Analytically Speaking

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X-ray Photoelectron Spectroscopy

-ray photoelectron spectroscopy \dot{X} (\dot{XPS}) involves electrons being knocked out of their shells. It was previously discussed that fluorescent analysis is also based on X-ray photons knocking out electrons in the lower shells of atoms and having electrons from shells of higher energy filling the vacancies. The difference in energy is given off as characteristic X-rays. Because this energy is different for each element, a chemical analysis can be made. The electron that is knocked out of the shells, creating a vacancy, is called a photoelectron. The energy of photoelectrons is weak, so that they can escape only from the near-surface layer.

XPS provides a means of determining the binding energy of the atoms in the surface layer. Highenergy X-rays should be used to produce the photoelectrons. It is preferable to use monochromatic Xrays. In this way, satellite peaks are avoided. The binding energy of an electron in the shell from which it came can be calculated, knowing the energy of the X-ray source and the kinetic energy of the photoelectrons. A constant, such as the work function of the spectrometer, must also be determined independently. The binding energy is the difference between the energy of the X-ray source and the sum of the kinetic energy of the photoelectrons and the constant. The binding energies provide information about the elements present in the surface layer and whether they are present in the elemental state or as compounds. Identification of the elements or compounds present can be made by comparison of the peaks with data

compiled in the literature. The detection limits vary from 0.1 to 1 atomic percent, which is comparable to AES.

An advantage of XPS over AES is that more precise information about the compounds present is provided. This information is obtained from shifts of the peaks. Another advantage over AES is that it can be readily used for insulating materials. The X-rays used for XPS do not cause a charge build-up in the way electrons do when they are not conducted away. Depth profiling can be carried out by sputtering off layers or with tapered sections in the same way as with AES. Because X-rays cannot be focused in the same way as electrons, however, AES can analyze a smaller area than can XPS. A larger database exists for the interpretation of XPS data than for AES. The two methods are often used together; if a precise value of the binding energy cannot be readily obtained, AES data can help.

Secondary Ion

Mass Spectroscopy Secondary ion mass spectroscopy is essentially a gas analysis. Layers are sputtered off the sample by a monoenergetic ion beam. Charged particles come off the surface as a result of the ion bombardment. Before they can be redeposited, they constitute a gas that can be analyzed by a mass spectrometer.

In most applications, the primary ion beam has energies ranging from 0.5 to 50 keV and is rastered over the sample surface. If the rate of material removal is known, data about depth profiling can be obtained from the gas analysis. The technique is very sensitive for detection of small impurities in the range of parts per million. It is particularly useful in the study of semiconductor materials. With suitable standards, the method can be made quantitative. If information about surface contaminants is desired, a low ion flux is employed so that only part of the top layer of molecules is sputtered off.

Low Energy

Electron Diffraction The arrangement of atoms (*i.e.*, the crystal structure in the surface layer) is different from that in the bulk of the material. The main reason for this difference is that the number of nearest neighbors is not the same. Also foreign species, such as oxygen, are more prevalent in the surface layer.

Determination of the crystal structure was discussed previously. If an electron beam of low energy, on the order of 5 keV, is diffracted by the surface layer, its crystal structure can be determined. Interpretation of the diffraction patterns is easier if the pattern of a single crystal is obtained.

Most transmission electron microscopes are not equipped to perform LEED unless they have a special chamber for it. For this technique, the electron beam is almost parallel to the surface. In the TEM for selected-area diffraction, as previously described, the electron beam is perpendicular to the specimen surface. Most work with LEED is performed in a special instrument that can also be used for high-energy electron diffraction. PESF