

Table 14.3 Specific Surface Analysis Applications

Type of analysis	Applications
Failure analysis	Surface contamination Particle identification Fracture due to grain boundary impurities
Adhesion failure	Adhesive failure Cohesive failure Silicone surface contamination
Corrosion	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 200 mm)
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 UHV Hydrated surfaces Samples that outgas at RT in UHV

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

Source: Information in Table provided by Physical Electronics USA, Inc. (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 (Fig. 14.1). An electron from an outer shell then drops into the inner shell and an X-ray

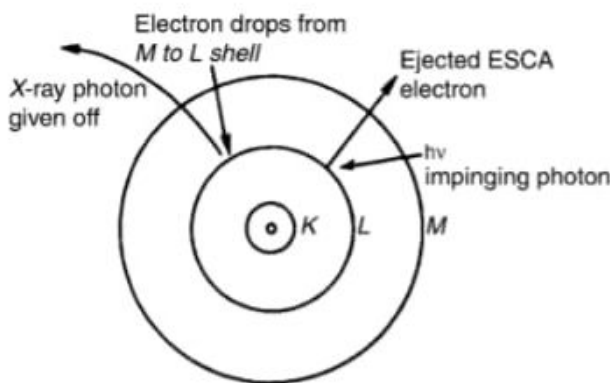


Figure 14.1 An impinging photon ejecting an inner shell ESCA electron. The kinetic energy of the ejected ESCA electron, E_k , is related to the binding energy of the electron in the atom, E_b . The binding energy is characteristic of the element. An X-ray photon of energy $E_M - E_L$ is emitted in the 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.)

photon is emitted simultaneously. The energy of the photon is equal to the difference between the energy of the orbital the electron was 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

photon is emitted simultaneously. The energy of the photon is equal to the difference between the energy of the orbital the electron was 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 UV absorption analysis. This variation is reflected as well in the energies of the inner shell electrons, but the changes in energy 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. XRF, as was discussed in Chapter 8, is therefore an elemental analysis technique. It tells us what elements are present, but does not give any 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 **electron spectroscopy for chemical analysis** (ESCA) was developed in the 1960s by Swedish physicist Kai Siegbahn and his coworkers. ESCA is also called **X-ray photoelectron spectroscopy** (XPS).

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. Electron Spectroscopy for Chemical Analysis (ESCA) or X-ray Photoelectron Spectroscopy (XPS)

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 ESCA, also called XPS, is based. ESCA was the original name for the technique, but the name XPS is now preferred by surface scientists; both terms will be used interchangeably. 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; $h\nu$, the energy of the photon (either X-ray or vacuum UV); E_k , the kinetic energy of the escaping electron; and ϕ , an instrumental constant called **the work function of the spectrometer**.

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 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 atom affects the energy E_b to a much smaller but measurable extent. 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 NIST electronic XPS database which can be found at www.nist.gov/srd/surface or tables in reference books such as that by Moulder et al. listed in the bibliography. Quantitative measurements can be made by determining the intensity of the ESCA lines of each element.

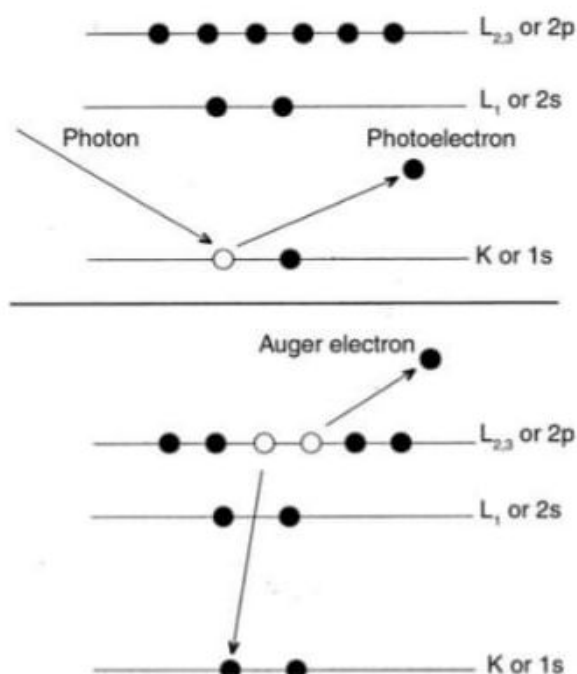


Figure 14.2 The XPS process for a model atom. The top diagram shows an incoming photon causing the ejection of the XPS (ESCA) photoelectron. The bottom diagram shows one possible relaxation process that follows the ejection of the photoelectron, resulting in the emission of an Auger electron. [From Moulder et al., courtesy of Physical Electronics USA, Inc. (www.pha.com).]