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PVD Processes: X-ray Photoelectron Spectroscopy (XPS)

X-ray photoelectron spectroscopy (XPS)—or as it is sometimes called, electron spectroscopy for chemical analysis (ESCA)—is a surface-sensitive analytical technique that analyzes the energy of the photoelectrons (50–2000 eV) that are emitted when a surface is bombarded with X-rays in a vacuum. The energy of these electrons is characteristic of the atom being bombarded, thereby allowing identification of elements in much the same way as in Auger electron spectroscopy (AES). (See February issue, *P&SF*, "SVC Topics" column, p. 60)

Atomic Shells

An atom consists of a nucleus containing protons and neutrons in nearly equal numbers, surrounded by electrons in specific energy ranges called shells or orbitals. All the shells except the inner shell are subdivided into several energy levels. The inner atomic shells can be filled to the specific number of electrons that they can contain (2, 8, 18 …).

The outermost or valence shell can be "full" or not, depending on the number of electrons available. For some materials, shells below the valence level may not be full. Electrons can be excited to such an extent that they leave the atom. They can be excited thermally (by an energetic photon such as an X-ray), or by collision with an energetic electron.

Photoelectron emission occurs by a direct process, whereby an X-ray is absorbed by an atomic electron and the emitted electron has a kinetic energy equal to that of the energy of the incident X-ray, minus the binding energy of the electron.

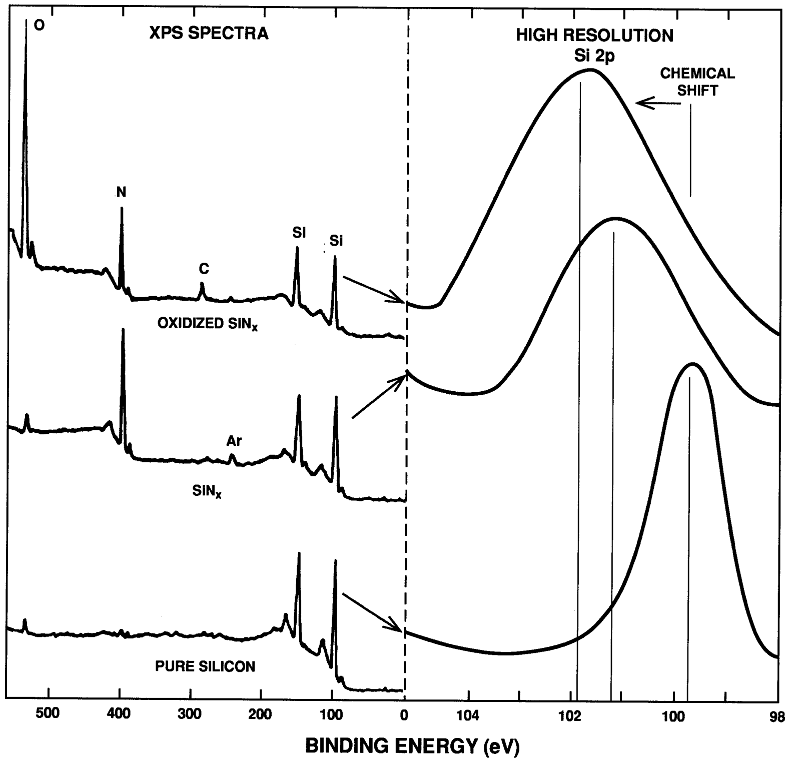
In contrast to the characteristic electron energies found in AES, the energy of the photoelectrons depends on the energy of the X-rays used to create the photoelectrons. Typically, the K-alpha X-ray radiation from magnesium (1253.6 eV) or aluminum (1486.6 eV) is used for analysis. The energy of the ejected electron is determined using an electron velocity analyzer, such as a cylindrical mirror analyzer.

The Auger electrons appear in the spectrum of emitted electrons, but they can be differentiated from the photoelectrons in that they have a characteristic energy that does not depend on the energy of the incident radiation.

Chemical Bonding

A compound is a material formed from two or more atoms of different elements bonding together by the interaction of the outermost (valence) electrons. The photoelectrons can come from all electronic levels, but the electrons from the outermost electronic states have energies that are sensitive to the chemical bonding between atoms.

Information on the chemical bonding can often be obtained from the photoelectron emission spectra by noting the "chemical shifts" of the low-energy (a few hundred eV) photoelectrons. AES, for example, can detect carbon on a surface, but it is difficult to determine the chemical state of the carbon. XPS detects the carbon and, from the chemical shifts, can determine if it is free



XPS electron energy spectrum of pure silicon, silicon in sputter-deposited SiN_X and silicon in oxidized sputter-deposited SiN_X, showing the chemical shifts associated with the changing binding energies of the valence electrons of the silicon.

carbon or carbon in the form of a metal carbide.

In some cases, chemical shift information is not capable of differentiating between chemical states. Iron in the Fe_2O_3 (ferric) state, for example, cannot be differentiated from iron in the FeO (ferrous) state.

The accompanying figure shows the photoelectron energy of silicon as:

- Pure silicon
- Sputter-deposited SiN_X
- Oxidized (contaminated) sputter-deposited SiN_X.

The figure also shows the chemical shifts of the silicon photoelectrons as a function of their chemical environments.

XPS vs. AES Techniques

X-ray photoelectron spectroscopy is the technique generally used to determine the ratio of the chemical states of compounds in the surface. (*e.g.*, the ratio of iron oxide to chromium oxide in an electropolished stainless steel surface, or the amount of unreacted titanium in a titanium nitride thin film). The spatial resolution of the XPS technique is not as good as with AES, because X-rays cannot be focused as easily as electrons.

The XPS analytical technique avoids the electron damage and heating that is sometimes encountered in AES. XPS is one of the primary techniques for analyzing the elemental, chemical and electronic structure of organic materials. It can determine, for example, the chemical environment of each of the carbon atoms in a hydrocarbon polymeric material. ***P&SF***

Reference

J.B. Lumsden, “X-ray Photoelectron Spectroscopy,” *Materials Characterization, Metals Handbook*, Vol. 10, ninth edition, p. 568. American Society for Metals (1986).