14
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 usually 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, 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,

Table 14.1 Selected Spectroscopic Techniques for Surface Analysis

Abbreviated	Primary	Secondary

Table 14.1 Selected Spectroscopic Techniques for Surface Analysis

Abbreviated name	Full name	Primary beam	Secondary beam
ESCA, XPS	Electron spectroscopy for chemical analysis, X-ray photoelectron spectroscopy	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

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 14.2 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
	Failure analysis
Optical coatings	Coating composition and thickness
	Adhesion layers
	Composition of surface defects
Automobile industry	Paint adhesion
	Paint weathering
	Catalyst poisoning
	Lubricant chemistry
Pharmaceutical industry	Tablet coating composition and uniformity
	Distribution of active ingredients in tablet
	Patent infringement monitoring
Polymer industry	Surface coatings
	Surface chemistry
	Multilayer composition and thickness
Biotechnology	Surface chemistry of metal and polymer medical implants
	Biocompatibility of implanted devices
	Implanted device performance

Source: Information in table provided by Physical Electronics USA, Inc. (www.phi.com).

Table 14.3 Specific Surface Analysis Applications

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

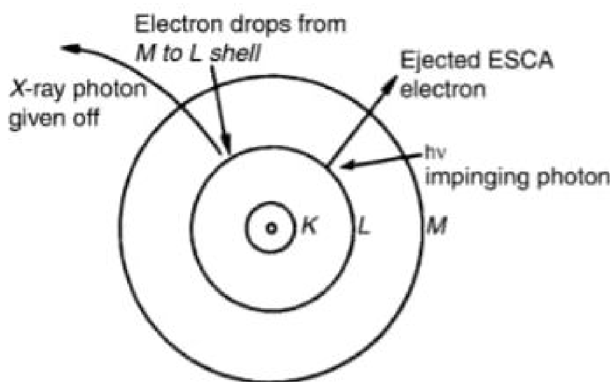

Figure 14.1 An impinging photon ejecting an inner shell ESCA electron. The kinetic energy of the ejected ESCA electron, E_k, is related to the binding energy of the electron in the atom, E_b. The binding energy is characteristic of the element. An X-ray photon of energy $E_M - E_L$ is emitted in the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