A COMBINED EXPERIMENTAL AND THEORETICAL APPROACH TO
ATOMIC SCALE CHARACTERIZATION*

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A Combined Experimental and Theoretical Approach to Atomic Scale Characterization

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Abstract
Recently, the scanning transmission electron microscope has become capable of forming electron probes of atomic dimensions. Through the technique of Z-contrast imaging, it is now possible to form atomic resolution images with high compositional sensitivity from which atomic column positions can be directly determined. An incoherent image of this nature also allows atomic resolution chemical analysis to be performed, by locating the probe over particular columns or planes seen in the image while electron energy loss spectra are collected. Such data represents either an ideal starting point for first principles theoretical calculations or a test of theoretical predictions. We present several examples where theory and experiment together give a very complete and often surprising atomic scale view of complex materials.

1. INTRODUCTION
A scanning transmission electron microscope (STEM) is designed to form a small electron probe which is scanned across a thin specimen as shown in the schematic of Fig. 1. With a crystalline specimen aligned parallel to the beam, the probe preferentially channels along the atomic columns, one by one as it is scanned across the specimen. A Z-contrast image results from mapping the intensity of electrons scattered through relatively large angles, using the annular detector. Because of the large size of the detector, phase contrast effects in the microdiffraction pattern are integrated to give an image based on total scattered intensity. As high angle scattering comes predominantly from the atomic nuclei, bright features in the image correspond directly to columns of atoms, with the brightness determined by their relative atomic number Z. Unlike conventional high resolution electron microscopy (HREM), this technique allows the positions of atomic columns to be determined directly and uniquely from the image to a high accuracy, without the need for extensive simulations of model structures. It provides an incoherent image of the atomic structure of materials and effectively bypasses the phase problem of HREM [1-5]. Such an image is sensitive to unexpected atomic arrangements, and by avoiding the need to search through large numbers of trial structures provides an ideal starting point for theoretical studies, with particular advantage for complex materials. The world's highest-resolution Z-contrast microscope is located at ORNL, a VG Microscopes HB603U with a 300 kV accelerating voltage, with a Scherzer resolution of 1.26 Å, although recently a resolution of 0.78 Å has been achieved in Si<110> using a higher than optimum defocus and large objective aperture [6]. This is sufficient to resolve and distinguish the sublattice in compound semiconductors for the first time, as seen in the image of GaAs shown in the schematic. For example, several different dislocation core structures at a CdTe/GaAs interface have been distinguished, including one structure not previously proposed [7].

Electron energy loss spectroscopy (EELS) can be performed simultaneously with the Z-contrast image, allowing atomic resolution chemical analysis to be achieved [8]. Furthermore, the fine structure on the core loss absorption edges maps the conduction band structure at the atomic
columns illuminated by the probe. Since the probe can illuminate a single plane of atoms at an interface, local changes in band structure, valence and bond angles can be detected. This is particularly valuable at a crystal/amorphous interface where it gives direct information on the structure in the amorphous phase adjacent to the last crystalline plane. At present the EELS capability is only installed on our older 100 kV STEM, which has a probe size of 2.2 Å, although a spectrometer is currently under construction for the 300 kV STEM.

Fig. 1. Schematic showing Z-contrast imaging and atomic resolution electron energy loss spectroscopy on a STEM. The image is of GaAs taken on our 300 kV STEM which directly resolves and distinguishes the sublattice.

2. ARSENIC SEGREGATION SITES AT A SILICON GRAIN BOUNDARY

Z-contrast imaging enables low concentrations of high-Z impurities to be directly observed. The most spectacular recent example of this capability is shown in Fig. 2, a Z-contrast image of a grain boundary in Si, after doping with As [9]. The atomic structure of the boundary is directly determined from the positions of the bright features in the image, and is different from all structures proposed previously. It comprises a continuous sequence of dislocation cores, a perfect edge dislocation (1) and two perfect mixed dislocations (2,3) arranged as a dipole, followed by the same sequence (1',2',3') mirrored across the boundary plane. In the (001) projection, these dislocations appear as a connected array of pentagonal and triangular arrangements of atomic columns. One of the dislocation cores contains columns that are 20% brighter on average than other similar columns, indicating the presence of As atoms. The increased intensity corresponds to an average of only 5% As concentration, approximately two As atoms in each atomic column.
Fig. 2. Z-contrast image of a 23° [001] tilt grain boundary in Si showing its unexpectedly complex structure. The five-fold rings (with black centers in the image) are dislocation cores arranged in a repeating sequence along the boundary. Columns shown black in the schematic are those seen brighter in the image due to segregated As.

This well-defined starting structure enables ab-initio theoretical studies to be performed efficiently, which added significant further insight. It was found that isolated As atoms have only a small segregation energy of \(\sim 0.1\) eV in all the dislocation cores, not showing preference for any site in the boundary. Arsenic dimers, on the other hand, were found to have a substantial segregation energy \([10]\). Most significantly, with a dilute concentration of As dimers, preference was found for those sites seen bright in the image, with the segregation energy being consistent with the As solubility limit in the bulk at the 700°C annealing temperature. This combined use of experimental and theoretical techniques has produced a remarkably detailed and consistent atomic-scale picture of impurity segregation at this grain boundary. Further theoretical work could build on this result to determine grain boundary diffusion coefficients, as well as to extend studies to other boundaries and polycrystalline materials.

3. IMPURITY-INDUCED GRAIN BOUNDARY TRANSFORMATION IN MgO

In this example, STEM imaging of an MgO grain boundary (Fig. 3) found a structure that was not consistent with the widely accepted structure of that boundary proposed by Harris et. al. \([11]\), but more like that proposed much earlier by Kingery \([12]\). These two structures are compared in Fig. 4, where the large empty core of the Harris structure is obviously very different from the more dense core of the Kingery model. Careful examination of the intensity patterns in the experimental image again suggested that impurities may in fact be present at certain sites. EELS measurements (Fig. 5) established that significant concentrations of Ca are present in the grain boundary, 0.3 monolayers, consistent with the bright intensity in the image, and also with theoretical calculations which determined a large segregation energy of 1 eV per Ca atom. Theory further established that the observed structure is in fact stabilized by the Ca segregation. Without the presence of the Ca impurity, the low energy structure is indeed that predicted by Harris et. al. Again, a synergistic approach between theory and experiment was crucial in arriving at the final conclusions.
4. ATOMIC STRUCTURE OF THE Si-SiO₂ INTERFACE

In the case of an amorphous material, no channeling of the probe can occur, and a Z-contrast image reflects only changes in density. This is in marked contrast to conventional HREM images where amorphous materials always show a speckle pattern due to random interferences. In addition, HREM images at interfaces show Fresnel fringes and other coherent interference phenomena. The model of Ourmazd et al [13] is based on a transition from crystal Si through crystal SiO₂ to amorphous SiO₂. The same phase contrast pattern is interpreted by Akatsu and Ohdomari [14] as indicating a direct transition from Si to amorphous SiO₂. The Z-contrast image shows no speckle pattern or interference phenomena at interfaces, as it is close to a direct projection of the atomic structure. In fact, because there is no channeling to concentrate the electrons onto the atomic nuclei, the image looks darker than crystal of the same composition, as seen in Fig. 6. The last monolayer of the crystalline Si is clearly visible in the image; the transition into the oxide is extremely abrupt, which is inconsistent with the presence of crystalline oxide at the interface as shown by the superimposed structure of the two possible oxide projections.
Fig. 5: EELS spectra from a MgO grain boundary and nearby bulk showing Ca segregation.

Fig. 6. Z-contrast image showing the interface between Si and SiO₂ with superimposed structure for a monolayer of crystalline oxide at the interface. The "dumbbells" characteristic of the Si [110] projection are still present at the interface ruling out the presence of any crystalline oxide.

A new model for the interface was deduced by combining the image data with electron energy loss spectroscopy (EELS) [15]. In the case of a thin amorphous material the spatial resolution of the EELS band structure measurement is comparable to the probe size of the microscope. Comparing spectra at the interface with spectra obtained far from the interface (~1-2 nm away) allows a direct determination of any changes to the local bonding. A shift in energy, and altered ratio of first to second peaks indicated the presence of excess Si at the interface, and a change in bond angles. A new structure model for the interface consistent with these effects is proposed in Fig 7.

- Silicon
- Oxygen
Fig. 7. Schematic model of the Si/SiO₂ interface consistent with the Z-contrast image and EELS data. The interface is Si rich and the SiO₄ tetrahedra adjacent to the Si substrate are significantly distorted.

5. CONCLUSIONS

It is now possible to determine, without prior knowledge, the structure, impurity content and local electronic states, at heterostructure interfaces, amorphous/crystal interfaces, as well as at defect sites such as steps and misfit dislocation cores. Although the particular microscopes used here are no longer commercially available, conventional TEM instruments are rapidly improving their probe sizes. A 350 kV TEM with an objective lens C₉ of 0.5 mm should allow a 1 Å electron probe to be formed, giving much greater image contrast and sensitivity to impurities than the results we have shown here. Atomic-scale total energy calculations are a natural complement and extension to these STEM techniques, giving critical insight into the underlying physics through the ability to study segregation energies, electronic states, and atomic scale dynamics.

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