ELNES: An Electron Spectroscopic Tool to Study Complex Microstructures

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The presence of internal boundaries can significantly influence many important properties of materials, such as fracture toughness, creep, electrical conductivity and magnetic behavior. Interfacial structure, chemical composition and bonding, on a nanometer length scale, are often controlling and sought after factors influencing these properties. An electron spectroscopic technique, known as energy-loss near edge structure (ELNES) analysis, can be utilized to probe compositional and bonding variations with a spatial resolution less than 1 nm and is therefore well suited to this endeavor.

When a fast electron passes through a material in an electron microscope, it collides with the electrons bound to the atoms in that sample. As a result, the fast electron often gives up a small fraction of its kinetic energy to the bound electrons. The laws of quantum mechanics dictate that these so-called inelastic scattering events will only take place if the bound electron can gain enough energy to enter an empty energy level. The number and energy distribution of these unoccupied electron energy levels (or states) are dependent upon the chemical bonding, structure and composition within the material. Spectroscopy is necessary to probe this energy distribution.

These ideas form the basis behind the technique of electron energy-loss spectroscopy (EELS). In every EEL spectrum characteristic edges are observed corresponding to the allowed scattering events. It turns out that each element has its own set of edges at well defined energies. Examples of these edges are shown in figures 1-3. This fact enables us to use EELS as an microanalytical tool. In addition, upon closer scrutiny one finds that the edges display a rich and complex fine structure. This has been termed the energy-loss near edge structure or ELNES. It is by analysis of this ELNES that information on the local atom arrangements, crystal symmetry, valence and chemical bonding can be extracted. Because of its complexity, a common analytical strategy[1] (analogous to "fingerprinting") is to compare spectra from materials containing unknown phases and microstructures with a library of standard spectra from well characterized materials.

In the modern scanning transmission electron microscope fitted with a field emission electron source, it is routine to focus the electron probe down to a spot size smaller than 1 nm in diameter. By acquiring the EELS data with such a finely focused electron probe, all information described above is accessible on a sub-nanometer scale. There are no other analytical tools available that can study chemistry, bonding, and structure at nanometer length scales at buried structures within bulk materials. The following example illustrates how characteristic ELNES fingerprints of known compounds can be used to identify the chemistry and microstructure of "unknowns".

A multilayer structure consisting of 10 nm thick layers of silicon enriched oxide in the sequence $SiO/SiO_2/SiO$ was deposited by chemical vapor deposition onto a silicon crystal substrate. Such structures are prospective materials for application in electrically erasable memory devices[2]. Silicon monoxide represents a 17 at. % enrichment of silicon in silicon dioxide and is thermodynamically unstable with respect to silicon and silicon dioxide and thus may be expected to separate into these two constituent parts. To interpret the measured electrical properties, it was inferred that the microstructure consists of sub-microscopic clusters of silicon matrix, probably below 1 nm in size, embedded in an amorphous SiO_2. Such very small clusters could have a disordered structure rendering them invisible to imaging in the conventional electron microscope. Figure 1 illustrates the silicon edge for standard spectra of (a) crystalline silicon and (b) quartz (SiO_2). The edge thresholds of Si and SiO_2 are at 99.8 and 105 eV respectively. The principal contribution to this chemical shift is the increased electrostatic attractive force on the bound electron to the tetravalently (4+) charged silicon ion in the oxide by comparison with a similar electron in silicon. An additional contribution is due to the increase in electronic band gap from silicon which is a semiconductor to quartz which is an insulator. The spectrum of SiO_2 is readily identified by its three intense peaks. The spectrum marked (c) in figure 1 was recorded in the first silicon rich oxide region deposited directly onto the substrate and can be constructed by combination of the two principal components of Si and SiO_2. It is concluded from this analysis that there exists small clusters of Si in this oxide layer. By measuring the relative intensities of each of the principal components it is possible to confirm that all of the excess Si is contained within such elemental Si clusters. In figure 2 the second SiO layer is compared with the first and the SiO_2 intermediate layer. The ELNES is similar above 105 eV but markedly different in the region below. The 100 eV threshold characteristic of elemental Si is absent, suggesting structural or compositional modification to the local environment of the excess Si component. It is likely that a metastable alloy of Si in intermediate oxidation states is formed. Confirmation of this has been elusive because there are no know stable reference compounds to which one can compare. Heating causes atoms to move and diffuse through the film more rapidly, enabling the film to decompose to the more stable Si island microstucture. This transition is illustrated in figure 3.

The ability of ELNES to provide electronic structure information on a nanometer or even sub-nanometer length scale provides an exciting prospect. The electronic and composition of specific defects and interface structures can be explicitly explored within bulk materials, and related directly to properties. ■

References:
(1) Brydson, R., in *Transmission Electron Energy Loss Spectrometry in Materials Science*, ed. M.M. Disko, C.C. Ahn, and B. Fultz, (The Minerals, Metals and Materials Society, Warrendale, PA, 1992).
(2) Dori, L., Bruley, J., DiMaria, D.M., Batson, P.E., Tornelio, J., and Arienzo, M., J. Appl. Phy., 69, 2317 (1991)

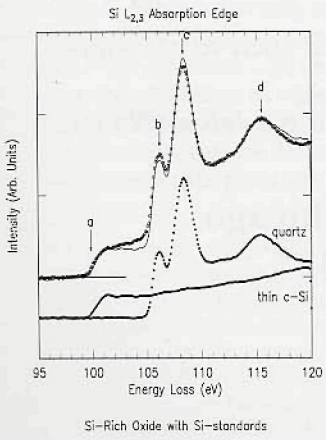

Figure 1: The upper curve (dots) is ELNES of the Si $L_{2,3}$ edge recorded from a silicon enriched oxide film. The underlying solid curve is the weighted sum of the elemental silicon and quartz edges. The ELNES indicates a microstructure composed of Si clusters/ islands in a SiO_2 matrix.

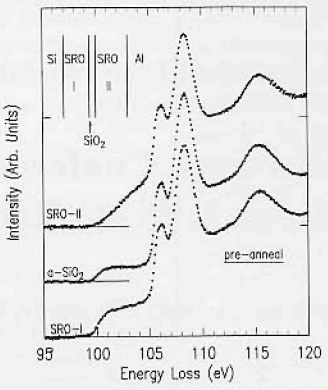

Figure 2: The Si ELNES of the different layers in the multilayer structure, as deposited by CVD. Note the differences in the energy region between 100 and 105 eV. The excess Si in the layer labeled as SRO II does not cluster to form Si islands.

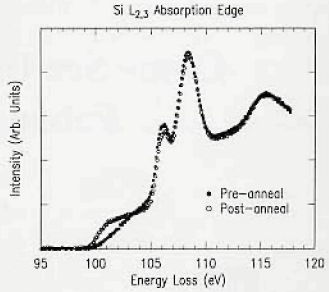

Figure 3: Upon annealing, the SRO II layer transforms to the more stable Si island microstructure.

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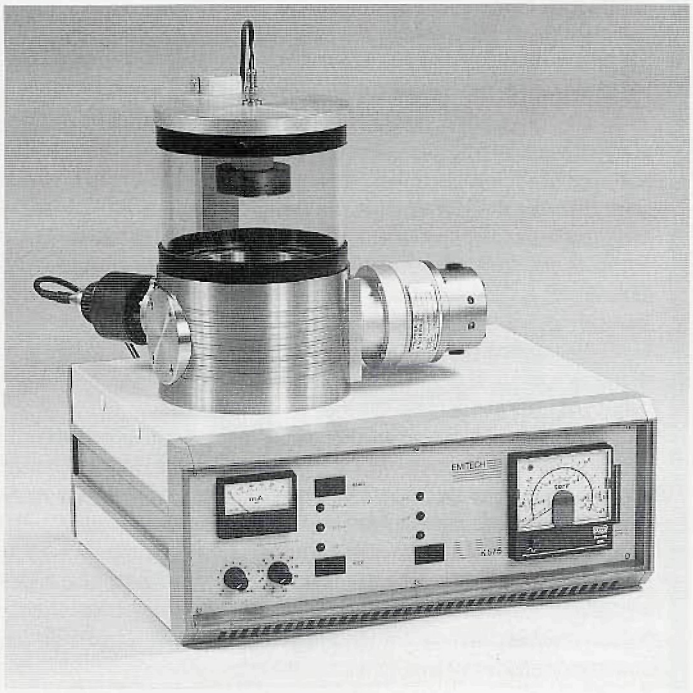

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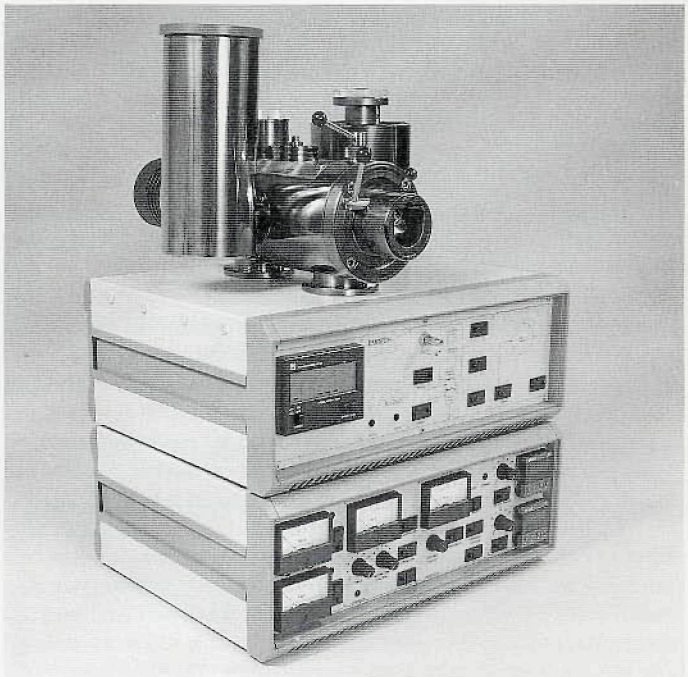

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