ATOMIC SCALE CHARACTERIZATION OF GRAIN BOUNDARIES IN OXIDES

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Grain boundaries play a major role in determining the overall electrical performance of oxide thin films and the electronic devices in which they are contained. Understanding how the grain boundaries affect these properties requires the ability to accurately quantify the structure, composition and bonding changes that occur at the boundary on the fundamental atomic scale. The ability to characterize grain boundaries at this level is possible through the combination of Z-contrast imaging and electron energy loss spectroscopy (EELS) in the scanning transmission electron microscope (STEM) [1].

The resolution in the STEM is primarily controlled by the ability to focus the electron beam down to a fine probe. Typically the probe size in conventional instruments is ~0.13nm [2] and in aberration corrected microscopes this can be reduced further, to <0.1nm. As this probe is scanned over the specimen, the integrated intensity collected in a variety of detectors is simultaneously displayed on a TV screen scanning at the same rate (Figure 1). In one of the detectors that is commonly used for imaging purposes, the high-angle annular dark field detector, the scattered intensity approximates to the Z^2 dependence of Rutherford scattering. For oxide materials in zone-axis orientations, the inter-atomic spacing is typically larger than the probe, allowing columns to be illuminated individually and an atomic resolution compositional map (Z-contrast image) of the sample generated (Figure 2). The high-angle detector does not interfere with the low angle scattering, meaning that EELS can be performed simultaneously with the image. In practice, the image is used to locate a structural feature of interest and position the probe to obtain a spectrum. As the energy loss spectrum maps out the density of states above the Fermi level, changes in the local electronic structure that have a direct impact on the local conductivity can be measured with the same resolution as the image (Figure 2).

An added benefit of these techniques is they provide direct input for ab-initio density functional theory calculations [3]. In these calculations, the structure from the image is used as the basic input parameter, along with composition measurements from the energy loss spectrum. The theory can be used to first minimize the starting structure (the experimental image will be limited by the stability and resolution of the microscope) and locate the optimum low-energy structure, and then to calculate the local density of states. Comparing this density of states with the fine-structure in the energy loss spectrum provides a self-consistent analysis, and allows a complete integration of experiment and theory. The model for the grain boundary structure can then be used to calculate vacancy formation energies, segregation energies etc, and investigate the properties of the boundary under a variety of conditions that are not directly accessible experimentally. Results from perovskite oxide systems that utilize this combination of techniques will be discussed in more detail. Furthermore, the potential for new levels of characterization that the recent development of monochromators and aberration correctors for STEM will permit, will also be discussed.

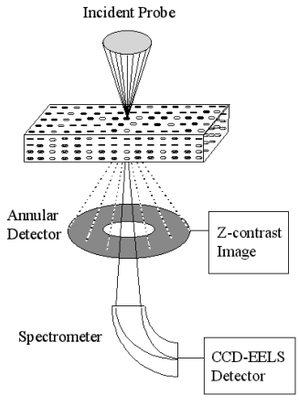

Figure 1: Schematic of the STEM.

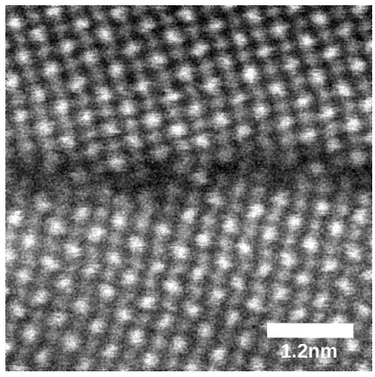

Figure 2: Z-contrast image of a high-angle $SrTiO_3$ grain boundary.

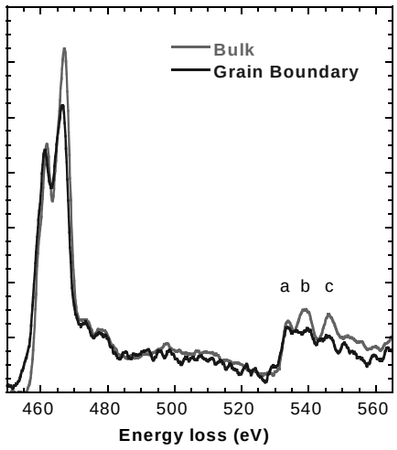

Figure 3: Oxygen K-edge and Titanium L-edge spectra from the bulk and grain boundary highlighting changes in the fine-structure.

[1] N. D. Browning, M. F. Chisholm & S. J. Pennycook, *Nature* **366**, 143 (1993)

[2] E. M. James & N. D. Browning, *Ultramicroscopy* **78**, 125 (1999)

[3] M. Kim et al, *Phys Rev Letts* **86**, 4056 (2000)