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Critical Issues In Ceramic Microstructures

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As the number and variety of ceramic materials have grown so rapidly in the last few decades, ranging from silicon nitride structural ceramics to the perovskite superconductors to the ferroelectric oxides to semiconducting sensors, the number of scientific and technical issues has also grown rapidly. Many of the basic questions relate to the role the microstructures play in determining the observed physical behavior, but increasingly it is not the geometric properties of the microstructure that are of central concern but rather compositional variations and associated electrical characteristics. These require the continued development of microscopy techniques to complement the tremendous advances in microstructural understanding that have already been made possible by microscopy in the past.

Since the role of microscopy is such a broad one, only a few of the most generic problems in microstructure characterization will be described in this article. The topics selected include the characterization of intergranular films in liquid-phase sintered ceramics, the charge distribution at interfaces and the associated space charge, the epitaxial growth of oxides on oxide substrates, and the use of fluorescence imaging to identify phases and non-destructively measure local strains.

Relatively speaking, the characterization of thin (~1 nm) intergranular films in liquid phase sintered ceramics is an old topic. Since the first identification of the presence of such thin films coating the grain boundaries in silicon nitride ceramics in 1974, a wealth of observations in a wide variety of other ceramics has been reported. It is now known that the films are a remnant, generally silica-rich, phase left wetting the grain boundaries after cooling from the sintering process used to densify the ceramic. It is also known from high-resolution electron microscopy that, rather unexpectedly, the thickness of the intergranular film does not vary from one grain boundary to another despite changes in the grain boundary plane and changes in the relative crystallographic misorientation of the grains on either side of the boundary. The reason for this is not known and represents an important challenge to our understanding of the densification of ceramics as well as the origin of grain boundary wetting by a liquid phase. One model proposes that the intergranular film is stabilized by the action of van der Waals forces and is present as a result of a gradient energy contribution to the overall free energy of the grain boundary. On the basis of the predictions of this model a number of critical observations have been proposed including accurate, high spatial resolution measurements of the composition across intergranular films and into their adjoining grains. Such measurements require the use of field-emission STEMs with EELS but without the radiation damage associated with the use of such high power densities. There is a continuing need for a microscopy that reveals, in quantitative detail and high resolution, the charge distribution along a grain boundary or interface as well as in

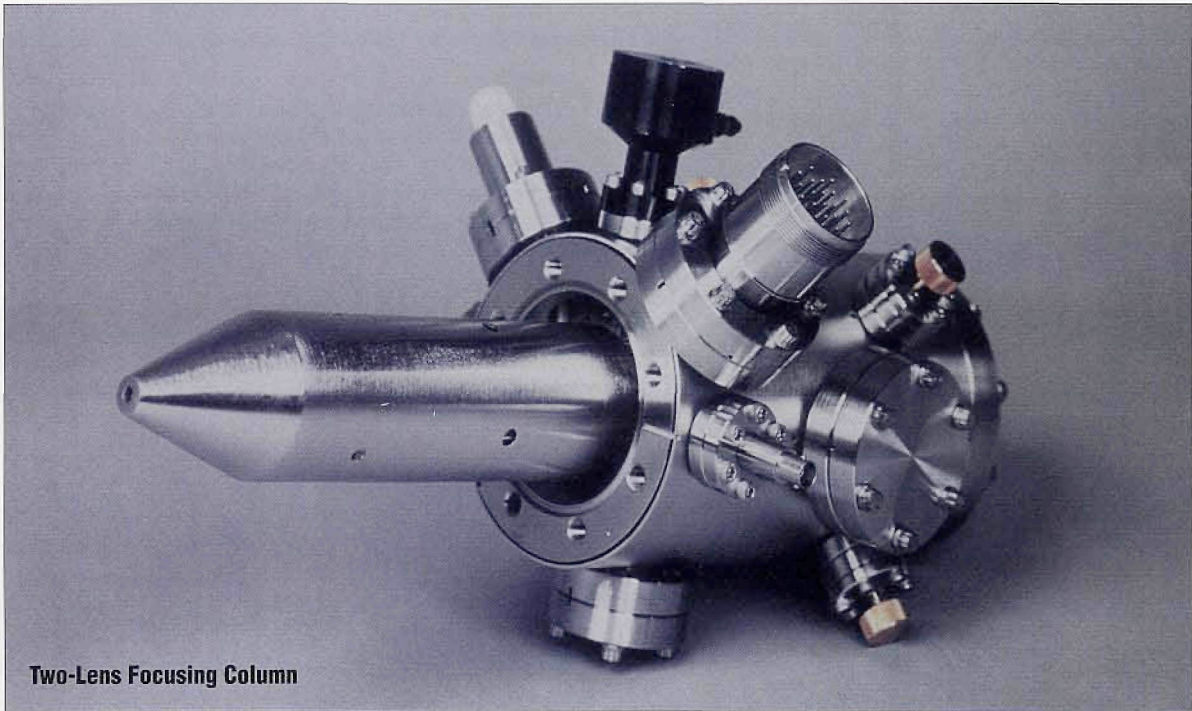
the associated space charge region. The lack of such a microscopy remains a major impediment to a wide range of subjects, including the charge distribution in Schottky barriers, the potential distribution at grain boundaries in varistor ceramics and solar cells, and the charge depletion at free surfaces. Traditionally the principal technique that has provided some of the required data, primarily the location of recombination centers, has been EBIC in the scanning electron (and optical) microscope. Defocus imaging in the TEM has also been used to examine field distributions at low magnifications in simple structures such as p-n junctions. There is, thus, a tremendous opportunity for electron beam holography once the imaging methodologies, the image reconstruction techniques and image contrast theory have been fully developed.

The successful epitaxial growth of defect-free oxides on oxide substrates is an essential pre-requisite for the use of high-Tc superconductors in device applications and the incorporation of ferroelectric memories in devices, to name just two. It can be argued that with continued process development the defect level will fall, just as occurred through largely empirical development in the silicon industry. However, it is important to recognize that microscopy played a key role in the identification of defects introduced during processing helping to define the direction of process development. Undoubtedly it will be again so for the epitaxial oxides but given that the bonding is different, the crystal structures more complex and the importance of charge effects, microscopies of all types will be required in defect identification.

The fact that most ceramics are, in actuality, wide band-gap semiconductors and hence transparent in the visible makes it possible to use optical based microscopies for analysis. One such methodology uses photoluminescence (fluorescence) in an optical microscope to form images of phases and uses piezospectroscopic shifts to determine local strains. Cr³⁺ fluorescence has proven to be particularly suited to the study of alumina-based ceramics, composites and coatings since the R-line fluorescence is both intense and sharp. On account of its similar size and same valence, Cr³⁺ is a substitutional solute for Al³⁺ in aluminum oxide. When the d³ outer electrons are excited, by an argon ion laser for instance, to higher energy states they return to the ground state emitting principally R-line fluorescence — a doublet at frequencies of 14448 and 14419 cm⁻¹. Other polymorphs, for instance, Q have similar fluorescence but at different frequencies. It is thus possible to map out the distribution of the polymorphs, and has recently been used to study the kinetics of the Q-a transformation in oxide scales formed on NiAl high temperature alloys. One of the surprising findings was that as distinct from the usual linear kinetics of interface controlled transformations, the kinetics were logarithmic. The R-line fluorescence also is suited to strain measurement. When the host lattice, for example a-alumina, is strained the crystal field at the Cr³⁺ ions is altered thereby changing the energies of the excited states and hence the frequency of the R-line fluorescence. These changes are relatively small (~ 1 cm⁻¹ per GPa) but by measuring the frequency shift the local strain can be calculated. ■

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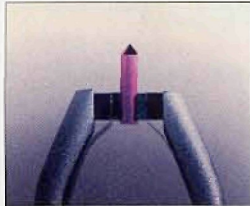
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