Chapter 42

Auger Electron Spectroscopy

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Summary

General Uses

- Identification of elements on surfaces of materials
- Quantitative determination of elements on surfaces
- Depth profiling by inert gas sputtering
- Phenomena such as adsorption, desorption, and surface segregation from the bulk
- Determination of chemical states of elements
- In situ analysis to determine the chemical reactivity at a surface
- Auger electron elemental map of the system

Common Applications

- Qualitative analysis through fingerprinting spectral analysis
- Identification of different chemical states of elements
- Determination of atomic concentration of elements
- Depth profiling
- Adsorption and chemisorption of gases on metal surfaces
- Interface analysis of materials deposited in situ on surfaces

Samples

State

Almost any solid can be analyzed.

Amount

Sample size depends on the instrument.

Preparation

Sample can be analyzed as it is. Because the analysis is done in high vacuum, some samples should be cleaned before loading in the chamber.

Analysis Time

Estimated time to obtain the survey spectrum from a sample varies from 1 to 5 min. High-resolution acquisition takes anywhere from 5 to 25 min per region of the spectrum and depends on the resolution required.

Limitations

General

- Analyzes conducting and semiconducting samples.
- Special procedures are required for nonconducting samples.
- Only solid specimens can be analyzed.
- Samples that decompose under electron beam irradiation cannot be studied.
- Quantification is not easy.

Accuracy

- The Auger spatial resolution common to most commercial instruments is of the order of 0.2 µm or less and is a function of analysis time.
- The sampling depth is about three monolayers.

Sensitivity and Detection Limits

The sensitivity is of the order of 0.3%.

Complementary or Related Techniques

- X-ray photoelectron spectroscopy.
- Atom probe field ion microscopy.

- Rutherford backscattering spectroscopy.
- Secondary ion mass spectrometry.
- Electron energy loss spectroscopy, X-ray absorption spectroscopy, Bremsstrahlung isochromat spectroscopy, inverse photoemission spectroscopy, and appearance potential spectroscopy. All provide complementary information on the unoccupied density of states.

Introduction

The Auger effect was discovered by Pierre Auger in 1925 while working with X rays and using a Wilson cloud chamber. Tracks corresponding to ejected electrons were observed along a beam of X rays (1).

Auger electron spectroscopy (AES) has now emerged as one of the most widely used analytical techniques for obtaining the chemical composition of solid surfaces. The basic advantages of this technique are its high sensitivity for chemical analysis in the 5- to 20-Å region near the surface, a rapid data acquisition speed, its ability to detect all elements above helium, and its capability of high-spatial resolution. The high-spatial resolution is achieved because the specimen is excited by an electron beam that can be focused into a fine probe. It was developed in the 1960s, when ultra-high vacuum (UHV) technology became commercially available (2, 3).

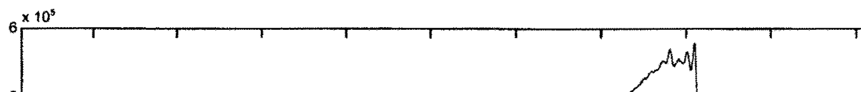
When an electron is ejected from an inner shell of an atom the resultant vacancy can be filled by either a radiative (X-ray) or nonradiative (Auger) process. In AES the atomic core levels are ionized by the incident electron beam and the resulting Auger electrons are detected with an electron spectrometer. These electrons form small peaks in the total energy distribution function, N(E) as shown in Fig. 42.1. The incident electrons entering a solid are scattered both elastically and inelastically. At the primary beam energy a sharp peak is observed, caused by electrons that have been elastically scattered back out of the specimen. For a crystalline specimen, these electrons carry the crystal structure information, which is exploited in techniques such as low-energy electron diffraction and reflection high-energy electron diffraction. At slightly lower energies there are smaller peaks due to electrons that have undergone characteristic energy losses. The information contained in this region is exploited in the technique of low-energy electron loss spectroscopy. At the other end of the spectrum (that is, on the low-energy side of the spectrum) there is a large peak corresponding to the secondary electrons. A few hundred eV above this peak is a loosely defined crossover energy. Above this point the distribution is dominated by backscattered primary electrons and below this point the secondary electrons form the major component. The crossover point depends on the primary beam energy and moves to higher energies with increasing primary beam energy. The peaks due to Auger electrons are superimposed on this distribution. The peaks become more pronounced by electronic spectral differentiation, which removes the large background.

The Auger process can be understood by considering the ionization process of an isolated atom under electron bombardment. The incident electron with sufficient primary energy, E_p, ionizes the core level, such as a K level. The vacancy thus produced is immediately filled by another electron from L_1. This process is shown in Fig. 42.2. The energy ($E_K - E_{L1}$) released from this transition can be transferred to another electron, as in the L_2 level. This electron is ejected from the atom as an Auger electron. The Auger electron will have energy given by

$$E = E_K - E_{L1} - E_{L2} \tag{42.1}$$

This excitation process is denoted as a KL_1L_2 Auger transition. It is obvious that at least two energy

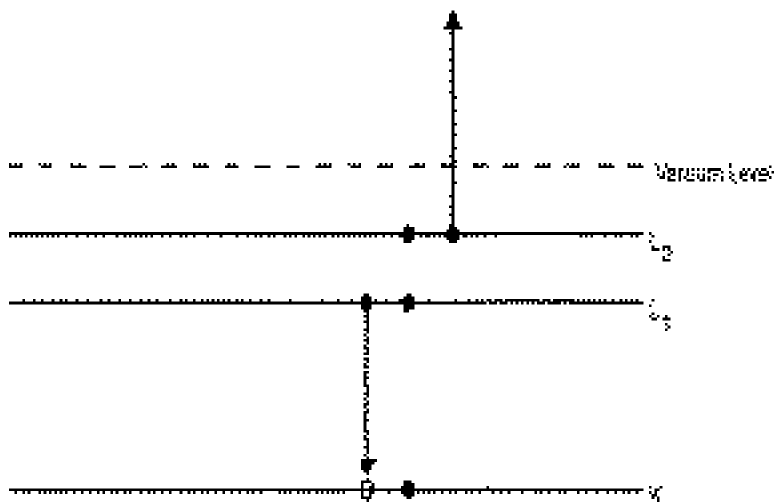
Figure 42.1 The energy distribution for an elemental Si sample. The $N(E)$ and dN/dE spectra are displayed. The energy of primary electrons is 20 keV. The spectra are taken using PHI 670xi system. *(Reproduced with permission from Physical Electronics, Eden Prairie, MN.)*



states and three electrons must take part in an Auger process. Therefore, H and He atoms cannot give rise to Auger electrons. Several transitions (KL_1L_1, KL_1L_2, LM_1M_2, etc.) can occur with various transition probabilities. The Auger electron energies are characteristic of the target material and independent of the incident beam energy.

Isolated Li atoms having a single electron in the outermost level cannot give rise to Auger elec-

Figure 42.2 Energy level diagram in an Auger process. Electron from L_1 drops into the K level with the emission of an L_2 electron.



trons. However, in a solid the valence electrons are shared and the Auger transitions of the type *KVV* occur involving the valence electrons of the solid. In general, the kinetic energy of Auger electrons originating from an ABC transition can be estimated from the empirical relation

$$E_{ABC} = E_A(Z) - E_B(Z) - E_C(Z + \quad) - {}_A \tag{42.2}$$

where ${}_A$ represents the work function of the analyzer material and Z is the atomic number of the atom involved. The term appears because the energy of the final doubly ionized state is somewhat larger than the sum of the energies for individual ionization of the same levels. Another expression for estimating Auger transition energies is

$$E_{ABC} = E_A(Z) - \frac{1}{2}[E_B(Z) + E_B(Z+1)] - \frac{1}{2}[E_C(Z) + E_C(Z+1)] - {}_A \tag{42.3}$$

The theoretical binding energies are discussed in the literature. A more detailed treatment of the Auger energies requires knowledge of a coupling in the final state that occurs between the two unfilled shells. For light elements the coupling scheme is pure *L–S*, for heavy elements *j–j*, and for elements in the middle of the periodic table intermediate coupling must be invoked.

The most pronounced Auger transitions observed in AES involve electrons of neighboring orbitals, such as *KLL*, *LMM*, *MNN*, *NOO*, *MMM*, and *OOO* families. The most prominent *KLL* transitions occur from elements with $Z = 3$ to 14, *LMM* transitions for elements with $Z = 14$ to 40, *MNN* transitions for elements with $Z = 40$ to 79, and *NOO* transitions for heavier elements. The Auger peak is commonly identified by the maximum negative peak in the $dN(E)/dE$ versus E spectrum.

How It Works

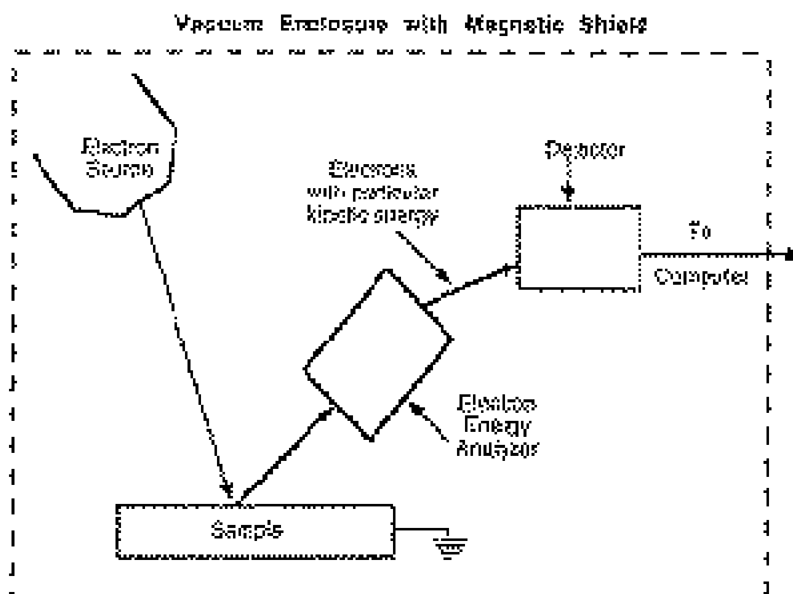
The schematic of the experimental arrangement for basic AES is shown in Fig. 42.3. The sample is irradiated with electrons from an electron gun. The emitted secondary electrons are analyzed for energy by an electron spectrometer. The experiment is carried out in a UHV environment because the AES technique is surface sensitive due to the limited mean free path of electrons in the kinetic energy range of 20 to 2500 eV. The essential components of an AES spectrometer are

- UHV environment
- Electron gun
- Electron energy analyzer
- Electron detector
- Data recording, processing, and output system

UHV Environment

The surface analysis necessitates the use of a UHV environment (4) because the equivalent of one monolayer of gas impinges on a surface every second in a vacuum of 10^{-6} torr. A monolayer is adsorbed on the surface of the specimen in about 1 second at 10^{-6} torr. Contamination of the specimen surface is critical for highly reactive surface materials, where the sticking coefficient for most residual gases is very high (near unity). The sticking coefficient for surfaces that are passivated through exposure to air is very low. The vacuum requirements are much less stringent for such samples. Generally, the background

Figure 42.3 Schematic arrangement of the basic elements of an Auger electron spectrometer.



pressure is reduced to the low 10^{-10}-torr range in order to minimize the influence of residual gases in surface analysis measurements.

Until 1960 the advancements in surface analysis techniques were inhibited by two difficulties: constructing an apparatus suitable for operation in a UHV environment and production and measurement of UHV. In the early 1960s the glass enclosures were replaced by standardized, stainless steel hardware. The UHV environment could be easily achieved by pumping a stainless steel chamber with a suitable combination of ion, cryo, turbo molecular, or oil diffusion pumps (5). It is also possible to bake these systems (up to 200 °C) to achieve UHV conditions.

Electron Gun

The nature of the electron gun used for AES analysis depends on a number of factors:

- The speed of analysis (requires a high beam current)
- The desired spatial resolution (sets an upper limit on the beam current)
- Beam-induced changes to the sample surface (sets an upper limit to current density)

The range of beam currents normally used in AES is between 10^{-9} and 5×10^{-6} A. The lower current gives high spatial resolution whereas the higher current may be used to give speed and high sensitivity where spatial resolution is of little concern. In certain samples the high current used may induce surface damage to the specimen and should be avoided.

The electron gun optical system has two critical components: the electron source and the focusing forming lens. In most cases the electron source is thermionic but for the highest spatial resolution the brighter field emission source may be used. The field emission sources have problems of cost and stability and are therefore limited in their use. The commonly used thermionic sources are as follows:

- A tungsten hairpin filament. This filament has a life of about 100 hr due to repeated exposure to air. As a result of introduction of a load-lock system in the modern Auger electron spectrometers the average filament life exceeds 1000 hr.
- Lanthanum hexaboride (LaB_6). This source is brighter than tungsten but is more expensive and a little more complicated to operate.

The electron lenses used to focus the beam may be either magnetic or electrostatic. The magnetic lenses have low aberrations and therefore give the best performance. However, these lenses are complicated and expensive. The electrostatic lenses are easier to fit in a UHV system. For spatial resolution of the order of a micron, a 10 keV electrostatic gun could be easily used. For spatial resolution below 100 nm electromagnetic lenses are used.

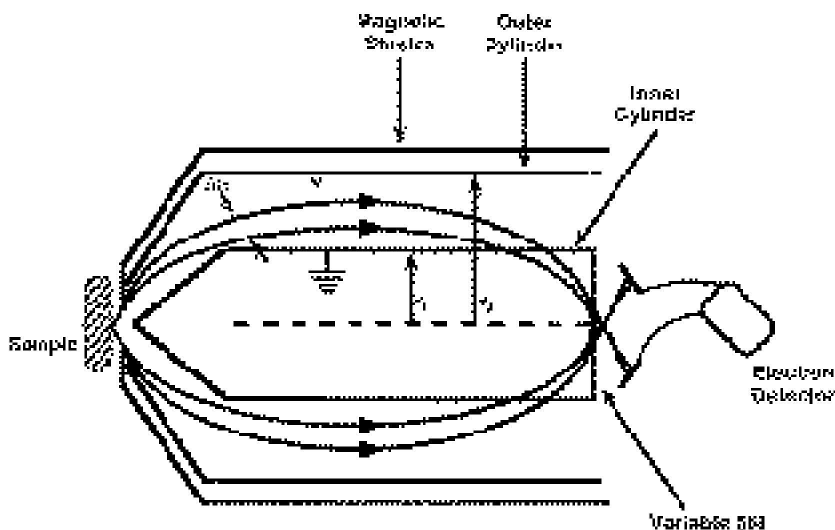
Electron Energy Analyzer

The function of an electron energy analyzer is to disperse the secondary emitted electrons from the sample according to their energies. An analyzer may be either magnetic or electrostatic. Because electrons are influenced by stray magnetic fields (including the earth's magnetic field), it is essential to cancel these fields within the enclosed volume of the analyzer. The stray magnetic field cancellation is accomplished by using Mu metal shielding. Electrostatic analyzers are used in all commercial spectrometers today because of the relative ease of stray magnetic field cancellation (6).

The Cylindrical Mirror Analyzer (CMA)

The schematic of the CMA is shown in Fig. 42.4. The CMA consists of two coaxial cylinders with a negative potential (V) applied to the outer cylinder (with radius r_2) and ground potential applied to the inner cylinder (with radius r_1). The sample and the detector are located along the common axis of the cylinders. Electrons emitted from the sample at an angle relative to the analyzer axis pass through the

Figure 42.4 Cross-sectional view of the single-pass CMA. *V* represents the voltage applied to the outer cylinder. The inner cylinder is grounded.



mesh-covered aperture in the inner cylinder. Only electrons that have a definite energy E_0 are deflected by the outer cylinder potential through the second mesh-covered aperture to a focus on the axis, where they pass into a detector. The focal condition is given by the relation

$$E_0 = \frac{KeV}{\ln(r_2/r_1)} \tag{42.4}$$

where e is the electron charge and K a constant. A variety of entrance angles, , can exist. However, in the special case where = 42°18 the CMA becomes a second-order focusing instrument. At this focus the electrons from a very wide range of s meet at the focal point. For this case the constant $K = 1.31$. Under this condition, the distance between the source and the focus is $6.1r_1$. All the CMA parameters scale with the radius r_1 of the inner cylinder. Once this is fixed, other parameters follow automatically. The energy resolution of the CMA is written in terms of the base resolution E_B, defined as

$$\frac{E_B}{E} = \frac{0.36w}{r_1} + 5.55(\quad)^3 \tag{42.5}$$

where w is the slit width (equal at the entrance and exit) and is the spread of the angle about (Fig. 42.4). The CMA has a very large acceptance angle, comprising a full cone about the spectrometer axis. This gives a high sensitivity and reduces the dependency of the signal on specimen topography (6). The electron gun may be incorporated into the inner cylinder, making the design of the system a compact unit. Because of its superior signal-to-noise capability, the CMA is used almost exclusively for modern AES apparatus.

Concentric Hemispherical Analyzer (CHA)

The CHA consists of two hemispherical concentric shells of inner radius r_1 and outer radius r_2, as shown in Fig. 42.5. A potential difference, V, is applied between the two surfaces such that the outer sphere is negative and the inner positive. Between the spheres there is an equipotential surface of radius r_0. The entrance and exit slits lie on a diameter and are centered at a distance r_0 from the center of curvature. The base resolution is given by

$$\frac{E}{E} = \frac{w}{r_0} + \quad ^2 \tag{42.6}$$

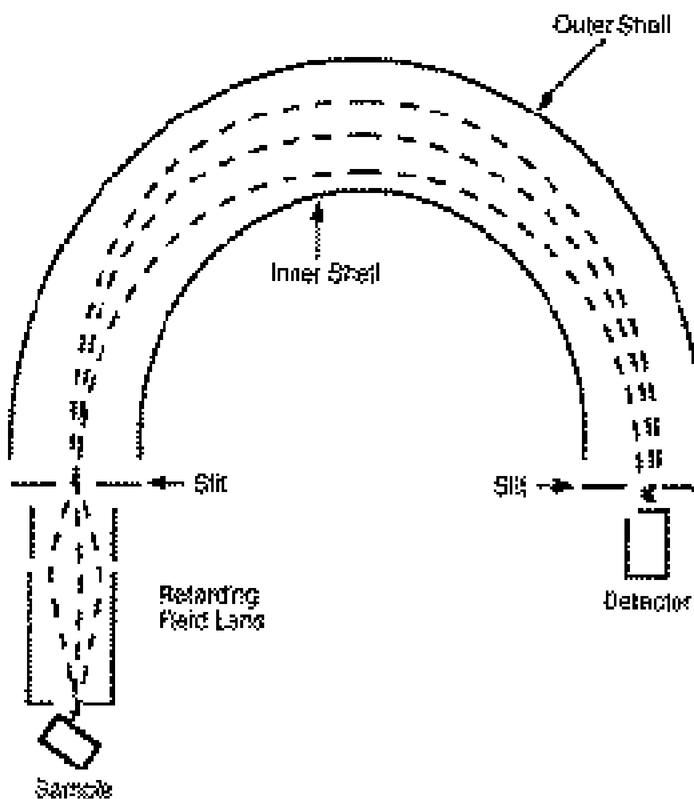
where is the entrance angle into the CHA and w is the width of the slit.

In the CHA, the sample must be placed at the slit of the analyzer. The working space between the sample and the analyzer is therefore increased by the use of an electron lens. The lens system takes electrons from the sample and injects them into the analyzer. The effective solid angle thus becomes comparable to that of a CMA. The main advantages the CHA has over the CMA are much better access to the sample and the ability to vary analyzer resolution electrostatically without changing physical apertures. Generally, a large entrance angle yields increased sensitivity. However, to reach a compromise between sensitivity and resolution it is a common practice to choose such that $^2 = w/2r_0$.

Electron Detector

Having passed through the analyzer, the secondary electrons of a particular energy are spatially separated from electrons of different energies. Various detectors are used to detect these electrons.

Figure 42.5 Cross-sectional view of the CHA with input lens. The outer sphere has a negative voltage and the inner sphere has a positive voltage. The dashed lines indicate the trajectories followed by the emitted electrons. The central dashed line represents an equipotential surface. The entrance and the exit slits lie on a diameter and are centered at the mean radius from the center of curvature.



Single-Channel Detector (SCD)

The detector used in conventional instrumentation is a channel electron multiplier. It is an electrostatic device that uses a continuous dynode surface (a thin-film conductive layer on the inside of a tubular channel). It requires only two electrical connections to establish the conditions for electron multiplication. The output of this detector consists of a series of pulses that are fed into a pulse amplifier/discriminator and then into a computer. The advantage of such a detector is that it can be exposed to air for a long time without damage. It counts electrons with a high efficiency, even at essentially zero kinetic energy, and the background is 0.1 count/sec or lower. The only drawback is that a high count rate (> 10^6 counts/sec) causes a saturation effect.

Multichannel Detector (MCD)

A multiple detection system can be added at the output of the analyzer. The system may be in the form of a few multiple, parallel, equivalent detector chains or position-sensitive detectors spread across the whole of the analyzer output slit plane. Such an arrangement can be devised in a number of ways (7): using phosphor screens and TV cameras, phosphor screens and charge-coupled devices, resistive anode networks, or discrete anodes.

Data Recording, Processing, and Output System

The Auger electrons appear as peaks on a smooth background of secondary electrons. If the specimen surface is clean, the main peaks would be readily visible and identified. However, smaller peaks and those caused by trace elements present on the surface may be difficult to discern from the background. Because the background is usually sloping, even increasing the gain of the electron detection system and applying a zero offset is often not a great advantage. Therefore, the Auger spectra are usually recorded in a differential form. In the differential mode it is easy to increase the system gain to reveal detailed structure not directly visible in the undifferentiated spectrum (Fig. 42.1). The most distinctive characteristic of an Auger peak in the differential spectrum is the negative going feature at the high-energy side of the peak. The minimum of this feature represents the point of maximum slope of the parent peak. By convention, this feature is used to define the energy of the transition. For systems that record data in an analog mode, the differential Auger spectrum has the following advantages over the direct undifferentiated spectrum:

- The background is zero away from the peaks, so the amplifier gain can be easily changed.
- The differential peaks are sharper than the direct peaks. This provides a reproducible energy reference point.
- The peak-to-peak height provides a convenient measure of peak intensity.

At present, the data in commercial instruments are acquired digitally and can be presented in either analog or digital mode. The majority of AES instruments are controlled by computer. Major functions of the computer control system are to acquire and store data efficiently.

A conventional Auger electron spectrometer uses a lock-in amplifier. The oscillator in this amplifier superimposes a sinusoidal modulation (frequency 10 to 20 kHz) on the potential applied to the outer cylinder of the analyzer. The AC component of the signal is decoupled from the multiplier high voltage and detected in the lock-in amplifier. The output is then fed to an x–y recorder. The amplitude of the modulation is chosen to yield a compromise between sensitivity and resolution. A typical modern Auger electron spectrometer collects the data in the $N(E)$ versus E integral mode. The data are then mathematically differentiated using computer software to yield $dN(E)/dE$ versus E Auger spectra (Fig. 42.1).

The CMA or the CHA is used in the constant retardation ratio (CRR) mode in AES, which determines the resolution. Therefore, while scanning a spectrum the optimum modulation voltage will change. High-energy peaks generally require high modulation. Although a constant modulation voltage may be used throughout the scan when recording a spectrum, some instruments can make the modulation proportional to the analyzer energy so that the ratio of modulation to analyzer resolution is constant. This point should be considered while comparing the Auger spectra from different instruments.

What It Does

The high surface sensitivity of AES is due to the limited mean free path of electrons in the kinetic energy range 20 to 3000 eV. Auger electrons, which lose energy through plasma losses, core excitations, or interband transitions, are removed from the observed Auger peaks and contribute to the nearly uniform background on which the Auger peaks are superimposed. Because phonon losses are small compared with the natural width of Auger peaks, they do not affect the Auger escape depth. Hence the Auger yield is not dependent on the sample temperature.

Because the Auger transition probability and Auger electron escape depth are independent of the incident electron beam energy, E_p, the dependence of the Auger peak amplitude on E_p is governed completely by the ionization cross-section of the initial core level. Ionization occurs primarily by the incident electrons during their initial passage through the escape depth region (5 to 25Å thick). The backscattered primary electrons can also contribute to the Auger yield when the incident beam energy is substantially greater than the binding energy of the core level involved.

Variables Involved in the Production of Auger Electrons

An inner shell vacancy can be produced through a variety of methods, such as irradiation with electrons and X rays or bombardment with argon ions. Electron impact is usually used for producing Auger lines for analytical purposes. It provides an intense beam that can be brought to a fine focus. X-ray irradiation has its value in providing less radiation damage and better peak-to-background ratios.

High-Energy Satellite Lines

High-energy satellite structures have been observed in the Auger spectra of solids. The presence of such a structure has been interpreted as being due to plasmon gains. It is also believed that the high-energy lines arise from an initial multiple ionization or perhaps resonance absorption. The question of Auger satellites in solids is still under active consideration.

Characteristic Energy Losses

Electrons ejected from a solid can suffer characteristic energy losses, usually due to plasmon losses (see p. 820). Because Auger spectra are generally rather complex and often not well resolved and are spread over a considerable range of energies, peaks from characteristic energy losses are much more difficult to disentangle from the normal Auger spectrum than is usual in the case of photoelectron spectroscopy. Also, the surface contamination will alter the nature of the characteristic loss peaks considerably.

Charging in Nonconducting Samples

Charging as a result of an impinging beam of electrons on a nonconductor is a particularly serious problem in Auger spectroscopy. Often the charging and the resulting nonuniform surface potential prevent a meaningful Auger spectrum. However, this problem often can be overcome by choosing the proper angle of incidence and the energy of the primary electron beam. The important factor is the ratio (the number of secondary electrons leaving the target to the number impinging on the target). If $= 1$, the charge is stabilized. If < 1, the charge is negative, and if > 1, it is positive. The choice of impact energy is also important. The factor becomes less than 1 if the energy of the impinging beam of electrons is either too large or too small. Generally, the primary beam energy lies between 1.5 and 3.0 keV depending on the application and the resolution required.

Scanning Auger Microscopy

With a finely focused electron beam for Auger excitation, AES can be used to perform two-dimensional

surface elemental analysis (8). In this setup, the electron gun operation is similar to that used in conventional scanning electron microscopy (SEM). A set of deflection plates raster the electron beam on the sample. The scanning Auger system can be used to perform point Auger analysis with a spatial resolution on the order of 3 μm by using a minimum beam size of about 3 μm or to obtain a two-dimensional mapping of the concentration of a selected surface element. The low-energy secondary electron or absorbed current displays are used to monitor the surface topography and locate the areas of interest on the sample. To obtain an elemental map, the intensity of the display is controlled by the magnitude of the selected Auger peak. The most negative excursion in the differentiated Auger spectrum is taken as a measure of the Auger current. A two-dimensional elemental map of the surface is obtained by setting the pass energy of the electron spectrometer at the negative excursion of the Auger peak of interest, while the output of the lock-in amplifier is used to modulate the intensity of the record display as the electron beam is rastered across the sample. Three-dimensional analysis of the surface of a sample can be obtained by using a combination of scanning Auger microscopy and sputter etching.

Analytical Information

Qualitative

Identification of Elements

Elements of an unknown sample can be identified easily by recording the AES spectrum over a wide range (generally 0 to 2000 eV). The kinetic energies of the intense peaks present in the spectrum are then compared with the elemental values.

Chemical Effects

The AES peaks involving valence electrons carry significant information about the chemical state of the surface. The chemical effect may appear as a simple peak shift, a change in peak shape, or both. In effect the valence of molecular orbital structure is convoluted into the Auger peak structure. Usually X-ray photoelectron spectroscopy is the preferred technique for investigating the chemistry of the surface as photoelectron peaks are sharper and chemical effects are more easily interpreted than in the case of the corresponding Auger peaks. The interpretation is limited by the beam-induced effects. Many compounds, particularly oxides, are readily decomposed under electron irradiation. Therefore, the current density must be limited so that the specimen damage is acceptable in the time taken to make the measurement.

Quantitative

The incident electron beam, on striking the solid, penetrates with both elastic an inelastic scattering and ionizes atoms in the depth of 1 to 2 μm depending on the density of the material. Therefore, quantitative analysis from the observed AES signal depends on the average concentration of the element and how it is distributed within the first few atomic layers of the surface. The sensitivity to Auger electrons in the outer surface layer is greater than that to electrons originating from subsurface layers because of strong inelastic scattering. The Auger electron source volume generated by an incident electron beam of diameter d and energy E_p produces an Auger current of an ABC Auger transition in an element x,

given by

$$I_x(ABC) = \int_{E_A}^{E_p} \int_0 I_p(E, Z) \; _x(E, E_A) N_x(Z) \; _x(ABC) \exp\left[-\frac{Z}{} \; d \;\; dEdZ \right] \tag{42.7}$$

where $I_p(E,Z)$ is the excitation electron flux density, $_x(E, E_A)$ is the ionization cross-section of the core level A, $N_x(Z)$ is the atomic density of the element x at a depth Z from the surface, exp(–Z/) is the Auger electron probability for escape, is mean free path of the electrons and is a function of depth or the matrix, and $_x(ABC)$ is the ABC Auger transition probability factor (9). In order to simplify this equation, it is assumed that the chemical composition is homogeneous over a depth of region for which the escape probability has a significant value. Also, the excitation flux density can be separated into two components:

$$I_p(E, A) = I_p + I_B(E, Z) \tag{42.8}$$

where $I_B(E,Z)$ is the excitation flux due to backscattered primary electrons and I_p is the primary electron current. With these assumptions, the detected Auger current can be expressed as

$$I_x(ABC) = I_p T N_x(Z) \; _x(ABC) \quad _x(E_p, E_A) \quad (1 + R_B) \tag{42.9}$$

where R_B is the backscattering factor and T is the energy-dependent transmission of the analyzer.

Thus, knowing the ionization cross-section, the Auger yield, and the backscattering factor, accurate quantitative analysis can be carried out using Eq. (42.9). In addition, the absolute Auger current must be accurately measured. A further complication is surface roughness, which generally reduces the Auger yield relative to flat surface. Because these requirements are generally not met for routine Auger analysis, quantitative analysis using first principles is not considered practical. Two methods are generally used for quantitative AES analysis.

Measurement with External Standards

In this method, the Auger spectra from the specimen of interest are compared with that of a standard with a known concentration of the element of interest. The concentration of element x in the unknown specimen, N_x^u is related to that in the standard, N_x^s using Eq. (42.9) and is given by

$$\frac{N_x^u}{N_x^s} = \frac{I_x^u}{I_x^s} \frac{^s}{^u} \frac{1 + R_B^s}{1 + R_B^u} \tag{42.10}$$

This method has an advantage in that ionization cross-section and Auger yield data are not required, and the Auger current is reduced to a relative measurement.

When the unknown sample composition is similar to that of the standard, the escape depth and backscattering factor are also eliminated from Eq. (42.10). The quantitative analysis thus reduces to the measurement of signal amplitude. The only requirement is that the measurements be made under identical experimental conditions. When the composition of the standard is not similar to that of the unknown sample, the influence of matrix on both the backscattering factor and the escape depth must be considered in detail.

The backscattering factor can be obtained by comparing Auger yield against E_p curves with theoretical ionization cross-section versus E_p curves or with Auger yield versus E_p data from gaseous specimens where the backscattering factor has negligible value.

Measurements with Elemental Sensitivity Factors

In quantitative AES analysis it is assumed that the composition of the sample in the near surface re-

gion is homogeneous. Quantitative analysis involving the use of elemental sensitivity factors is less accurate but is highly useful. The atomic concentration (C) of an element x in a sample is given by

$$C_x = \frac{I_x / S_x}{(I_i / S_i)} \tag{42.11}$$

where I_x is the intensity of the Auger signal from the unknown specimen and S_i is the relative sensitivity of pure element i. The summation is for the corresponding ratios for all other elements present in the sample. Because it neglects variations in the backscattering factor and escape depth with material, this method is semiquantitative. The main advantages of this method are the elimination of standards and insensitivity to surface roughness. In order to avoid the need for a large number of pure elemental standards, the signal from the specimen is compared with that from a pure silver target. Thus, the elemental sensitivity factors relative to silver can be conveniently used in Eq. (42.11). Because the data are finally represented in the differential mode, it is necessary to base the sensitivity factors on the peak-to-peak height. This is valid only when the peak shape is invariant with the matrix. The atomic concentration of element x is then given by

$$C_x = \frac{I_x}{I_{Ag} S_x D_x} \tag{42.12}$$

where I_x is the peak-to-peak amplitude of the element x from the test specimen, I_{Ag} is the peak-to-peak amplitude from the Ag standard, and D_x is a relative scale factor between the spectra for the test specimen and silver. If the lock-in amplifier sensitivity (L_x), modulation energy ($E_{m,x}$), and primary beam current ($I_{p,x}$) settings used to obtain the test spectrum are different from those of the Ag spectrum (that is, L_{Ag}, $E_{m,Ag}$, and $I_{p,Ag}$) the relative scale factor is

$$D_x = \frac{L_x E_{m,x} I_{p,x}}{L_{Ag} E_{m,Ag} I_{p,Ag}} \tag{42.13}$$

Depth Profiling

Depth profiling is one of the most important applications of AES because it provides a convenient way of analyzing the composition of thin surface layers. It is a destructive technique. In this technique the sample is eroded by ion sputtering. The sample is bombarded with ions accelerated in an ion gun to an energy in the range 1 to 4 keV. As these energetic ions strike the sample a small amount of energy is transferred to the surface atoms, which causes them to leave the sample. The ion beam is rastered on the surface for a known time to remove a uniform layer of the sample. Under controlled conditions the layer removed can be calculated. The residual surface is then analyzed by AES, giving the depth distribution of different species in the sample. Inert gases (usually Ar) are commonly used as the ion sources (10).

Applications

Auger electron spectroscopy is a very powerful surface analytical technique that has found applications in many fields of solid-state physics and chemistry. AES is used to monitor the elemental composition of surfaces during physical property measurements. Several phenomena such as adsorption, desorption,

surface segregation from the bulk, measurement of diffusion coefficients, and catalytic activity of surfaces have been investigated using AES. It has also been used to study the surface compositional changes in alloys during ion sputtering. Chemical properties such as corrosion, stress corrosion, oxidation, and catalytic activity and mechanical properties such as fatigue, wear, adhesion, resistance to deformation processes, and surface cracking depend on surface properties. Similarly, grain boundary chemistry influences mechanical properties such as low- and high-temperature ductility and fatigue, chemical properties such as intergranular corrosion and stress corrosion, and electrical properties. AES has been used to relate surface and grain boundary chemistry to properties of materials. AES has proved to be extremely valuable compared to most other techniques, which are limited by either large sampling depth or poor sensitivity. The main advantages of AES can be summarized as follows:

- Spatial resolution is high.
- Analysis is relatively rapid.
- Surface or subsurface analysis can be performed.
- It is sensitive to light elements (except H and He).
- It provides reliable semiquantitative analysis.
- Chemical information is available in some cases.

The disadvantages of this technique are as follows:

- Insulators are difficult to study due to surface charging.
- Surface may be damaged by the incident electron beam.
- Precise quantitative analysis may require extensive work.
- Sensitivity is modest (0.1 to 1 atom%).
- Depth profiling by ion sputtering or sectioning is destructive.

AES is expected to find increasing applications in many areas of science and technology requiring detailed information on elemental identification, surface composition, oxidation states, and chemical bonding.

Nuts and Bolts

Relative Costs

Vendors for Instruments and Accessories

Comstock, Inc.
1005 Alvin Weinberg Dr.
Oak Ridge, TN 37830
phone: 423-483-7690
fax: 423-481-3884
email: salesinfo@comstockinc.com
Internet: http://www.comstockinc.com

Kurt J. Lesker Company
1515 Worthington, Ave.
Clairton, PA 15025
phone: 800-245-1656
fax: 412-233-4275
Internet: http://www.lesker.com

Physical Electronics
6509 Flying Cloud Dr.
Eden Prairie, MN 55344
phone: 612-828-6100
fax: 612-828-6322

Vacuum Generators-Microtech
Bellbrook Business Park
Bolton Close, Uckfield
East Sussex, United Kingdom TN22IQZ
phone: 44 (0) 1825 761077
fax: 44 (0) 1825 768343
e-mail: sales-microtech@vacgen.fisons.co.uk

Vendors	Model and Description	Accessories	Cost
PHI	Model 680 Scanning Auger microprobe AES, SIMS, RGA, EDS	CMA, MCD 25-kV field emission Electron gun Multiple analysis points for simultaneous profiles Fracture stage	$$$$
PHI	Model 5600 Multitechnique system AES, XPS, ISS, SIMS	CHA, MCD, IG Sample manipulator (single or multiple) with x-, y-, and z-translations and tilt	$$$$
Comstock, Inc.	Model 1951 Auger assembly	Retarding and focusing lens Electrostatic energy analyzer 50 eV to 5 kV electron source with focusing lens and x, y deflection Microchannel plate detector	$
VG Microtech	VG 100AX Multitechnique AES, XPS	100-mm CHA Mu-metal analyzer housing Any orientation of sample possible Mounting flange: FC64 (114 mm/4.5-in. outside diameter)	$$
Kurt J. Lesker	CHA Electron sources Data acquisition software		$$, $$$ $ $

$ = 10,000 to 25,000, $$ = 25,000 to 50,000, $$$ = 50,000 to 100,000, $$$$ = 500 to 800 k$.
IG = ion gun (for sputter etching), RGA = residual gas analyzer, EDS = energy dispersive spectroscopy, ISS = ion scattering spectroscopy

Required Level of Training

The operation of the instrument requires a good knowledge of vacuum pumps. An understanding of the computers and familiarity with the software are essential because the instruments are computer-controlled. Extensive training is required for each kind of instrument as these instruments are designed differently. The design of the experiment for the sample to be analyzed requires knowledge of the sample chemistry. A graduate-level knowledge regarding the spectroscopy, atomic physics, solid-state physics, and chemistry is required for understanding and interpreting the spectra.

Service and Maintenance

Routine adjustment and calibration of the energy analyzer are needed. The vacuum pumps need maintenance. Care must be taken to load only samples that are vacuum compatible, that is, ones that do not outgas in vacuum. The detection of malfunctioning electronic components is facilitated by plug-in cards. The detector is expensive and cumbersome to replace. The filament of the electron gun must be replaced often. Due to the design of the modules, most of these replacements must be carried out by trained personnel. The electron optics and the ion gun focusing components are not normally aligned

on-site. They need regular attention to ensure proper operation of the instrument. Most companies offer service contracts but they are expensive.

Suggested Readings

BRIGGS, D., AND M. P. SEAH, EDS., *Practical Surface Analysis by Auger and X-ray Photoelectron Spectroscopy.* New York: Wiley, 1983.

CHILDS, K. D., AND OTHERS, in C. L. Hedberg, ed. *Handbook of Auger Electron Spectroscopy.* Eden Prairie, MN: Physical Electronics Publishing, 1995.

CZANDERNA, A. W., in S. P. Wolsky and A. W. Czanderna, eds. *Methods of Surface Analysis.* Amsterdam: Elsevier, 1988.

ERTL, G., AND J. KUPPERS, *Low Energy Electrons and Surface Chemistry.* Deerfield Beach, FL: VCH, 1985.

MCGUIRE, G. E., AND OTHERS, "Surface Characterization," *Analytical Chemistry*, 65 (1995), 199R.

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