentic until 1974, when the Yale Library hired a surface analysis group (McCrone Associates) to make a detailed examination. Since that time, scientists have used a wide variety of surface analytical techniques to look at the parchment and the ink used in the map. As discussed in the following, many of the measurements indicate that the map is a forgery. However, not all scientists agree, and several nagging questions remain.

Instrumental Techniques

In their comprehensive investigation of the map, McCrone Associates\(^1\) made a careful preliminary examination using optical microscopy. These observations revealed that the drawing consisted of an apparently hand-drawn map with a black ink outline on vellum. The outline is bordered with an underlying pale yellow layer, which is typical of ancient manuscripts. A key early observation was that the black outline was not in perfect registration with the yellow underlayer.

The map was then examined using polarized light microscopy to reveal the likely presence of particles of calcite and titanium dioxide (TiO\(_2\)), probably anatase. These observations also suggested that the anatase particles were similar to those of commercial white pigments produced since the early twentieth century. Following microscopic examination, particles from various parts of the map were subjected to several other ultramicroanalytical methods.

Powder X-ray diffraction (Section 12D-1) measurements were performed on sub-nanogram samples of the yellow pigment layer, which confirmed the presence of both calcite and anatase. Particles of the pigments were examined in a scanning electron microscope (Section 21F-2) equipped with an X-ray fluorescence detection system (Section 12A-3). The yellow pigment particles showed relatively high concentrations of titanium, and the black particles showed high concentrations of iron and chromium. The transmission electron microscope (Section 21F-2) was used to compare the particle shape and size distribution of anatase from the Vinland map to those of the commercial product. These results also suggested that the anatase particles were of modern origin.

The electron microprobe (Section 21F-1), which is capable of elemental analysis on femtogram samples with a beam diameter of 1 µm, was used to show that the yellow pigment contained substantial amounts of titanium, but neither the parchment nor the black pigment contained titanium. Ion microprobe analysis (Section 21D-1) of the pigment samples provided results consistent with those of the electron microprobe. The ion microprobe was also used to compare the pigments of the Vinland map with the inks in the “Tartar Relation” and the “Speculum Historiale.” The results from the Vinland map did not match those from the Tartar Relation or the Speculum Historiale, and they did not match results from any known ink. McCrone concluded that the Vinland map was a clever forgery produced by drawing the map with the yellow, anatase-containing pigment and then redrawing the map using a black, carbon-based ink. This conclusion appears to have been triggered by the lack of registration of the yellow and black layers and was consistent with all of the ultra- microanalytical results.

An interdisciplinary group led by Cahill used particle-induced X-ray emission (PIXE) techniques (Section 12C-1) to determine that although titanium is indeed often present in the yellow pigment of the Vinland map, it is found only in minute quantities, far less than is consistent with the impression given by the early results from the McCrone group.\(^2\) The Cahill group, which had previously tested hundreds of other early manuscripts, had detected comparable levels of titanium in several other undisputedly medieval parchments. In his summary report, McCrone\(^3\) disputed the Cahill study by stating that

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3See note 1.
PIXE, although a trace analysis technique, is not an appropriate tool for ultramicroanalysis. In other words, the sampling area of PIXE is considerably larger than the microanalytical techniques used by McCrone, which leads to apparently lower concentrations of titanium in significant areas of the map.

Raman microprobe measurements (Section 18B-2) on the map by Brown and Clark confirm that the yellow pigment contains anatase, that the black pigment is carbon based, and that these pigments are entirely different than the inks of the “Tartar Relation.” These results are consistent with McCrone’s conclusion that the map is a forgery. Finally, the age of the parchment of the Vinland map has been determined by radiocarbon dating using accelerator mass spectrometry (Section 11F-1), and these results suggest that the parchment was created sometime between AD 1411 and AD 1468 (95% CL). Therefore, if the parchment is a modern forgery, the forger used an authentic piece of parchment to produce the map.

In 2013, a Scottish amateur historian, John Paul Floyd, conducted a series of Internet searches and claimed to have found proof that the Vinland map is a forgery. Floyd found references in two Spanish books dated before the map came to light again that described a fifteenth century manuscript that he identified as the “Speculum Historiale.” No map was reported in these books. The “Tartar Relation” was put on display in Madrid in 1892 with no map bound in it. Manuscripts for the Madrid exhibition were loaned from the Cathedral Church of Zaragoza, which was the subject of numerous thefts in the 1950s just prior to the reemergence of the Vinland map. Floyd also found details in the Vinland map that matched those of an engraving printed in 1782. He concluded that the map was a forgery.

The Analytical Perspective
The controversy regarding the Vinland map points out several important aspects of any analytical study. The first involves defining exactly the analytical sample and keeping it in mind during the determination. In our case specifically, several different samples could be defined: the parchment, a broad area containing the map’s ink and parchment, or small particles of the ink itself. In many analytical studies, we seek to homogenize a sample or average our results over a certain area.

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In others, however, it is important to look at the individual local heterogeneities in a sample. Our case study shows that scientists looking at small particles may come to conclusions about concentrations that are different from those of others looking at a broader spatial region. The spatial resolution of analytical techniques is also an important aspect of this study. We cannot hope to determine local effects or local concentrations with techniques that observe or average over large spatial regions. In our example, PIXE, although a sensitive trace analysis method, does not have the spatial resolution of many of the surface techniques used to study the map. Another aspect that our case study brings out is the difference between a technique that determines elemental composition and one that determines molecular composition. In our case, X-ray diffraction and Raman microscopy were used to determine conclusively the presence of TiO$_2$ in the ink. The other techniques used can establish the presence of specific elements and determine their quantities in the sampled volume. Finally, we should note that the Vinland map controversy is undoubtedly not over. If the map is a forgery, questions remain about how such an old parchment could be obtained. Likewise, if the map is real, the presence of TiO$_2$ in the particle size and particle distribution must be explained. New and more powerful analytical techniques will certainly be used in the future to help put to rest these and other remaining questions.$^7$

It is interesting that Yale University itself has chosen not to comment on the authenticity of the map, but merely to claim custodianship of this very interesting, but controversial document.