

Surface Analysis

14.1 INTRODUCTION

The term **surface analysis** is used to mean the characterization of the chemical and physical properties of the **surface layer** of **solid** materials. The surface layer of a solid often differs in chemical composition and in physical properties from the bulk solid material. A common example is the thin layer of oxide that forms on the surface of many metals such as aluminum upon contact of the surface with oxygen in air. The thickness of the surface layer that can be studied depends on the instrumental method. This layer may vary from one atom deep, an atomic **monolayer**, to 100–1000 nm deep, depending on the technique used. Surface analysis has become increasingly important because our understanding of the behavior of materials has grown. The nature of the surface layer often controls important material behavior, such as resistance to corrosion. The various surface analysis methods reveal the elements present, the distribution of the elements, and sometimes the chemical forms of the elements in a surface layer. Chemical speciation is possible when multiple surface techniques are used to study a sample.

Surface analysis has found great use in understanding important fields such as materials characterization of polymers, metals, ceramics, and composites; corrosion; catalysis; failure analysis; and the functioning and failure of microelectronics and magnetic storage media. In the pharmaceutical industry, it can be used to investigate the multilayered materials and coatings used in packaging and time-release products. In medicine, it has been used to study bone structure and the surface of teeth, indicating why SnF_2 fights tooth decay, for example, and to study the biocompatibility of metallic and polymeric implantable devices.

Spectroscopic surface analysis techniques are based on bombarding the surface of a sample with a beam of X-rays, particles, electrons, or other species. The bombardment of the surface by this **primary beam** results in the emission or ejection of X-rays, electrons, particles, and the like from the sample surface. This emitted beam is the **secondary beam**. The nature of the secondary beam is what provides us with information about the surface. A number of techniques have been developed for surface analysis but only the most common will be discussed in this chapter. The names of these spectroscopic techniques and the primary and secondary beams used for each technique are listed in Table 14.1. These techniques are frequently quite different in physical approach, but all provide information about solid surfaces. Applications of these surface analysis techniques are presented in Tables 14.2 and 14.3.

The student should be aware that there is another class of surface analysis instruments based on analytical microscopy, including scanning electron microscopy, transmission electron microscopy, atomic force microscopy, and scanning tunneling microscopy. A discussion of these microscopy techniques is beyond the scope of this chapter. Most industrial materials characterization laboratories will have some combination of electron spectroscopy, X-ray analysis, surface mass spectrometry, and analytical microscopy instrumentation available, depending on the needs of the industry.

Table 14.1 Selected Spectroscopic Techniques for Surface Analysis

Abbreviated Name	Full Name	Primary Beam	Secondary Beam
XPS (ESCA)	X-ray photoelectron spectroscopy (electron spectroscopy for chemical analysis)	X-rays	Electrons
AES	Auger electron spectroscopy	Electrons	Electrons
ISS	Ion scattering spectroscopy	Ions	Ions
SIMS	Secondary ion mass spectrometry	Ions	Ions
EM, EPMA	Electron microprobe, electron probe microanalysis	Electrons	X-rays

Table 14.2 Surface Analysis Applications by Industry

Industry	Application
Microelectronics	Composition of deposited layers
	Thickness of deposited layers
	Defect characterization
	Particle identification
	Process residue identification
Magnetic data storage media	Lubricant type and thickness
	Carbon overcoat composition
	Magnetic layer composition
	Magnetic layer thickness
	Defect/contamination identification
Optical coatings	Failure analysis
	Coating composition and thickness
	Adhesion layers
Automobile industry	Composition of surface defects
	Paint adhesion
	Paint weathering
	Catalyst poisoning
Pharmaceutical industry	Lubricant chemistry
	Contamination identification
	Distribution of active ingredients in tablets
	Drug distribution in time-release coatings
Polymer industry	Patent infringement monitoring
	Surface coatings
	Surface chemistry
Biotechnology	Multilayer composition and thickness
	Contamination identification
	Correlation of surface chemistry and biocompatibility
	Biosensor development
	Promotion of cell growth on surfaces

Source: Information in table provided by Physical Electronics, Inc., Eden Prairie, MN, www.phi.com.

14.2 ELECTRON SPECTROSCOPY TECHNIQUES

In the discussion on X-rays (Chapter 8), it was mentioned that the source of an X-ray photon is an atom that is bombarded by high-energy electrons or photons. This can displace an inner shell electron, which is ejected from the atom, leaving an ion with a vacancy in an inner shell (Figure 14.1). An electron from an outer shell then drops into the inner shell and an X-ray photon is emitted simultaneously. The energy of the photon is equal to the difference between the energy of the orbital the electron was

Table 14.3 Specific Surface Analysis Applications

Type of Analysis	Applications
Failure analysis	Surface contamination Particle identification
Adhesion failure	Fracture due to grain boundary impurities Adhesive failure Cohesive failure
Corrosion	Silicone surface contamination Thickness and composition of surface oxides Identification of corrosive elements (e.g., Cl) Passivation layer composition and thickness
Surface cleanliness	Detergent residue identification Solvent residue identification Type and amount of surface impurities
Reverse engineering	Composition and identification of competitors' materials
Semiconductor wafers	Analysis of complete surface of wafer (up to 300 mm) Defect/particle identification Thin-film composition
Hot sample stage analysis (up to 700°C)	Volatility of surface components Temperature dependence of surface chemistry Migration of bulk components to surface
Cold sample stage analysis (to -100°C)	Surface species that are volatile at RT in ultrahigh vacuum (UHV) Hydrated surfaces Samples that outgas at RT in UHV

Source: Information in table provided by Physical Electronics, Inc., Eden Prairie, MN, www.pha.com.

Note: RT, room temperature; UHV, ultrahigh vacuum.

in originally and that of the one to which it descends. The energy levels of these two inner orbitals are almost independent of the chemical form of the atom, combined or otherwise. However, we know from Chapter 5 that the energy of a valence electron varies with the chemical form and chemical environment of the combined atom and provides the basis for ultraviolet (UV) absorption analysis. This variation is reflected as well in the energies of the inner shell electrons, but the changes in energy

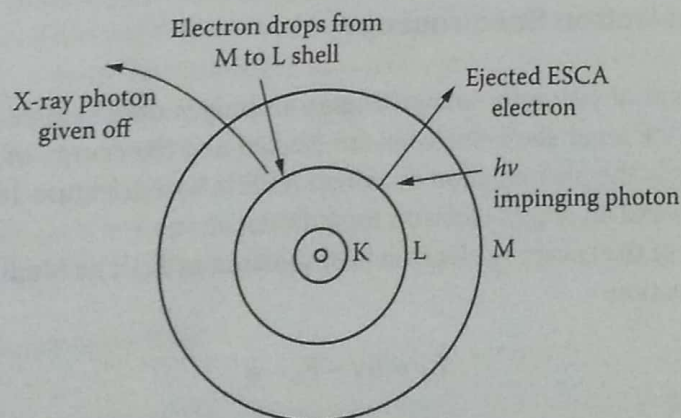


Figure 14.1 An impinging photon ejecting an inner shell XPS (or ESCA) electron. The kinetic energy of the ejected XPS (ESCA) electron, E_k , is related to the binding energy of the electron in the atom, E_b . The binding energy is characteristic of the element. An X-ray photon of energy $E_M - E_L$ is emitted in the process. An alternative process to the emission of the X-ray photon is emission of an Auger electron, which is shown in the next figure.

involved are very small compared with the energy of the emitted X-rays themselves. The slight differences in X-ray wavelength are extremely difficult to measure, since they are such a small fraction of the nominal wavelength of the X-rays generated. It is therefore normally accepted that the energies of the emitted X-rays are independent of the chemical form of the generating atoms and differences in energy cannot be observed except under very high resolution. X-ray fluorescence (XRF), as was discussed in Chapter 8, is therefore an elemental analysis technique. It tells us what elements are present, but does not give information on the oxidation state of the element or the chemical species present.

However, the energy E of the original electron ejected from the atom is the difference between the energy E_1 of the impinging electron (or photon) and the energy E_b required to remove the electron from the atom, that is, $E = E_1 - E_b$. The energy E_b will be slightly different depending on the chemical environment of the atom. We can determine this small difference by making the energy E_1 of the impinging electron just slightly greater than the energy E_b required to eject the electron. The residual energy E of the emitted electron will then be small, but any variation in E_b will produce a larger relative variation in the energy E of the emitted electron. In this way, small differences in E_b can be measured. For example, if the energy of the K_α line for Al is 1487 eV, the effect of chemical environment may change this by 2 eV, resulting in Al K_α at 1485 eV. The relative shift ($2/1487$) is slight, and the 1485 eV X-ray line would be difficult to distinguish from the original 1487 eV line in X-ray emission and XRF. If the energy of the *impinging electrons* generating X-rays is 1497 eV, then the energy of the ejected electron is $1497 - 1487 = 10$ eV. But if the chemical environment changes the energy needed to eject the electron to 1485 eV, then the energy of the emitted electron is $1497 - 1485 = 12$ eV. It is easier to distinguish electrons with 10 eV energy from electrons with 12 eV energy than to distinguish between photons with energies of 1487 and 1485 eV. These slight changes in the energy of the ejected electron can provide information about the chemical species present and the oxidation state of the atoms present. Based on this phenomenon, the field of ESCA was developed in the 1960s by Swedish physicist Kai Siegbahn and his coworkers. More recently, the term **X-ray photoelectron spectroscopy (XPS)** has become the accepted name for the field and will be used preferentially.

A companion field, **Auger electron spectroscopy (AES)**, was developed simultaneously. AES does not provide chemical species information, only elemental analysis, as we will see. Since the electrons ejected in these two techniques are of low energy and the probability of electron interaction with matter is very high, the electrons cannot escape from any significant depth in the sample. Typical escape depths for XPS and AES electrons range from 0.5 to 5 nm for materials. The phenomenon is therefore confined to a few atomic layers, combined or otherwise, which are at the surface of the sample, and provides a method of surface analysis.

14.2.1 X-Ray Photoelectron Spectroscopy

When an X-ray beam of precisely known energy impinges on a sample surface held under an ultrahigh vacuum (UHV), inner shell electrons are ejected and the energy of the ejected photoelectrons is measured. This is the phenomenon on which XPS is based. Figure 14.2 shows the emission of both a photoelectron and an Auger electron for a model atom.

The kinetic energy of the escaping electron is designated as E_k . The binding energy of this electron is given by the equation

$$E_k = h\nu - E_b - \phi \quad (14.1)$$

where

E_b is the binding energy of the electron

$h\nu$ is the energy of the photon (either X-ray or vacuum UV)

E_k is the kinetic energy of the escaping electron

ϕ is an instrumental constant called **the work function of the spectrometer**

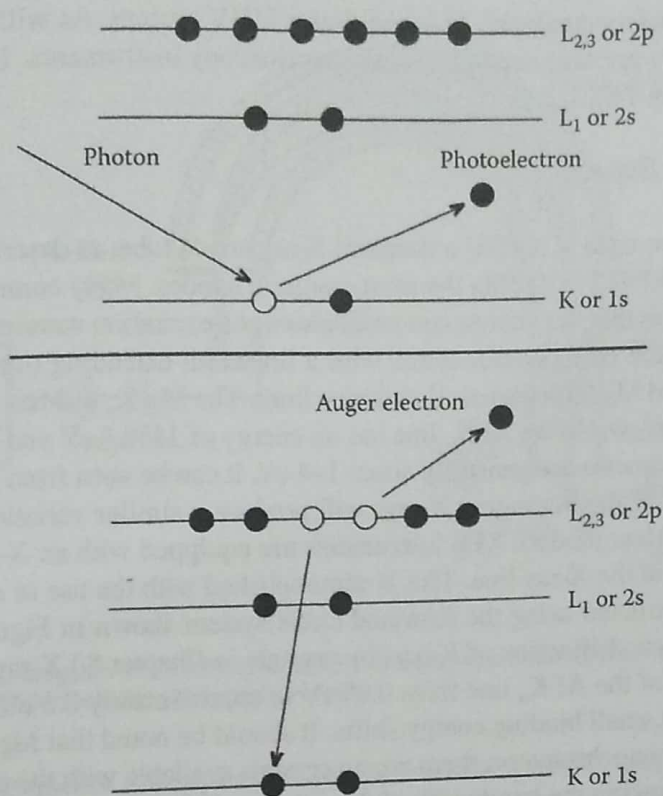


Figure 14.2 The XPS process for a model atom. The top diagram shows an incoming photon causing the ejection of the XPS photoelectron. The bottom diagram shows one possible relaxation process that follows the ejection of the photoelectron, resulting in the emission of an Auger electron. (From Moulder, J.F. et al., In *Handbook of X-Ray Photoelectron Spectroscopy*. Chastian, J. and King, R.C., eds., Physical Electronics, Inc., Eden Prairie, MN, 1995; Courtesy of Physical Electronics, Inc., Eden Prairie, MN, www.phi.com.)

The XPS spectrum is a plot of the number of emitted electrons per energy interval vs. their kinetic energy. The work function of the spectrometer can be measured and is constant for a given instrument, allowing the binding energies of the electrons to be determined.

Since E_b , the original binding energy of the electron is emitted, it can be used to identify the element present. In addition, the chemical form or environment of the emitted electron, depends on the energy of the electronic orbit and the element from which the electron is emitted, it can be used to identify the element present. In addition, the chemical form or environment of the emitted electron, depends on the energy of the electronic orbit and the element from which the electron is emitted, it can be used to identify the element present. In addition, the chemical form or environment of the emitted electron, depends on the energy of the electronic orbit and the element from which the electron is emitted, it can be used to identify the element present. In addition, the chemical form or environment of the emitted electron, depends on the energy of the electronic orbit and the element from which the electron is emitted, it can be used to identify the element present. These minor variations give rise to the **chemical shift** and can be used to identify the valence of the atom and sometimes its exact chemical form. Databases of binding energies for elements and compounds are available, such as the National Institute for Standards and Technology (NIST) electronic XPS database that can be found at www.nist.gov/srd/surface or tables in reference books such as that by Moulder et al. (1995) listed in the bibliography. Quantitative measurements can be made by determining the intensity of the XPS lines of each element.

14.2.1.1 Instrumentation for XPS

A commercial XPS instrument consists of four major components housed in a UHV system with magnetic shielding: (1) the radiation source, consisting of an X-ray source and a means of providing highly monochromatic X-rays; (2) the sample holder; (3) the energy analyzer, which resolves the electrons generated from the sample by energy; and (4) an electron detector. Modern instruments have computerized data recording and processing systems. The pressure required for XPS must be very low, often less than 10^{-7} Pa, in order to prevent adsorbed residual gas from

interfering with the surface analysis. This requires a UHV system. As will be seen, many of the instrument components are also used for Auger spectroscopy instruments. The sample holder will be discussed in Section 14.2.1.2.

14.2.1.1.1 Radiation Source

The radiation source used in XPS is a standard X-ray anode tube, as described in Chapter 8. Soft X-rays are used, with Al and Mg being the most common anodes. Many commercial systems offer a dual anode X-ray tube so that the analyst can switch between excitation wavelengths. It is very important that the X-ray source be monochromatic, with a linewidth extending over as narrow an energy range as possible. Al and Mg have narrow K emission lines. The Mg K_{α} line has an energy of 1253.6 eV and a linewidth of 0.7 eV, while the Al K_{α} line has an energy of 1486.6 eV and a linewidth of 0.85 eV. Linewidths for other elements are generally about 1–4 eV. It can be seen from Equation 14.1 that any variation in the energy of the impinging X-rays will produce a similar variation in the energy of the ejected XPS electron. Most modern XPS instruments are equipped with an X-ray monochromator to narrow the bandwidth of the X-ray line. This is accomplished with the use of a quartz crystal monochromator that is constructed using the Rowland circle system shown in Figure 14.3. (If necessary, the student should review diffraction of X-rays by crystals in Chapter 8.) X-ray monochromators can narrow the bandwidth of the Al K_{α} line from 0.85 eV to approximately 0.3 eV, dramatically improving the ability to detect small binding energy shifts. It should be noted that Mg cannot be used as the source with an X-ray monochromator; there are no crystals available with the proper lattice spacing.

In addition to narrowing the bandwidth of the primary X-ray beam, the monochromator eliminates X-ray satellites, radiant heat from the X-ray source, high-energy electrons, and background radiation (**Bremsstrahlung**) from the X-ray anode. This simplifies photoelectron spectra and minimizes the potential for chemical damage to the sample from the X-ray source. For nonmonochromatic X-ray sources, an aluminum window is typically placed at the end of the X-ray tube to reduce unwanted radiation from the X-ray source. The Al window must be very thin (no more than a few microns) to provide good X-ray transmission. This restriction limits the effectiveness of the Al window in reducing unwanted radiation.

Historically, XPS instruments have relied upon the energy analyzer to define the analysis area because technology was not available to finely focus the X-ray beam, limiting the spatial resolution of XPS. A commonly used approach to improve the spatial resolution is shown in Figure 14.4, where an aperture is placed in the analyzer's input lens to restrict the analysis area. Only the photoelectrons from a given small area of the sample pass through the aperture and into the analyzer. The practical lower limit for small-area XPS analysis with this approach is 25 μm .

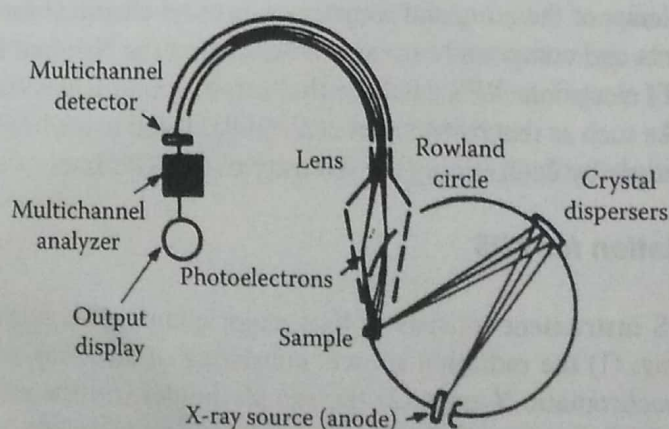


Figure 14.3 Schematic diagram of an XPS instrument using an X-ray monochromator and a multichannel detector.

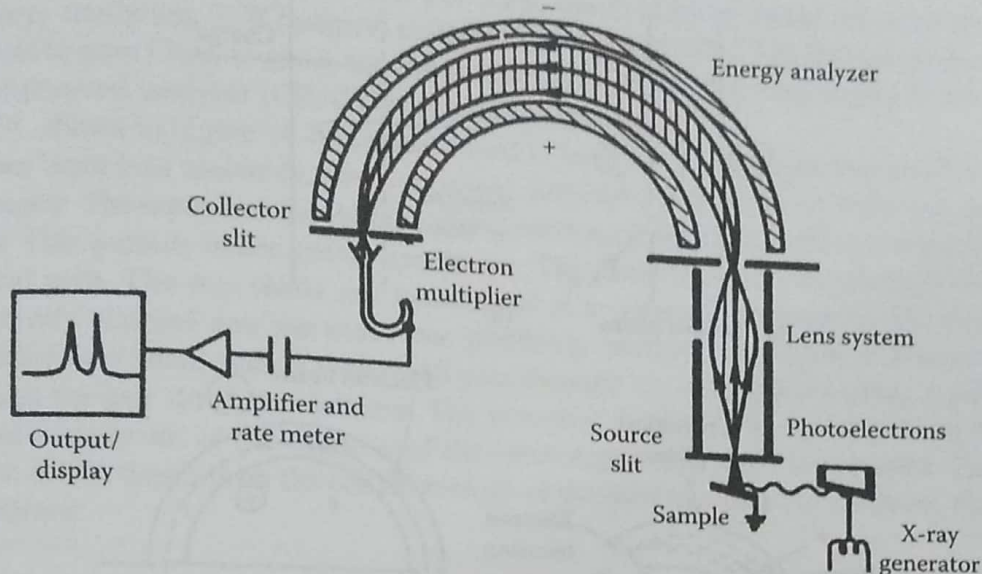


Figure 14.4 Schematic diagram of an XPS instrument with a single-channel electron multiplier detector, and an aperture for selecting the analysis area.

Modern XPS instruments are typically equipped with a specially shaped crystal monochromator that, in addition to decreasing the bandwidth, also focuses the X-ray beam. Currently, it is possible to produce X-ray beams that are less than $10\ \mu\text{m}$ in diameter with this approach. XPS instruments of this type provide much higher sensitivity for small-area XPS analysis than those using an aperture to select the analysis area.

14.2.1.1.2 Electron Energy Analyzers

Electron energies can be filtered with energy discriminators as shown in Figure 14.5. Figure 14.5a shows two parallel charge plates with two openings. The electrons with the required energy enter and leave the holes as in a slit system. Electrons with other energies do not exit the second hole. Figure 14.5b shows a second type of energy discriminator, which is a simple grid discriminator. Electrons with insufficient energy are repelled by the second grid and do not penetrate. This system only discriminates against electrons with low energies. Any electrons that have sufficient energy penetrate the second grid. A third system uses cylindrical plates (Figure 14.5c). If the angle between the planes of the entry and exit slits is 127.17° (i.e., $\pi/(2)^{1/2}$ rad), a double-focusing effect is obtained and the intensity of the electron beam is maintained as high as possible. Electrons with the incorrect energy are lost either to the sides of the cylindrical plates or on the sides of the exit slit. Similar modifications have led to the development of a 180° cylindrical system rather than parallel plates (Figure 14.5d). This system does not provide such fine-tuning of the energy bandwidth, but it increases the intensity of the electron beam. This is another example of gaining in beam intensity but losing in energy discrimination or gaining in power and losing in resolution.

Electron energy analyzers are equivalent to the monochromators used in spectroscopy. Their function is to disperse the emitted photoelectrons based on their energies. The most commonly used electron energy analyzers incorporate an electrostatic field that is either symmetrical or hemispherical. These systems are in essence an extension of the electron energy filters shown in Figure 14.5. All electron energy analyzers require shielding from stray magnetic fields as described subsequently. One system is shown schematically in Figure 14.6; it is based on the system of Figure 14.5a and is called a cylindrical mirror analyzer (CMA). The "plates" are now two coaxial cylinders, thus providing an efficient electron-trapping system while maintaining resolution. The electron source

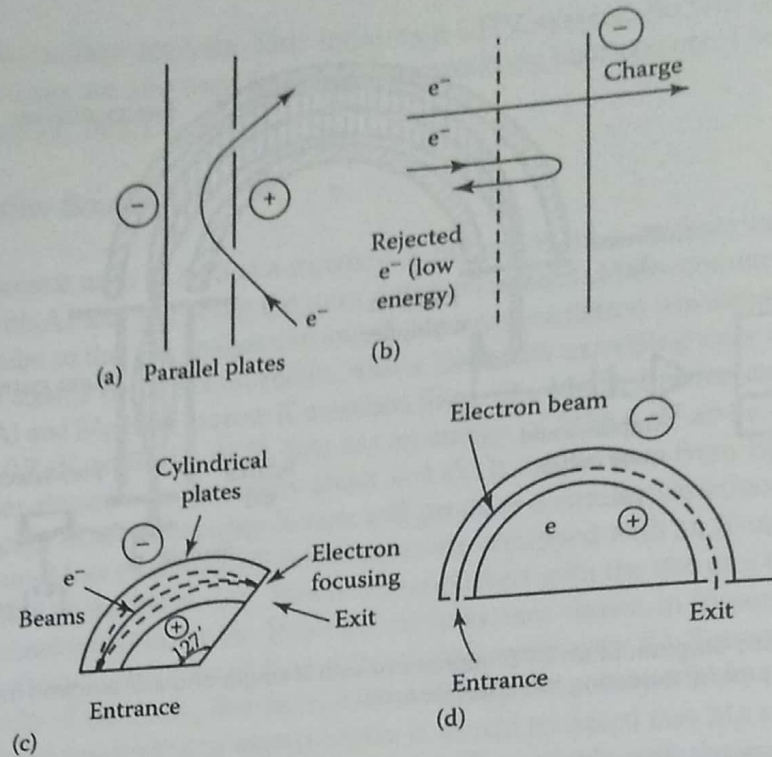


Figure 14.5 Schematic diagrams of several electron energy discriminators.

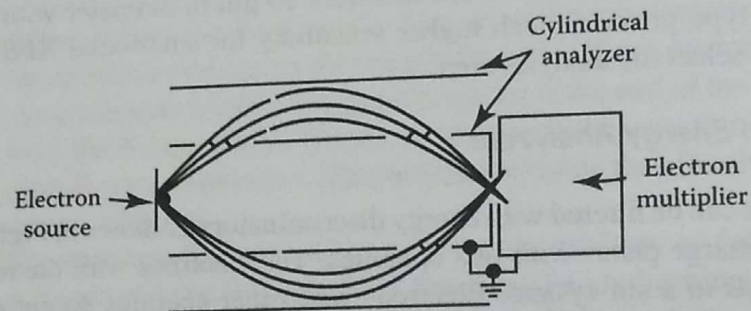


Figure 14.6 Cross section of an electrostatic cylindrical electron energy analyzer. The electron source is the excited sample surface that is emitting photoelectrons.

labeled on the figure is of course the sample surface, emitting photoelectrons. A voltage (negative potential) is applied to the outer cylinder; the inner cylinder is grounded. Only photoelectrons with the appropriate energy pass through the apertures and are focused onto the detector.

Photoelectrons of energy E will be focused when

$$E = \frac{KeV}{\ln(r_o/r_i)} \quad (14.2)$$

where

K is a constant

e is the charge on the electron

V is the applied voltage

r_i is the radius of the inner cylinder

r_o is the radius of the outer cylinder

The CMA as shown is used for AES. For XPS, two CMAs in series are used to obtain the required energy resolution. This design is called a double-pass CMA. The transmission of electrons through a double-pass CMA is good, but the resolution is poorer than that obtained using the concentric hemispherical analyzer (CHA) described subsequently.

The CHA, shown in Figure 14.4, is widely used in both XPS and Auger instruments. The CHA consists of an input lens assembly, two concentric hemispherical shells of differing radii, and an electron detector. The input lens focuses the photoelectrons from the sample and lowers (or retards) their energy. This permits better energy resolution. The electrons then pass through a slit into the hemispherical path. The two shells are maintained at a potential difference, ΔV , with the outer sphere negatively charged and the inner one positively charged, as shown in Figure 14.4. Only electrons with a very small energy range will pass through the hemispheres along a path of radius r_0 and through the exit slit to the detector. The potential difference is varied to scan the electron energies, and a spectrum of the energies of the ejected photoelectrons is recorded. Resolution of this analyzer, $\Delta E/E$, depends on the entrance angle of the electrons into the analyzer, the slit width, and r_0 , as follows:

$$\frac{\Delta E}{E} = \frac{w}{r_0} + \alpha^2 \quad (14.3)$$

where

$\Delta E/E$ is the resolution

w is the slit width

r_0 is the radius of the equipotential surface within the analyzer

α is the angle at which the electrons enter the analyzer

Two approaches to retardation (deceleration) of the electrons are used. One mode of operation is called **fixed-analyzer transmission (FAT)** or **constant-analyzer transmission (CAT)**. In this mode, the electrons are retarded to a constant energy. This results in the absolute resolution of the system being independent of the kinetic energy of the incoming electrons. Energy analyzers operating in the FAT mode provide high sensitivity when the pass energy is high and high energy resolution when the pass energy is low. The other operating mode is called **fixed retardation ratio (FRR)** or **constant relative ratio (CRR)**. In this mode, the incoming electrons are decelerated by a constant ratio from their initial kinetic energies. Energy analyzers operating in the FRR mode provide relatively uniform sensitivity across the energy spectrum. However, absolute energy resolution degrades as the measured kinetic energy increases.

Other analyzers have been designed based on the magnetic deflection of electrons, but in general, these have not been very successful because of the difficulty of maintaining a uniform magnetic field. Electrostatic systems are used in all commercial instrumentation.

The instrument is calibrated regularly with known conductive standards such as gold or copper to establish the linearity of the energy scale and its position.

14.2.1.1.3 Detectors

Both single-channel and multichannel detectors are used in XPS and Auger spectroscopy. The most common single-channel detector is the channel electron multiplier. The channel electron multiplier functions much like the photomultiplier tube (PMT) used in optical spectroscopy (discussed in Chapter 5). The major difference is that electrons constitute the signal that is being amplified, not photons. The channel electron multiplier consists of a continuous dynode surface inside a tube as depicted in Figure 14.7a. Channels may be straight tubes as shown or curved. The surface is a thin-film conductor with a high resistance. When a voltage is supplied across the input and output,

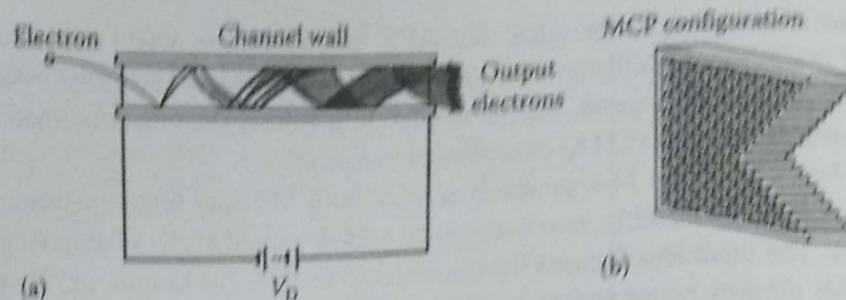


Figure 14.7 (a) A schematic channel electron multiplier. A thin-film conductive layer inside the tube serves as a continuous dynode surface. (b) A schematic microchannel plate (MCP) configuration. (Courtesy of Hamamatsu Corporation, Bridgewater, NJ, www.usa.hamamatsu.com.)

a potential gradient exists along the channel direction. The dynode surface and potential gradient permit electron amplification throughout the channel. An incoming electron strikes the inner wall and secondary electrons are emitted. These are accelerated by the potential gradient and travel a parabolic path until they strike the opposite wall, releasing more electrons. An ejected photoelectron from the sample enters at one end and an amplified pulse of electrons exits at the other end. Gains of up to 10^6 are possible with a 1 kV supply voltage. This detector is very efficient at counting electrons, even those with very low energy. Like the PMT, the detector can be saturated at high electron intensity.

Multichannel electron detectors of various types can be placed to cover the exit plane of the analyzer. Charge-coupled devices (CCDs) (discussed in Chapter 7), phosphor-coated screens, and position-sensitive detectors are some of the multichannel devices in use. One type of position-sensitive detector consists of a **microchannel plate** (MCP) electron multiplier. The MCP (Figure 14.7b) consists of a large number of very thin conductive glass capillaries, each 6–25 μm in diameter. The capillaries are fused together and sliced into a thin plate. Each capillary or channel works as an independent electron multiplier, exactly as the single-channel electron multiplier described earlier, thereby forming a 2D electron multiplier. Used in conjunction with a phosphor screen, 2D imaging of surfaces is possible.

Electrons are detected as discrete events, and the number of electrons for a given time and energy is stored and then displayed as a spectrum.

14.2.1.1.4 Magnetic Shielding

The ejected electrons have low energy. They are affected significantly by local magnetic fields, including the Earth's and those of any stray electrical impulses as generated by wiring to lights, equipment, elevators, and so on. These stray fields must be neutralized in the critical parts of the instrument in order to obtain useful data. One method is to enclose the critical regions with high-permeability magnetic alloy, which shields the sample from stray magnetic fields. Another method is to use Helmholtz coils, which produce within themselves a homogeneous field. This field may be made exactly equal and opposite to the Earth's magnetic field. A feedback system to the coils can also be used; this senses variations in local magnetic fields and varies the current in the Helmholtz coils, neutralizing transient magnetic fields as they arise. This system not only neutralizes the Earth's magnetic field but also local fields as they are generated.

14.2.1.1.5 Electron Flood Gun

In practice, when the sample is irradiated, electrons are ejected. An electron takes with it a negative charge, leaving the sample positively charged. Depending on the conductivity of the sample, this positive charge builds up at a steady but unpredictable rate on the surface of the sample, changing the work function of the sample itself and therefore the net energy of the ejected electrons.