

Analytically Speaking

Dr.RolfWeil ProfessorEmeritus StevensInstitute of Technology Hoboken, NJ 07030

Characterization of Deposits, Coatings & Electroforms-Methods of Surface Analysis

There are several methods to characterize the surfaces of electrodeposits, coating and electroforms. Auger electron spectroscopy (AES) is used mainly to obtain a chemical analysis of essentially the top layers of atoms that constitute the surface. X-ray photoelectron spectroscopy (XPS), also known as electron spectroscopy for chemical analysis (ESCA), provides information about compounds in the surface layer. Secondary ion mass spectroscopy (SIMS) is used primarily for measurements of depth penetration. Low energy electron diffraction (LEED) provides information about the crystal structure of the surface layer.

The surface analysis methods are used primarily for adhesion problems and adhesives. In corrosion studies, they yield information about corrosion products, especially about passive films. They are also applied to investigate conversion coatings and for the degree of coverage of a substrate by very thin deposits and interactions between them.

Auger Electron Spectroscopy To understand Auger electron spectroscopy, it is first necessary to review the production of characteristic X-rays, which was discussed in Part I of this series. It may be recalled that characteristic X-rays are produced when an electron knocks out another one in the levels close to the nucleus, such as the K shell. The vacancy is then filled by an electron from the L shell, for example, which has a higher energy. The energy difference can then be emitted as Xray photons. In this case, the radiation is called K_{α} . It was previously discussed in conjunction with

microstrain and particle size measurements, that there are two slightly different wavelengths of K radiation, namely $K_{\alpha l}$, and $K_{\alpha 2}$. The reason for two wavelengths of K radiation is that there are three energy levels in the L shell. They are designated as L_{l} , L_{ll} and L_{III} . When an electron from the L_{III} level fills the vacancy in the K shell, $K_{\alpha l}$ X-rays result. If the electron filling the vacancy in the K shell originated in the L_{II} level, the resulting radiation is $K_{\alpha 2}$.

A process other than production of characteristic X-rays, such as K_{α} , can take place, especially in elements with atomic numbers less than 31, which is gallium. If a vacancy in the K shell, for example, is filled by an electron from the L_{π} level, the resulting $K_{\alpha 2}$ radiation may not escape from the atom. Instead, an electron is ejected from the L_{III} level, for example. This electron is called an Auger electron and it has an energy or wavelength characteristic of the energy difference between the K and L shells. This energy difference is unique to each element and can, therefore, be used to identify it.

The energy of Auger electrons is very small. Consequently, they are absorbed by the material being tested, except for the very top layers of atoms in the surface. In this way, the surface can be chemically analyzed, as only Auger electrons from it can escape. The principal application of Auger electron spectroscopy is, accordingly, chemical analysis of the surface layer. The various energies of the emitted Auger electrons result in peaks that can be identified, resulting in a qualitative analysis.

There are related applications of AES. A quantitative analysis can be

obtained from the intensity of the AES peaks with suitable standards. A depth profile can be achieved by sputtering off successive surface layers by inert ion bombardment and determining the composition of each one by AES. The uniformity of layer removal by sputtering limits the depth resolution. A depth profile can also be obtained by polishing a cross section of the deposit at a shallow slant. In this way, the area of a layer is greatly increased. Because electrons can be focused, a very small area can be analyzed. This capability can be applied to the newly created surface of each layer. Small shifts in the wavelength of the peaks can provide information about the oxidation state or valence of the elements, and so indicate whether they exist in compounds. For example, aluminum has an Auger peak at 68 eV. The peak of aluminum in Al₂O₃ occurs at 51 eV. It is then possible to differentiate between elemental aluminum and its being combined in the oxide. There should be no other elements present with peaks near the ones in question. As will be discussed next month, XPS is more suitable for the determination of specific compounds.

There are some problems and limitations associated with AES. Insulating materials can present problems in that they can develop a charge. This problem is especially acute if the surface is not smooth. It is best to limit the AES analysis to conducting materials. Hydrogen and helium cannot be analyzed because they do not have L shells. The low energy of the Auger electrons can cause them to be absorbed by air molecules; an ultra-high vacuum is therefore required. PESF