Ab initio calculations of rigid-body displacements at the $\Sigma5$ (210) tilt grain boundary in TiO$_2$

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Through extensive *ab initio* total energy calculations of the $\Sigma5$ (210) grain boundary in TiO$_2$ (rutile), the remarkably large rigid-body contractions found by high resolution electron microscopy and Z-contrast imaging are explored. Unlike previous calculations, this work emphasizes the importance of the displacements of the two halves of the bicrystal towards one another. Previous experimental work suggests that the stochiometry and ionic charges at the boundary are preserved at their bulk values and therefore vacancies and impurities within the grain boundary core were not considered. The calculations predict no significant rigid-body contraction or expansion. The implications of this result for both computational and experimental studies of rigid-body displacements at grain boundaries are discussed.

It is well known that the grain boundaries in polycrystalline materials have a profound effect on their electronic and vibrational properties, but the exact nature of these defects is not well understood even in Si, the most studied electronic material. Transition metal oxides have many physical properties that are important for such diverse applications as catalysis,[1,2] electronic devices,[3] and electrochemical cells,[4] to name a few. One of the most widely used transition metal oxides is TiO$_2$, a semiconducting ceramic used in catalytic processing of organic wastes,[5] photovoltaic cells,[6] protective coatings and paints,[7] and gas sensors.[8] Many other technologically important materials have the rutile and similar structures.[9] In these materials, as in Si, it is essential to understand grain boundaries on the atomic level, where the electronic and vibrational states are determined and to relate this structure to the various physical properties.

From a fundamental perspective, TiO$_2$ has become of great importance because well characterized bicrystals of it can be readily grown and studied by a variety of powerful experimental techniques such as Z-contrast scanning transmission electron microscopy (STEM), electron energy loss spectroscopy (EELS), and high resolution electron microscopy (HREM). Unfortunately, on the theoretical side, TiO$_2$, like all oxides, is difficult to work with because of the O ions whose electronic structure is quite sensitive to the crystalline environment (the O^{2-} ion is unstable in free space). This problem becomes potentially severe near surfaces and interfaces where the crystalline environment may differ greatly from that of the bulk material. It was found by Dahman *et al.*[10] using HREM that the lattice around the $\Sigma5$ (210) TiO$_2$ grain boundary is *contracted* through a rigid-body shift by a remarkably large amount ($\sim$1 Å). This result has defied theoretical explanation in terms of either *ab initio* or semiempirical calculations, leading Dahman *et al.* to attribute it to defects (a loss of oxygen) and/or nonstochiometry (excess Ti with a +3 valence). But the subsequent EELS measurements of Wallis *et al.*[11] gave details about the oxidation states at cation sites and the atomic structure around anion sites from multiple scattering theory. It was found that to a

large degree the stochiometry and ionic charges at the boundary are preserved at their bulk values. Further, the Z-contrast image of the grain boundary in Ref. 11 agrees with the HREM results[10] in that a large rigid-body contraction is indicated. In addition, it is clear from the Z-contrast image that some of the projected Ti-Ti distances across the grain boundary are significantly contracted (11–18 %) compared to the bulk. In the work described here, we explore the structure at the grain boundary through very extensive *ab initio* calculations, with particular emphasis on the relative stabilities of grain boundary structures that include rigid-body shifts of various magnitudes.

Structural calculations have generally proceeded by two approaches. One uses semiempirical methods such as the shell model developed by Dick and Overhauser[12] for the calculation of phonon dispersion curves, while the other uses first principles calculations, perhaps augmented by semiempirical considerations.[13] In this work only first principles calculations are used. It should be noted that a paper by Dawson *et al.*[14] employed techniques quite similar to those used here to study the same grain boundary in TiO$_2$ but with a few significant differences as discussed below.

Our calculations, like many others, are based on density functional theory using the local density approximation combined with nonlocal, norm-conserving pseudopotentials and plane wave expansions.[15] The calculations used the band-by-band conjugate gradient technique to minimize the total energy with respect to plane-wave coefficients. Pseudopotentials of the Kleinman-Bylander[16] representation were generated in real space using a well established optimization scheme. The O potential was generated using the reference atomic configuration $2s^2 2p^4$ for the s and the p angular momentum components. For the d component, $2s^1 2p^{1.75} 3d^{0.25}$ was used. For all three components, the core radii were 1.8 a.u. The Ti potential used $3d^2 4s^2$ for the s and d components and $3d^2 4s^{0.75} 4p^{0.25}$ for the p component. Core radii of 2.5 a.u. were used for all three components. Brillouin-zone sampling used the lowest-order set of k points.[17] After extensive experimentation, a plane-wave cutoff of 1000 eV was used.
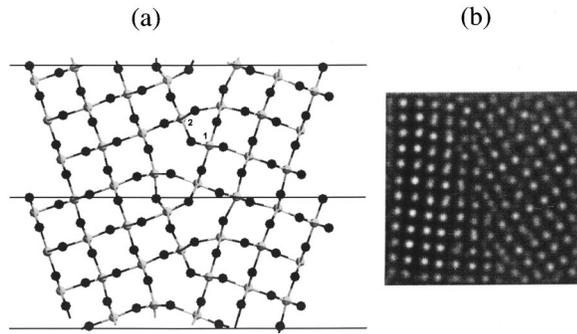
(a)   (b)

FIG. 1. The $\Sigma5$ (210) grain boundary in TiO_2: (a) sixty-six-atom unit cell used in the preliminary calculations where the lines indicate the unit cell boundaries and (b) Z-contrast image.

The energy per unit cell was converged to 0.001 eV/atom (0.066 eV/unit cell) and residual forces on the ions were less than 0.1 eV/Å.

Before the grain boundary calculations, a bulk TiO_2 unit cell was allowed to relax and the results are as follows:

Parameter	Theory (this work)	Theory (Ref. 14)	Experiment (Ref. 18)
a (Å)	4.603	4.603	4.594
c (Å)	2.976	2.976	2.956
Ti-O (short) (Å)	1.953	1.961	1.949
Ti-O (long) (Å)	1.989	1.978	1.980

It should be noted that the calculations in Ref. 14 used a 500 eV cutoff rather than the 1000 eV cutoff used in this work.

Figure 1(a) shows the grain boundary structural model used in the initial calculations. The large unit cell of these calculations is enclosed by the solid lines. The grain boundary structure was generated by matching the two halves of the bicrystal at one of the O sites in the bulk unit cell, carrying out the necessary rotations to get the $\Sigma5$ coincident site lattice and removing all ions that were within 0.5 Å of one another. The large unit cell contains sixty-six ions and is electrically neutral for formal valences of $+4$ and -2 for Ti and O, respectively. We also constructed structural models by taking the match points at the Ti ions, but this generated only symmetric boundaries that did not agree with the microscopy results unless an additional translation along the boundary was introduced, as others[10] have noted.

It is seen that our unit cell does not contain two grain boundaries of opposite orientation as in Ref. 14. Instead we include several ''layers of vacuum'' before repeating the structure to form a periodic slab configuration. While this approach introduces surface states, it allows more atoms per grain boundary unit cell to be treated and eliminates the interaction of close-lying, oppositely directed grain boundaries. Numerous calculations were made to study the effects of varying the vacuum layer thickness. As the bicrystal was expanded and contracted, the number of vacuum layers also increased and decreased such that the length of the bicrystal minus the length of the vacuum layers is constant at 5.5 Å. This was done to satisfy long-range interactions of the crystal atoms and at the same time prevent orbital overlap at the surface edges. This approach will be discussed in detail in a later paper.

Initially, the connectivity in the c direction was the same as in the bulk but subsequently the two sides of the grain boundary were displaced relative to one another along c, as described below. The ions on the outer extremities of the slab were fixed and all others were allowed to relax. The very lengthy calculations (carried out on an Intel Paragon supercomputer) with this structure gave results so similar to those of Dawson *et al.* that they will not be discussed further here. While the grain boundary structure is quite similar to the experimental images, reproduced in Fig. 1(b), the large inward rigid-body shift could not be obtained. Although these calculations, like those of Ref. 14, were unsuccessful in this respect, they provided some important insights. It became clear that only those ions in the immediate neighborhood of the grain boundary plane undergo significant displacements during relaxation. In contrast, other ions near the grain boundary plane moved only slightly and still more distant ones hardly at all. This implied that some other approach would have to be taken if the large observed contraction was to be obtained.

The results of Ref. 10 suggest that one side of the grain boundary is simply rigidly displaced toward the other while maintaining essentially the bulk distances within each half of the bicrystal. Thus, all atoms on one side of the bicrystal must undergo large displacements relative to those on the other side. Obviously, then one cannot fix one or more layers of ions on both sides of the grain boundary, as is sometimes done, and expect to find the observed result. To implement this rigid displacement constraint in our calculations, the number of atoms in the unit cell was reduced to forty-eight. This simplification, which appears well justified in view of the results for the sixty-six ion calculation, made it possible, though computationally still extremely intensive, to carry out the series of calculations discussed next.

It should be emphasized that, with the exception of the rigid-body displacements of the two sides of the grain boundary relative to one another, the atoms at the slab/vacuum surfaces are held rigid throughout the calculations. This is because the slab is cut out of, and is meant to mimic, a bulk TiO_2 material. The surface states are the same for each structure considered and it is assumed that their effect on the *relative stabilities* should be negligible. Some evidence for this is that the relaxation of grain boundary core atoms in the sixty-six atom unit cell (with more rigid ''bulklike'' atoms between the grain boundary core and the surface of the slab) was approximately the same as the relaxation of grain boundary core atoms in the comparable forty-eight atom unit cell (with fewer ''bulklike'' atoms between the grain boundary core and the surface of the slab).

Figure 2 summarizes the results of the calculations. Curve 1 shows the total energy for the forty-eight ion configuration discussed above and shown in Fig. 3 as a function of the rigid projected displacement, x_p, of Ti atoms *at the edges of the slab* towards and away from one another. The atoms at the edge are shifted in such a way that their relative position in the c direction is maintained at the level given in Fig. 1(a). This means that the projected distance observed by TEM is shortened while keeping the $+4$ Ti atoms fairly far apart since they are on different levels in the c direction. The atoms that were allowed to relax are the twenty-seven inside and at the perimeter of the grain boundary, indicated by the
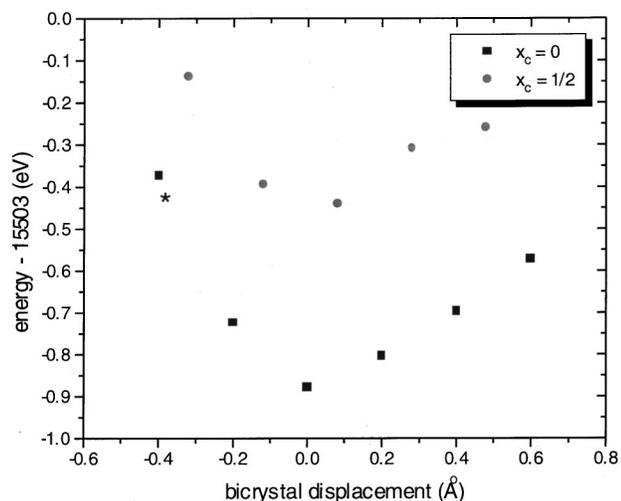
FIG. 2. Relative stability of grain boundary structures as the two sides of the boundary are shifted relative to one another. The two curves represent structures that are shifted relative to one another in the c direction as discussed in the text. The asterisk indicates a contraction comparable to that found experimentally.

FIG. 3. The minimum-energy structure for the forty-eight-atom unit cell where $x_c = 0$. The shaded areas mark the grain boundary core where atoms were allowed to relax. Two unit cells are shown for clarity.

shading in Fig. 3. In addition to the rigid-body displacement, we calculated the relaxed projected Ti-Ti distance across the grain boundary. The results show no rigid-body contraction of the bicrystal but there is a large contraction of the Ti-Ti projected distance across the grain boundary of 12% (0.4 Å) that does agree with the Z-contrast image obtained by Wallis *et al.* However, the calculations also give a projected Ti-Ti distance that is 10% (0.33 Å) greater than the bulk on one side of the grain boundary region not seen in the Z-contrast image. These expansions and contractions effectively cancel each other out.

In the second series of calculations, the two sides of the grain boundary were displaced relative to one another by $c/2$. This is equivalent to interchanging the up-down positions of all ions in the bulk unit cells as the grain boundary is crossed. It also puts the 1 and 2 Ti atoms shown in Fig. 1(a) on the same level in the c-direction. Thus, in this case the actual and projected Ti-Ti distances are the same. The results are shown in curve 2 on Fig. 2. The total energy is ~0.44 eV (0.009 eV/atom) higher than that of the preceding calculations and the minimum again occurs at a position where there is little or no rigid-body contraction of the bicrystal. A smaller contraction of the Ti-Ti projected distances across the grain boundary relative to the bulk of 4.3% (0.14 Å) is predicted for this structure.

The results of these calculations argue strongly that the experimentally observed rigid-body contractions must be due to some phenomena not considered in these calculations,
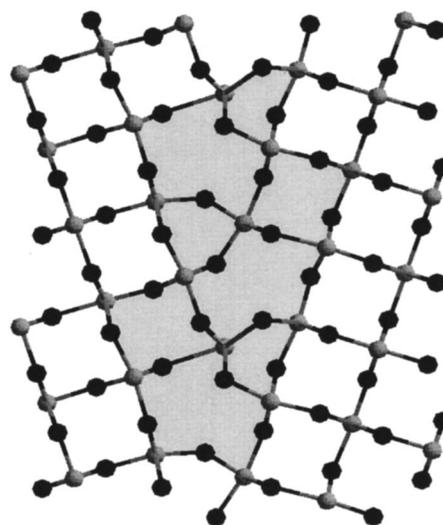
such as half-filled columns, vacancies, or impurities that are present at this grain boundary and not detected in the EELS work of Wallis *et al.*[10] Whatever the origin of the contraction, the implication for the computational side is disturbing in that long series of calculations for even more complex structures will have to be considered, requiring greatly increased computational power. However, for the experimental side, the implications may be even more significant. Clearly, the whole question of the growth of bicrystals, which is still in its infancy, becomes crucial. How can it be established that an ''intrinsic'' grain boundary, devoid of impurities, vacancies, half columns, etc. has been obtained under given growth conditions? The crucial need for microscopes with even higher resolution that are able to detect all the ionic species in a given sample is evident. Recent progress in correcting the large spherical aberration of present objective lenses promises to make such microscopes a reality.[19,20]

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