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DETERMINATION OF INTERFACE STRUCTURE AND BONDING AT ATOMIC RESOLUTION IN THE STEM

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DETERMINATION OF INTERFACE STRUCTURE AND BONDING AT ATOMIC RESOLUTION IN THE STEM

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1. INTRODUCTION

The scanning transmission electron microscope now routinely produces probes of atomic dimensions, 2.2Å at 100 kV and 1.3Å at 300 kV. This capability opens up a new strategy for determining the structure and bonding of materials at the atomic scale, which is particularly advantageous for complex interfaces such as grain boundaries. The Z-contrast image allows the high-Z column locations to be determined by direct inspection, and quantified through maximum entropy methods to a positional accuracy of currently ~0.2Å. With the same electron probe, located to sub-Ångstrom precision with reference to the Z-contrast image, parallel detection EELS can determine light element coordination from core edge fine structure, in principle around a single atomic column (Browning et. al 1993, Batson, 1993).

2. COLUMN-BY-COLUMN IMAGING AND SPECTROSCOPY

There are several attractive features to combining Z-contrast imaging with EELS. First, the incoherent nature of Z-contrast imaging provides higher resolution, $0.44 \text{ Cs}^{1/4} \lambda^{3/4}$ compared with $0.66 \text{ Cs}^{1/4} \lambda^{3/4}$ for phase contrast imaging, freedom from contrast reversals (see Fig. 1.) and a highly local image. This allows a greatly extended régime of intuitive image interpretation. For example, the presence of dumbbells, with a spacing of 1.36Å, in a Si<110> image is seen directly at 2.2Å resolution from the elongation of the image features. For microanalysis, the Z-contrast image facilitates the accurate placement of the probe over selected atomic columns, either a single atomic column or using a line scan to reduce the effects of beam damage.

Column-by-column analysis by EELS is possible, without beam broadening, through the columnar channeling effect that occurs when a highly convergent *coherent* probe is incident along a low order crystal zone axis. The large angular range of the coherent STEM probe ensures that for localized interactions *s*-type Bloch states are preferentially selected around each atomic column (Pennycook et. al. 1992, 1993). These are the most local type of states, little influenced by their surroundings at typical column spacings. They may also be selected in phase contrast imaging by choosing very thin specimens, but then it is their emergent phase that is imaged, which is strongly thickness dependent and also sensitive to potential tails from surrounding strings. At thicknesses above a small fraction of the *s*-state extinction distance, other types of states will also affect the phase contrast image, and it is important to realize that different states are present at an interface than in a perfect crystal. The phase contrast image from an interface therefore is not generally given by a linear combination of perfect crystal images, but should be interpreted through supercell calculations to include these interface states explicitly. In Z-contrast imaging, it is the *s*-state intensity that is important, which is not sensitive to the potential tails of surrounding strings. Also, since the other states are suppressed, supercells are unnecessary, and an intuitive interpretation then remains valid at complex regions such as grain boundaries and interfaces. This intuitive interpretation extends to thicknesses comparable to the *s*-state absorption length, an order of magnitude greater than with phase contrast imaging, although it should be noted that absorption effects can be quite strong for heavy strings at 100 kV. In thick crystals, this means that only the first few hundred Ångstroms of a high-Z column contributes to the image. However, such effects can be substantially reduced by increasing the accelerating voltage to 300 kV.

Figure 1: Comparison of (a) coherent and (b) incoherent contrast transfer functions for a 300 kV microscope with 1mm C_s and appropriate Scherzer optimum conditions, (a) a defocus of $1.15 (C_s \lambda)^{1/2}$, (b) a defocus of $(C_s \lambda)^{1/2}$, with an objective aperture semiangle of $(4\lambda/C_s)^{1/4}$.

3. MAXIMUM ENTROPY IMAGE RESTORATION

The major disadvantage of Z-contrast imaging is the inherently low signal to noise ratio. Here we expect that the maximum entropy method (Gull and Skilling, 1984) will prove very useful in quantifying images. It appears to be particularly suitable for the reconstruction of phaseless data consisting of discrete points, which is precisely the nature of the Z-contrast object function. As an example, Fig. 2. shows an image of GaAs taken with the VG Microscopes HB603U operating at 300 kV (McGibbon et. al., 1994). The dumbbells are clearly resolved, though noisy, but the maximum entropy analysis brings out the column positions after 100 iterations to an accuracy of $\pm 0.2\text{\AA}$, and distinguishes the polarity of each dumbbell even though the two columns are only two atomic numbers and $1.4\text{\AA}$ apart.

Figure. 2: (a) 300 kV Z-contrast image of GaAs, with maximum entropy restoration for (b) 25, and (c) 100 iterations, revealing the lattice polarity. (d) projected structure.

The reconstruction uses MaxEnt Solutions software based on the Cambridge MemSys 5 software of Gull and Skilling and is available through VG Microscopes. It runs on an IBM 486 PC equipped with a specially designed accelerator card. No prior assumptions are made concerning the nature of the specimen; the routine applies Bayesian statistics, using a given instrumental point spread function, to deduce the most likely positions of the scattering centers in the image. It appears reasonably robust to the choice of probe, giving good reconstructions using a simple Gaussian for example (McGibbon et. al., 1994). In the future it would seem promising to attempt to extract the actual effective probe profile from an area of perfect crystal adjacent to the region of interest. In this way it should be possible to account for probe broadening

in amorphous layers covering the specimen, and perhaps to compensate for the effects of tilt and astigmatism to some extent. This should allow column positions to be determined to greater accuracy. The analysis also provides quantitative intensity data, which gives a direct indication of column composition.

The maximum entropy approach appears to provide an attractive alternative route to sub-Ångstrom resolution (Pennycook et. al., 1994). Since the Z-contrast image does not involve reconstructing the exit face wave function at the specimen it does not have the phase problem or the inverse dynamical diffraction problem associated with coherent imaging methods. The incoherent imaging of columnar scattering powers is a powerful approach to direct structure determination, and the nature of the contrast transfer function suggests that reconstruction to higher resolutions than the Scherzer limit would be relatively straightforward. Provided not all the spacings are below the resolution limit this can be done using the Scherzer optimum probe. Alternatively, the probe profile can be sharpened through the use of higher defocus values; for the optimum conditions shown in Fig. 1., a defocus of 438Å, the first zero of the probe intensity occurs at 1.22Å, but reduces to only 0.82Å by increasing the defocus to 700Å. Such probes must be used with care however, since they are accompanied by a secondary maximum at about 1.5Å which may illuminate some surrounding columns and lead to a less local, less intuitive image.

4. ANALYSIS OF A GRAIN BOUNDARY IN SrTiO₃

To illustrate the strategy for determining high-Z column positions from the Z-contrast image, and low-Z coordination by EELS, we have studied the SrTiO₃ bicrystal grain boundary shown in Fig. 3. This is nominally a near Σ 13 symmetric boundary, although it can be seen that considerable segments are actually faceted along the (001) plane of one of the grains. The Z-contrast image distinguishes the heavier Sr columns from the TiO columns, and their positions can be traced into the boundary to derive an initial structural model. These images were taken at 100 kV with the HB501UX (Browning et. al. 1994). The Sr and Ti column positions can be obtained more accurately from the maximum entropy analysis shown in Fig. 4., in which two different structural arrangements are seen to comprise the boundary, differing by the presence or absence of a TiO column. EELS can now be used to study the oxygen coordination at the boundary. The Ti-L edge fine structure shows striking differences between tetrahedral and octahedral coordination (Brydson et. al., 1992) Spectra taken from the boundary showed a strong resemblance to the octahedral form, with slight changes in the relative strengths of the π^* and σ^* transitions consistent with the distortions across the boundary. Hence the Ti atoms have been placed in octahedral cages in the structural model of Fig. 4(c). Note that the two Sr columns at the center of each triangular Sr unit are very close and are therefore assumed to be half occupied. A bond valence sum analysis validates this structure and shows that both types of unit, with and without a TiO column, can be charge balanced. These Ti voids naturally suggest themselves as candidate sites for the impurities used to tailor the electrical response of this material.

Figure. 3: 100 kV Z-contrast montage of a near Σ 13 tilt grain boundary in SrTiO₃.

Figure. 4: (a) Z-contrast image with (b) maximum entropy restoration revealing boundary units with and without (crosses) TiO columns (c).

5. CONCLUSIONS

Combined Z-contrast and EELS studies of interfacial structure and bonding would benefit from the higher resolution of the 300 kV instrument. Although the impact parameter for core edges increases at the higher voltage, it is more than offset by the decrease in probe size. The ultimate analysis would be achievable with a 300 kV STEM equipped with parallel EELS.

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