The influence of atomic structure on the formation of electrical barriers at grain boundaries in $SrTiO_3$

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An experimental atomic resolution analysis of an undoped Σ5 36° [001] tilt grain boundary in $SrTiO_3$ shows that the structure contains incomplete oxygen octahedra. These incomplete octahedra act as *effective* oxygen vacancies and lead to a fixed, positive boundary charge. Annealing the boundary in the presence of MnO_2 does not change the atomic structure of the boundary plane, and results in a high concentration of Mn^{3+} (acceptor) enrichment at the specific Ti^{4+} locations in closest proximity to the effective oxygen vacancies. This result can be explained in terms of standard charge compensation models and indicates that the formation of electrical barriers at oxide grain boundaries may be influenced by the atomic structure of the boundary plane. © *1999 American Institute of Physics.* [S0003-6951(99)00618-X]

Grain boundaries are known to have a dominating effect on the macroscopic electrical properties of oxides.[1] This can be used advantageously, as with nonlinear current–voltage characteristics for varistors and thermistors,[2] or limit technology, as with the decrease in critical current in high-T_c superconductors.[3] While it is accepted that these effects arise because of a high concentration of donor sites at the boundary, which creates back-to-back Schottky barriers, as yet there is no generally accepted explanation for their origin. In this letter, we report a detailed atomic-scale study of nominally undoped and boundary diffused Mn-doped Σ5 36° [001] tilt grain boundaries in $SrTiO_3$. We find that both grain boundaries, despite their different electronic structures and compositions, have the *same* atomic structure framework, containing incomplete oxygen octahedra. We propose that these incomplete octahedra act as the boundary donor states that influence the electrical activity of the boundary.

Determination of the structure, composition, and local electronic structure at the boundary is provided by the combination of *Z*-contrast imaging and electron energy loss spectroscopy (EELS) in the scanning transmission electron microscope (STEM).[4,5] Figure 1 compares *Z*-contrast images of undoped and Mn-doped 36° [001] bi-crystal tilt boundaries in $SrTiO_3$. In this [001] projection of $SrTiO_3$ (space group $Pm3m$, $a=3.905$ Å), the brighter spots in the image correspond to Sr columns and the less bright spots correspond to Ti–O columns. Oxygen columns are not visible above the background. The Mn doping, which was achieved by annealing a bi-crystal covered with MnO_2 paste at 1350 °C in air for 5.5 h, does not result in the formation of a boundary phase. In fact, it can be seen that both grain boundaries have symmetric (310) grain boundary planes, with *similar atomic structural units*. Of particular interest for both boundaries are the positions where the atomic column separation is very small; like-ion repulsion should preclude such a structure. It has been determined previously that these atomic positions are partially occupied, i.e., there is a 2×1 reconstruction along these atomic columns.[6,7]

Using the *Z*-contrast image to position the probe over specific columns, EELS can be used to determine the Mn concentration at defined locations in the structure. Figure 2 shows oxygen *K*-edge and Mn $L_{2,3}$-edge spectra acquired from the atomic positions marked on the schematic. As can be seen from the oxygen *K* edge, there are significant changes in the fine structure at the doped boundary. This is in marked contrast to the small changes observed at several nominally undoped boundaries.[6] Furthermore, significant quantities of Mn were found up to 3 nm on each side of the boundary plane. However, as can be seen from Fig. 2(c), the highest density of Mn atoms occurs at the atomic positions corresponding to the most dramatic changes in the oxygen *K*

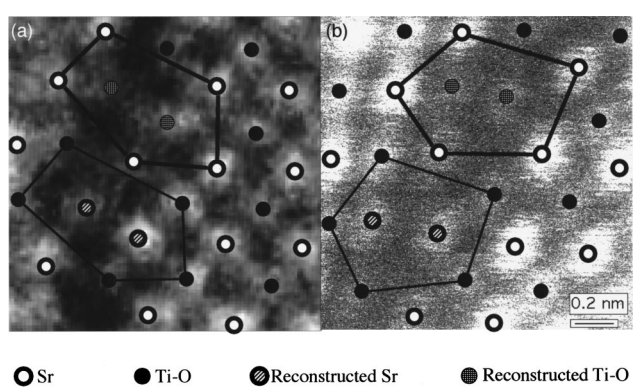

FIG. 1. (a) *Z*-contrast image of a nominally undoped Σ5 36° [001] tilt grain boundary in $SrTiO_3$. (b) *Z*-contrast image of the Σ5 36° [001] tilt grain boundary after Mn doping.

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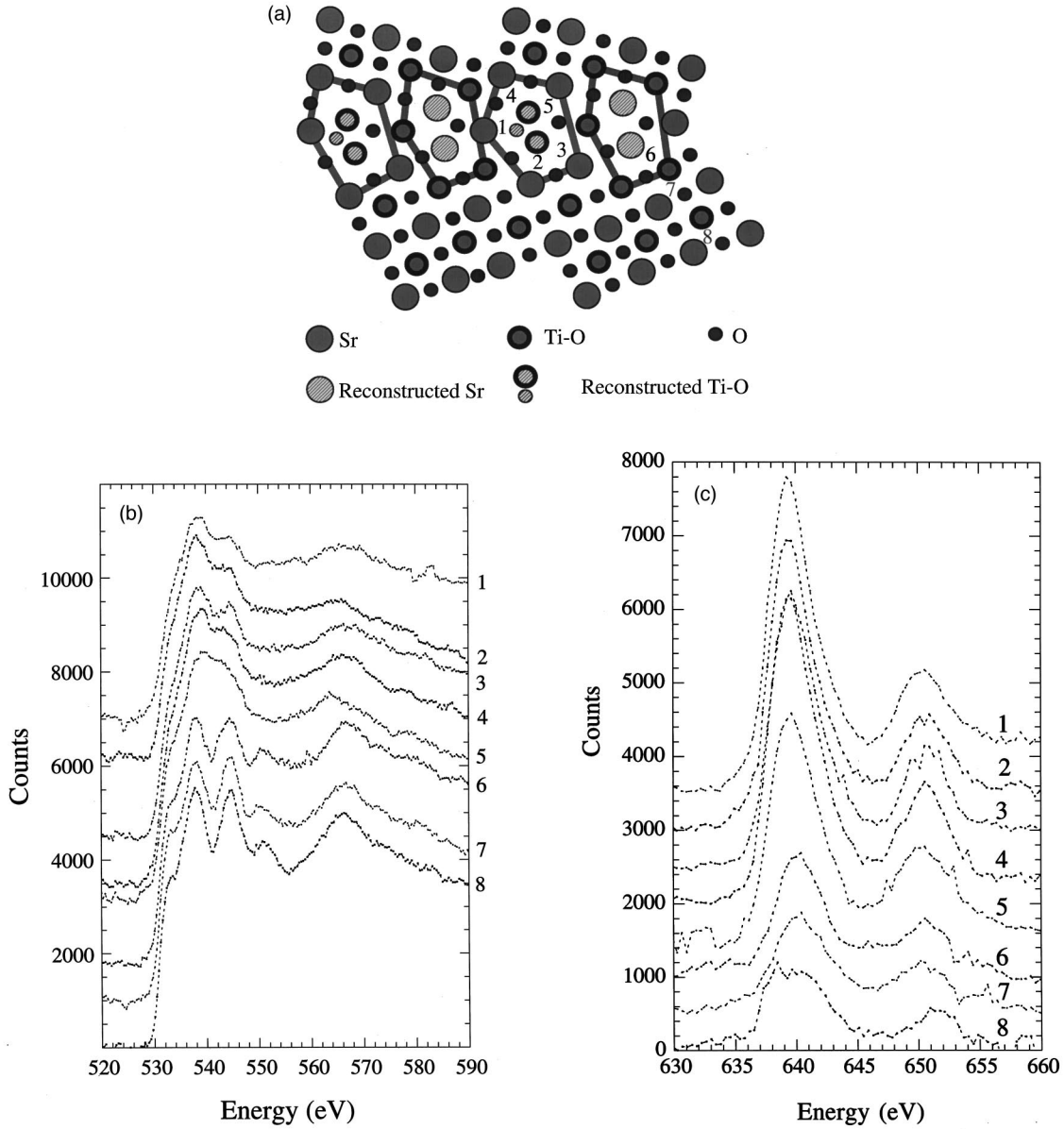

FIG. 2. (a) Schematic of the undoped and Mn-doped boundary structure. (b) Experimental oxygen *K*-edge spectra. (c) Mn $L_{2,3}$-edge spectra obtained from defined locations in the grain boundary plane.

edge (also corresponding to the reconstructed atomic column positions). Detailed analysis of the Mn $L_{2,3}$-edge fine structure shows that the L_3/L_2-edge ratio is 3.6 at the boundary and only 3.0 in the bulk. Comparing these numbers to literature values for bulk manganese oxides[8] indicates that the nominal valence of the Mn in the boundary plane is 3+, while in the bulk it is 4+. Although cluster calculations have predicted this decrease in nominal Mn valence at the grain boundary,[9] this is the first experimental measurement of a spatial variation in the nominal Mn valence. This result suggests it is the *structure* of the boundary plane that plays a critical role in *defining* the valence state of the Mn dopants.

Although the *Z*-contrast image only gives us the location of the cations in the structure, we can include the oxygen atoms using bond-valence pair potentials.[6,10] This analysis reveals that the near neighbor atomic spacings in the boundary are within a small fraction of an angstrom (± 0.2 Å) of the bulk values. This means that we can define the same coordination shells as in the bulk,[10] and that we might, as a first approximation, interpret *changes* in coordination at the grain boundary in the *same manner as the bulk*, i.e., as donor and acceptor states (Fig. 3). This assumes that the energy levels due to incomplete coordination in the boundary are similar to those for vacant sites in the bulk (rigorous proof will require extensive first principles calculations). However, if in a simplistic first approximation we assume this is the case, then it is immediately obvious from Fig. 3 that the cations in the undoped boundary have a reduced oxygen coordination and the structure is therefore *effectively* donor doped. We emphasize that this intrinsic charge imbalance results from broken symmetry and boundary reconstruction and is not due to real dopants. All of the possible lattice sites in the boundary are occupied. Inserting an extra oxygen into the boundary plane to complete the octahedron results in a nearest neighbor separation ~1 Å; it is therefore quite clear that this cannot be the case.

Invoking the well-known ionic charge compensation models for $SrTiO_3$,[11] these incomplete octahedra naturally

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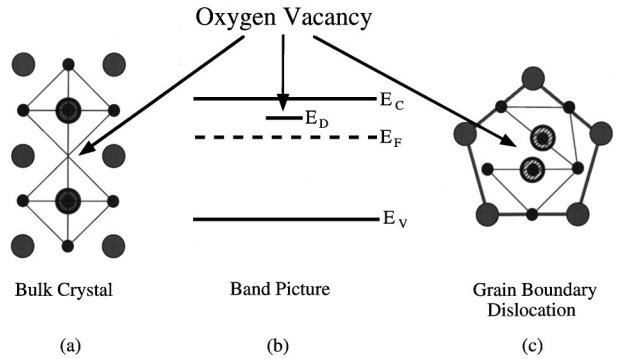

FIG. 3. (a) Reduced atomic coordination of cations in the bulk due to an oxygen vacancy results in donor states being formed near the conduction band edge (b). A similar reduced coordination is present in the dislocation cores of the grain boundary (c).

explain the presence of Mn^{3+} in the boundary core. The energy loss spectra identify the location of the majority of Mn^{3+} (acceptors) at the sites in closest proximity to the effective vacancies (donors), thereby compensating for the excess charge. As the distance from the boundary increases, the spectra show that Mn exists in the nominal 4+ valence state, i.e., it is not an acceptor. Again, this is to be expected as the influence of the effective donors decreases with distance and is compensated by the presence of Mn^{3+} in the boundary core. It should also be noted that, although this result is obtained from a single, well defined boundary plane, the presence of reconstructed atomic columns at tilt grain boundaries in perovskite structured materials appears to be ubiquitous.[10,12,13]

The lack of space to incorporate more oxygen atoms in the grain boundary plane means that these effective vacancies are immobile and unable to diffuse, thereby explaining much of the existing electrical data in the literature.[2] For example, although we have not considered the thermodynamics of compositional variations and bulk donor/acceptor impurities, these effects will only increase the potential barrier at the interface. Therefore, this grain boundary plane will always be positive. This is consistent with the universal observation of a positive boundary with a negative space charge potential[14] in all undoped and bulk acceptor/donor doped $SrTiO_3$ (there are no observations of donor segregation[14]). Additionally, it is expected that in the undoped material the isoelectric point should occur very close to the stoichiometric mix, $Sr+Ti+O_3$. However, from this model it can be seen that there is no feasible way to overcome the intrinsic boundary charge on the atomic level. The inability to reach the isoelectric point has been observed experimentally in $SrTiO_3$.[14]

In conclusion, we have shown how the intrinsic structure of this $\Sigma 5$ 36° [001] tilt grain boundary leads to incomplete oxygen octahedra. These act as immobile effective vacancies, and lead to the formation of a positively charged grain boundary plane and electrical barriers consistent with those reported in the literature. We point out especially that reconstructions similar to those discussed here have been observed in *all* [001] and [011] tilt grain boundaries in $SrTiO_3$[6,10,12] so far observed, implying that this phenomenon is generic to all grain boundaries, not just this particular special boundary. Additionally, as the high-T_c superconductor $YBa_2Cu_3O_{7-\delta}$ also has similar structural units, we therefore expect that a similar explanation lies behind the observed reduction in grain boundary critical current.[13] Further analysis of these ideas may lead to a comprehensive atomic model for conductivity at grain boundaries and other internal interfaces in oxides.

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