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DIRECT DETERMINATION OF GRAIN BOUNDARY ATOMIC STRUCTURE IN SrTiO\textsubscript{3}

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ABSTRACT

In the electroceramic SrTiO\textsubscript{3} the grain boundary atomic structure governs a variety of electrical properties such as non-linear I-V characteristics. An understanding of this atomic structure-property relationship for individual grain boundaries requires a technique which probes both composition and chemical bonding on an atomic scale. Atomic structure models for [001] tilt boundaries in SrTiO\textsubscript{3} bicrystals have been determined directly from experimental data by combining high-resolution Z-contrast imaging to locate the cation columns at the boundary, with simultaneous electron energy loss spectroscopy to examine light element coordination at atomic resolution. In this paper we compare and contrast the grain boundary structure models of symmetric and asymmetric boundaries in SrTiO\textsubscript{3}.

SYMMETRIC GRAIN BOUNDARIES IN SrTiO\textsubscript{3}

Following the experimental procedure described recently (1), a Z-contrast image from a symmetric 36.8° [001] tilt boundary is shown in figure 1. The brighter spots in the image correspond to the strongly scattering Sr columns (Z=38) with the less bright spots corresponding to the lighter Ti-O columns (Z=22 for Ti, 8 for O). The pure O columns are not visible. The maximum entropy image analysis technique (2,3) has been applied to determine the positions and intensities of each atomic column directly from the maximum entropy object function of figure 1(b) without the need for a reference atomic model. Although a relative tilt between the two grains or changes in specimen thickness may result in long range variations in the intensity of the Z-contrast image, the short range variations due to differences in scattering cross-section between the Sr and Ti-O columns always remain intuitive on a local scale.

Figure 1. (a) Z-contrast image of 36.8° symmetric grain boundary in SrTiO\textsubscript{3} with (b) the maximum entropy image providing scattering intensities and coordinates of the Sr and Ti atomic columns directly from the image.
The Sr and Ti-O column coordinates in the maximum entropy object function of figure 1(b) give direct information on the misorientation between the two grains and any rigid body translation or grain boundary expansion present at the boundary. The boundary is symmetrical with a (310)-type boundary plane common to both crystals, which corresponds to a Σ = 5 (310) symmetrical tilt grain boundary in coincident site lattice notation. By constructing a series of corresponding (310) planes in each unit cell across the grain boundary an expansion of ~10% normal to the boundary plane was measured (4). Similarly by constructing the (130) planes normal to the grain boundary a rigid body translation of (0.7 ±0.2)Å was measured.

Figure 2. A comparison of (a) Ti L23 and (b) O K edge spectra acquired from the bulk and boundary of a SrTiO3 bicrystal, showing that the octahedral Ti-O coordination is maintained across the boundary.

Figure 2 compares the Ti L23 and O K edges acquired from the bulk and the grain boundary regions of the sample. The spectra were acquired in line scans parallel to the grain boundary to reduce radiation damage effects. Previous studies have shown that the Ti L23 fine structure is sensitive to changes in Ti-O coordination from octahedral to tetrahedral (5). Since we probe the unit cells forming the boundary plane, and find no significant change, we conclude that the Ti atoms remain octahedrally coordinated to O in the grain boundary, although the bonds themselves are distorted across the boundary. In addition, since no chemical shift is observed in the Ti edge onset in figure 2(a), we conclude that the average Ti valency remains 4+ in the grain boundary region (6,7). In the O K edge spectra from the grain boundary, figure 2(b), the increased σ* intensity relative to the π* peak may also be attributed to the disrupted linear Ti-O coordination across the boundary (8).

By combining the PEELS information on Ti-O coordination with the Sr and Ti-O column positions determined from the Z-contrast image, a model for the grain boundary structure was proposed directly from the experimental evidence. In order to test the validity of the proposed structural model and to refine the positions of the O atoms, bond-valence sum calculations were performed (9,10). In these calculations, the contribution of a particular bond to the formal valence of each of the atoms involved in the bond is calculated from the bond length. Using the coordinates of the metal columns determined from the maximum entropy object function, the oxygen column positions were refined so as to maintain charge neutrality with the correct valence on all the atoms. The refined grain boundary structure model is shown in figure 3. There is a distinct grain boundary structural unit (outlined in figure 3) which consists of half occupied Sr and Ti-O columns at the grain boundary. This observation is consistent with the half occupied Sr columns observed in a 25° symmetric boundary (1) and the reduced density at the grain boundary noted in studies by Merkle and Smith (11) in NiO and Fonda and Luzzi (12) in NiAl.
Figure 3. Grain boundary structural model for a 36.8° symmetric grain boundary in SrTiO₃. The grain boundary structural units are shown outlined.

Comparison of the grain boundary structural units found experimentally in 25°, 36.8° and 67° symmetric boundaries in SrTiO₃ revealed six distinct grain boundary structural units from which all symmetric [001] tilt boundaries between 0° and 90° can be constructed (13).

ASYMMETRIC GRAIN BOUNDARIES IN SrTiO₃

Figure 4 shows the Z-contrast image of a 45° asymmetric grain boundary in SrTiO₃ which is faceted along the (100) and (110) planes. The Z-contrast image can be used to accurately position the probe at the grain boundary for PEELS analysis. Figure 5 compares the Ti L₂₃ and O K edges acquired from the bulk and the grain boundary regions of the sample and again there is no significant change in the Ti L₂₃ edge between the bulk and boundary spectra implying that the Ti atoms remain octahedrally coordinated to O across this asymmetric grain boundary. The O spectra at the grain boundary in figure 5(b) also show the same loss of linear coordination indicated by the increase in the σ* intensity relative to the π* intensity seen in the symmetric boundaries. However, the O K-edge spectra taken at the apex of the grain boundary shows an O configuration similar to that of the bulk suggesting that the O environment has returned to a linear coordination at these regions of the grain boundary.

Figure 4. Z-contrast image of a 45° asymmetric grain boundary in SrTiO₃.
Figure 5. A comparison of (a) Ti L\textsubscript{23} and (b) O K edge spectra acquired from the bulk and boundary regions of a 45° asymmetric grain boundary in SrTiO\textsubscript{3}.

The cation positions were obtained from the maximum entropy analysis of figure 4 and combined with the Ti-O coordination from PEELS to produce a grain boundary structure model directly from experimental results. Figure 6 shows the structure model for the 45° asymmetric grain boundary after bond-valence sum calculations to refine the O positions and verify the half occupied Ti columns at the grain boundary. There are two distinct grain boundary structural units (outlined in figure 6) consisting of a small pentagon of Sr atoms surrounding two half occupied Ti columns and a larger pentagon of Sr atoms surrounding two half occupied and one fully occupied Ti-O column. The frequency of half occupied Ti columns at this grain boundary may explain the (17±8)% grain boundary contraction measured directly from the maximum entropy analysis of figure 4.

Figure 6. Grain boundary structural model for a 45° asymmetric grain boundary in SrTiO\textsubscript{3}. The grain boundary structural units are shown outlined.
In the original study of the 25° symmetric grain boundary in SrTiO$_3$ bicrystals (1) the boundary plane was found to wander from the symmetric (920) common boundary plane to an asymmetric (100) facet. Figure 7 shows the structure model for the 25° asymmetric grain boundary after bond-valence sum calculations to refine the O positions and verify the half occupied Ti columns at the grain boundary. Again there are two distinct grain boundary structural units (outlined in figure 7) consisting of a pentagon of Sr atoms surrounding two half occupied Ti columns (as seen in the 45° asymmetric boundary) and a slightly distorted SrTiO$_3$ unit cell.

Figure 7. Grain boundary structural model for the asymmetric faceted region of a 25° grain boundary in SrTiO$_3$. The grain boundary structural units are shown outlined.

Figure 8. The predicted grain boundary structure for a 33.7° (100/320) asymmetric grain boundary in SrTiO$_3$. 
Comparison of the experimentally derived grain boundary structures for the 25° and 45° asymmetric boundaries shows that these boundaries are composed of 3 distinct grain boundary structural units and that the half occupied columns are an important feature in the structure of asymmetric grain boundaries as well as symmetric grain boundaries in SrTiO₃. The two larger grain boundary structural units represent dislocation cores which is consistent with the need for two types of dislocations to describe asymmetric boundaries. These three distinct grain boundary structural units form the building blocks for asymmetric [001] tilt boundaries in SrTiO₃. This is demonstrated in figure 8 which shows that the predicted grain boundary structure for a 33.7° (100/320) asymmetric boundary is comprised entirely of these three grain boundary structural units.

SUMMARY

In summary, by combining the cation coordinates obtained from the Z-contrast image with the Ti-O coordination from PEELS grain boundary structure models can be derived directly from experimental data for a number of symmetric and asymmetric grain boundaries in SrTiO₃. Bond valence sum calculations were then carried out on these structures to refine the positions of the O atoms and to verify the presence of half filled Sr and Ti-O columns observed in both the symmetric and asymmetric boundaries. These half columns are an important feature of these grain boundary structures which minimize the long range strain fields and avoid self ion repulsion in the dislocation cores. The structural units derived from the experimental images can be applied to determine the structure for all symmetric and asymmetric [001] tilt boundaries in SrTiO₃ in the range 0 to 90°.

REFERENCES

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