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Structure, Composition and Strain Profiling of Si/SiO₂ Interfaces

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Recently, the scanning transmission electron microscope has become capable of forming electron probes of atomic dimensions. This makes possible the technique of Z-contrast imaging, a method of forming incoherent images at atomic resolution having high compositional sensitivity. An incoherent image of this nature also allows the positions of atomic columns in a crystal to be directly determined, without the need for model structures and image simulations. Furthermore, atomic resolution chemical analysis can be performed by locating the probe over particular columns or planes seen in the image while electron energy loss spectra are collected. We present images of the Si/SiO₂ interface showing no crystalline oxide, compositional profiles across a nitrided sample at 2.5 Å resolution showing an extended sub-stoichiometric zone, and strain profiles at a rough interface showing static rms displacements ~ 0.1 Å extending 10 Å into the crystalline Si.

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 between different Bragg reflections 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 [1-4].

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. 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 [5].

FIGURE 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.

Electron energy loss spectroscopy (EELS) can be performed simultaneously with the Z-contrast image, allowing atomic resolution compositional profiling to be achieved [6]. Furthermore, the fine structure on the core loss ionization 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. 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.

To eliminate the possibility of beam damage affecting the energy loss results, a time sequence of spectra are taken from each region. This is particularly important at an interface, which typically damages before the perfect crystal adjacent to it. The spectra may then be compared, and if no evolution is seen through the sequence they can be added to improve statistics. Similarly, it is also simple to assess the contribution of ion milling surface damage to the shape of the edge by comparing spectra taken from different thicknesses.

THE STRUCTURE OF THE Si/SiO₂ INTERFACE

Conventional HREM images of amorphous materials always show a speckle pattern due to random interferences which tends to obscure the image at the interface and makes it difficult to infer atomic column positions. In addition, HREM images from the interface may show Fresnel fringe effects that can change the contrast of the last one or two Si layers. The direct nature of the Z-contrast image, however, makes it particularly simple to determine the structure at the Si/SiO₂ interface. Because there are no interference phenomena in an incoherent image, there are no Fresnel fringes or speckle pattern, and the last atomic columns of the crystal may be clearly seen.

The sample shown in Fig. 2 was prepared by thermal oxidation of a Si(111) wafer, which was subsequently used as a substrate for liquid phase epitaxy of Si. In this way a single microscope sample contained two Si/SiO₂ interfaces grown in different ways [7]. Both interfaces were found to be atomically smooth and abrupt, as evident in Fig. 2. The oxide appears dark in the Z-contrast image because of the reduced atomic number (Z) and scattering power of the O, and also because the atoms are not aligned in well ordered atomic columns and no channelling of the electron probe occurs.

Superimposed on the image is the structure proposed by Ourmazd et al. [8] from HREM studies, based on a transition from crystal Si through crystal SiO₂ to amorphous SiO₂. Clearly the positions of the Si atoms are inconsistent with even a single monolayer of crystalline oxide at this particular interface. An alternative interpretation of the same phase contrast pattern has been

made by Akatsu and Ohdomari [9]. These authors proposed that interface roughness was responsible for the phase contrast effects. Clearly interface roughness will vary significantly from sample to sample. However, a sample having a rough interface is shown later for strain profiling (Fig. 6) and again there is no evidence for the presence of crystalline oxide at the interface.

FIGURE 2. Z-contrast image of a Si/SiO₂ interface with superimposed structure of crystalline oxide. The "dumbbells" characteristic of the Si [110] projection are still present at the interface ruling out the presence of any crystalline oxide.

COMPOSITIONAL PROFILING AT THE Si/SiO₂ INTERFACE

There is no information in the Z-contrast image from the amorphous oxide. Its atomic structure is unresolved because of the limited resolution and detection sensitivity. Columns of atoms are visible in a crystal, but images from individual Si atoms are below the detection limit. However, information on composition and bonding can be readily obtained with EELS. Fig. 3 shows a series of Si-L_{2,3} ionization edges from a nitrated Si/SiO₂ interface. Each spectrum is obtained with the probe located at a different distance from the interface, as determined from the Z-contrast image. Due to the large band gap of the SiO₂, the onset of the ionization edge is 104 eV in the SiO₂ compared to 99 eV in the Si. It is clear that the edge profile evolves from Si to SiO₂ over a surprisingly extended region, greater than 2 nm.

It is worth stressing that this large interface width is more than an order of magnitude greater than the resolution of the measurement. Allowing for beam broadening in the amorphous oxide and the intrinsic delocalization of the inelastic scattering process [4,10] we calculate an instrumental resolution of 2.7 Å for this measurement.

Figure 4 shows the corresponding set of spectra at the O-K edge. Again, the shape of the edge evolves over a significant distance from the interface, only becoming characteristic of stoichiometric SiO₂ after 24 Å. The ratio of the first to second peak following the ionization threshold may be used to quantify the stoichiometry of the

oxide [11,12]. The resulting quantitative profile in Fig. 5 provides an independent verification of an extended sub-stoichiometric zone with an interface width comparable to that estimated from the Si-K edge spectra.

FIGURE 3. Si-L_{2,3} spectra across a nitrided Si/SiO₂ interface showing evolution of the SiO₂ band gap. The full gap is not established until 2.4 nm into the oxide.

FIGURE 4. O-K spectra across a nitrided Si/SiO₂ interface. No further changes in the edge shape were seen closer to the interface than 0.7 nm.

STRAIN PROFILING ACROSS THE Si/SiO₂ INTERFACE

With a crystalline sample in a zone axis orientation, the intensity reaching the annular detector is predominantly thermal diffuse scattering. The cross section σ per atom depends on scattering angle and temperature through the atomic form factor f and the Debye-Waller factor M^T , as

$$\sigma = f^2 (1 - \exp(-2 M^T s^2)), \quad (1)$$

FIGURE 5. Profile of oxide stoichiometry obtained from the ratio of first to second peaks in the O-K edge spectra shown in Fig. 4 showing providing independent verification of an extended sub-stoichiometric zone.

where s = scattering angle, $M^T = 8\pi^2 \overline{u_r^2}$, and $\overline{u_r^2}$ is the mean square thermal vibration amplitude of the atom. In the presence of static random atomic displacements due for example to the proximity of an incoherent oxide interface, and assuming a Gaussian distribution of strain with a mean square static displacement of $\overline{u_s^2}$, the atomic scattering cross section will be modified to

$$\sigma^s = f^2 (1 - \exp(-2 (M^T + M^s) s^2)). \quad (2)$$

It is clear from the form of these expressions that both tend to the full atomic scattering cross section f^2 at a sufficiently high scattering angle. At lower angles where the Debye-Waller factor is significant, static strains comparable to the thermal vibration amplitude may lead to a significantly enhanced scattering cross section.

An example of strain contrast of this nature is shown in Fig. 6. Here we show a bright field phase contrast image (a), showing dark contrast that could be due to a number of effects, such as strain, thickness variation, bending of the crystal or a combination of these mechanisms. Fig 6(b) shows a Z-contrast image collected simultaneously using a low (25 mrad) inner radius for the annular detector. Now there is a bright band near the interface indicating additional scattering. With this image alone, this additional scattering could be due either to strain or to the presence of some heavy impurity atoms. However, when the inner detector angle is increased further to 45 mrad the bright line disappears, showing that the contrast can not be due to the presence of heavy impurity atoms. It must therefore be due to a strain effect.

In Fig 7 we show a higher magnification Z-contrast image from this interface which can now be seen to have significant roughness, much more than the interface shown

FIGURE 6. Z-contrast image of a rough Si/SiO₂ interface; (a) bright field phase contrast image, (b) Z-contrast image with 25 mrad inner detector angle showing strain contrast. The vertical line marks the last Si plane used for strain profiling. (c) Z-contrast image with 45 mrad inner detector angle.

in Fig. 2. Even 10 Å into the oxide, local intensity maxima are seen at exactly the positions expected for a continuation of the Si lattice, although at a much reduced intensity. This implies that small crystalline regions must be protruding into the oxide, still connected to the Si substrate and so maintaining their correct relative positions. The interface width is therefore several monolayers, and we presume that this extended interface width is the source of the significant strain contrast in this specimen.

FIGURE 7. High magnification Z-contrast image of a rough Si/SiO₂ interface showing a gradual transition into the oxide.

The image intensity is not a direct measure of atomic scattering cross section. In a perfect zone-axis crystal, the electron flux is concentrated into the vicinity of the atomic nuclei, increasing the effective columnar cross section. This channelling effect means that the intensity I scattered by a column in a zone-axis crystal is given by

$$I = \phi^{ts} \sigma, \quad (3)$$

where ϕ^{ts} is the thickness integrated flux at the nuclei (given by the thickness integrated 1s Bloch state intensity at the column in question). Since this channelling effect is not dependent on detector angle (provided scattering angles remain sufficiently high) then images taken at a high angle (where the exponential factor is zero) are a direct measure of the channelling effect, and can be used to normalize images taken at lower detector angles.

For example, to quantify the strains seen in Fig. 6, intensity profiles are taken across the Z-contrast images and normalized to the same intensity far from the interface, as shown in Fig. 8. As the interface is approached, the intensity in the high angle image reduces because the columns are distorted and channel less effectively. The image at 25 mrad detector angle shows increased intensity due to the increased scattering cross section. Dividing this

FIGURE 8. Intensity profiles across the Z-contrast images with 25 and 45 mrad inner detector angles.

FIGURE 9. RMS atomic displacement due to static strain induced by the Si/SiO₂ interface and an exponential decay fitted to the data. Profile ends at the vertical lines shown in Figs. 6 and 8.

trace by the high angle profile normalizes out the channelling effect to give the relative scattering cross section at each position in the crystal. This in turn can be simply converted into a mean square atomic displacement as shown in Fig. 9. It is interesting to note that this displacement falls exponentially from the interface as would be expected for a planar periodic array of misfit dislocation cores. The $1/e$ decay length is 10 Å. Note that this simple normalization procedure assumes that the

column is entirely Si, and therefore is not valid across the diffuse oxide interface itself.

SUMMARY

The STEM techniques presented in this paper show how the atomic resolution Z-contrast image combined with EELS can give insights into the atomic structure, composition, and strain in the vicinity of a Si/SiO₂ interface, at a spatial resolution limited primarily by the size of the electron probe. Plans are underway to install an EELS spectrometer on the ORNL 300 kV STEM, which would increase the available spatial resolution from ~2.5 Å to ~1.5 Å. With shrinking device dimensions, these techniques would seem to be ideally suited for the characterization of gate dielectrics and correlation with electrical properties.

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