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STRUCTURE, ENERGY, AND ELECTRONIC PROPERTIES OF THE $\Sigma = 13$ {510} TILT GRAIN BOUNDARY STRUCTURE IN SI

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J. R. Morris*, Z.-Y. Lu*, D. M. Ring*, J.-B. Xiang*, K.-M. Ho*, C. Z. Wang*, C.-L. Fu†
*Ames Laboratory–U. S. Department of Energy, Department of Physics and Astronomy, Iowa State University, Ames, IA 50011
†Metals and Ceramics Division, Oak Ridge National Laboratory, Oak Ridge, TN 37831

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ABSTRACT

We have examined a variety of structures for the {510} symmetric tilt boundary in Si, using first-principles calculations. These calculations show that the observed structure in Si is the lowest energy structure. This structure is more complicated than what is necessary to preserve four-fold coordination. We compare the results to classical and tight-binding models, in order to test these empirical approaches.

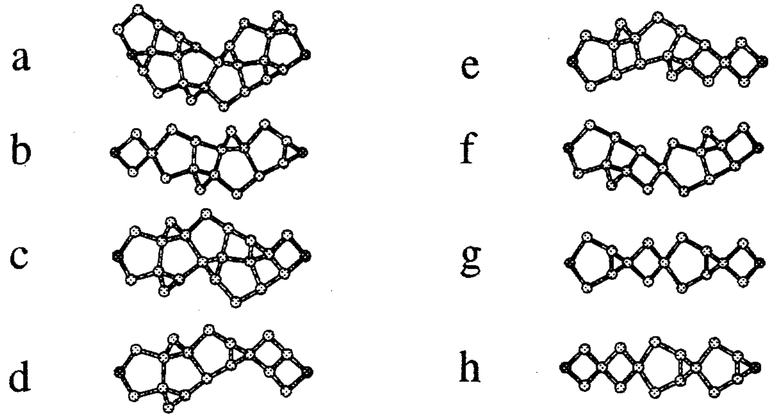
INTRODUCTION

Grain boundaries in semiconductors have been of interest for some time [1], due to the importance of polycrystalline semiconductors in the microelectronic industry, the interest in micromechanical materials, in solar energy applications, and in nanocrystalline Si [2]. The grain boundaries can provide preferential sites for dopants [3, 4], and act as low energy diffusion pathways. For low energy tilt boundaries, which usually retain the four-fold coordination found in bulk [1], the dominant electronic effects are presumed to be due to dopant segregation to the grain boundary; however, intrinsic gap states localized to the grain boundary may still occur if the bonding is sufficiently distorted.

The atomic structure of grain boundaries in Si and Ge has received some attention both experimentally [5, 6, 7, 8, 9] and theoretically [1, 10, 11, 12], but both types of studies are difficult. The experimental resolution necessary to examine the atomic structure of a grain boundary is difficult to achieve. The theoretical studies are complicated by the presence of multiple structures for a given angle. For special low-energy boundaries, such as the {210} and {310} tilt boundaries, there are only two boundaries to be considered. For other boundaries, including the {510} boundary considered here, there are considerably more possibilities, all of which preserve four-fold bonding. Complicating the calculations is the questionable ability of empirical potentials to correctly predict the lowest energy structure. Also, the large system sizes necessary for the calculations ($\sim$ 400 atoms for the boundaries in this study) makes first-principles calculations very costly in terms of computer time. Furthermore, experiments on Ge have observed multiple structures for the same grain boundary, suggesting that several configurations may be very close in energy, and that energetics are not the complete story in predicting the structures [7, 8].

We have begun examining grain boundaries in Si and Ge, using first-principles calculations. In this paper, we briefly present work on the {510} symmetric tilt boundary. (A more detailed account has been submitted elsewhere [13].) This boundary has been studied in Si and Ge experimentally [6, 7, 8, 9], and has also been simulated using empirical potentials. The empirical potentials do not predict that the structure observed in Si [9] is the lowest energy. The same structure (shown in fig. 1a) has also been seen in Ge [6, 7, 8], but another disordered structure has also been observed.

Figure 1: Eight possible structures for the {510} symmetric tilt boundary. The structures are shown in order of increasing grain boundary energy. The lowest energy structure (A) has been experimentally observed in both Si and Ge. All structures are fully four-fold bonded.



The crystallography of the [001] symmetric tilt boundaries has been examined thoroughly [1, 10]. For (510) boundaries, the repeat distance along the boundary is $\frac{1}{2}\sqrt{26}$ times the cubic lattice constant a_0. This boundary contains a number of dislocations, with a total Burger's vector of $\mathbf{b} = [100]$. The individual dislocations that occur are either $\mathbf{b} = \frac{1}{2}[110]$ and $\mathbf{b} = \frac{1}{2}[1\bar{1}0]$ pairs of edge dislocation, or $\mathbf{b} = \frac{1}{2}[101]$ and $\mathbf{b} = \frac{1}{2}[10\bar{1}]$ 45° mixed dislocation pairs. Grain boundaries made up solely of the edge dislocation structures are shown in [001] projection in figs. 1e and 1f, and are characterized by a set of five-fold and three-fold rings sharing a vertex. The mixed dislocation core structures, which can form the (510) grain boundaries shown in fig. 1g and 1h, also appear as a combination of a five-fold and a three-fold rings, but sharing an edge.

THEORY

The first step in studying these boundaries is to generate a set of possible structures. A number of structures have been studied previously [6, 10, 12]. We felt that in addition to including previously studied structures, we should also search for possible new structures. This was done by constructing a system with two (510) boundaries, such that the system had periodic boundary conditions. This system was then simulated at 1900 K using a Tersoff potential [14]. Thirty two independent simulations were performed, each for 10^6 time steps of 0.54 fs. At this temperature, with the 0 K lattice constants, the bulk was stable. The grain boundaries, on the other hand, changed structures occasionally, without melting. By examining structures time averaged over 20,000 time steps, we identified eight different structures, shown in fig. 1. These structures (appropriately relaxed) formed the basis of the rest of the calculations. With the exception of structure b, these structures had been previously considered as candidates [6]. Structure b is new, though it is similar to structure d.

These structures were then fully relaxed using the Tersoff potential. This was done in two ways: first, a single grain boundary was studied using open boundary conditions along the direction perpendicular to the boundary. Second, a fully periodic system with two identical boundaries was relaxed. The two boundaries were approximately 50 Å apart, depending upon the details of the structure. The numbers of atoms ranged from 380 to 416. The grain boundary energies calculated from these two techniques were nearly identical.

Table I: Silicon grain boundary energies in units of mJ/m^2. The structures are labeled both according to their order in fig. 1, and by the notation used by Bourret.

Structure		Ab Initio	Tersoff	Tight-Binding
			mJ/m^2	
a	M	620	416	548
b	none	686	443	617
c	IV±	733	486	664
d	IH±	736	459	665
e	$Z_{2,0}$	744	451	695
f	$Z_{1,1}$	784	481	719
g	$S_{1,1}$	798	479	740
h	$S_{2,0}$	808	469	757

These energies are given in Table I. Within the Tersoff calculations, all of the different structures had very similar energies, with the highest energy structure having an energy about 20% higher than the lowest energy structure.

The relaxed, periodic structures were then used as starting points for a first-principles conjugate gradient plane wave calculation of the atomic structure and energy. The calculations have been performed using the pseudopotential plane-wave self-consistent method which is based on the density functional theory within the local density approximation (LDA) [15, 16]. We adopted the Ceperley-Alder exchange and correlation potential functional with the parameterization of Perdew and Zunger [17, 18]. We modeled the electron-ion interaction using a norm-conserving pseudopotential [19] in the Kleinman-Bylander form [20] with s and p nonlocality. The Kohn-Sham orbitals were expanded in plane waves with an energy cutoff of 10 Ryd.

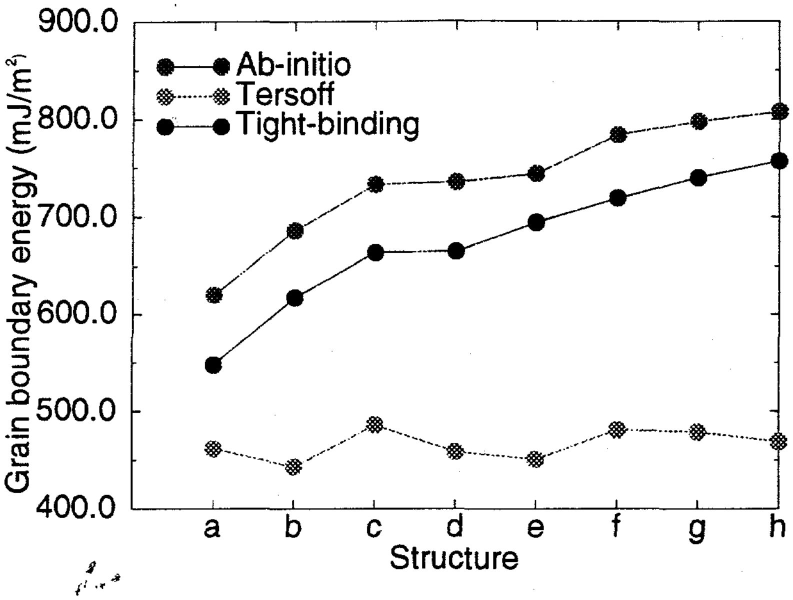
In these calculations, the dimensions normal to the grain boundaries are roughly ten times larger than the dimensions along grain boundaries. This case is similar to that in typical surface slab calculations. *Ab initio* calculations done for Si and Ge surfaces show that a 10 Ryd energy cutoff is enough to correctly reflect the electronic and atomic structures of Si and Ge surfaces (for example, see refs. [21, 22]). This is the reason why we chose 10 Ryd as an energy cutoff in our grain boundary slab calculations (note that no vacuum is involved in our slabs). So we can approximately consider the Brillouin Zone as two-dimensional. A set of four special k-points is therefore chosen to sample the two-dimensional rectangular Brillouin Zone[23].

We allowed all atoms in the system to relax until the forces were less than 10 meV/Å. We computed the bulk diamond energy using a slab cell with equivalent k-point sampling and slab size as ones in the grain boundary calculations, in order to eliminate the error induced by different k-point samplings and slab geometries. We can therefore compare different calculated grain boundary energies with reliable accuracy.

RESULTS

The Si grain boundary energies are shown in Table I. Structure a is clearly the lowest in energy. This structure has been observed in Si [9] and in Ge [7]. The structures shown

Figure 2: Grain boundary energies for different structures. Letters indicate the appropriate structure, as labeled in fig. 1.



in fig. 1 are labeled in order of increasing energy. The highest energy structures are those that contain regions that are structurally similar to the bulk, with a minimal number of dislocation cores. The new structure that we located is also low in energy.

In fig. 2, we show the energies of the different structures, using the ab-initio values, the Tersoff values, and the values obtained from an environment-dependent tight-binding potential developed for Si by Pan *et al.* [24]. The tight-binding results accurately predict the differences in energy, producing the correct ordering, and reasonable results for the actual grain boundary energies as well. The Tersoff potential, on the other hand, does not correctly predict the lowest energy structure; indeed, the Tersoff results suggest (incorrectly) that the energy is only weakly dependent upon the actual grain boundary structure.

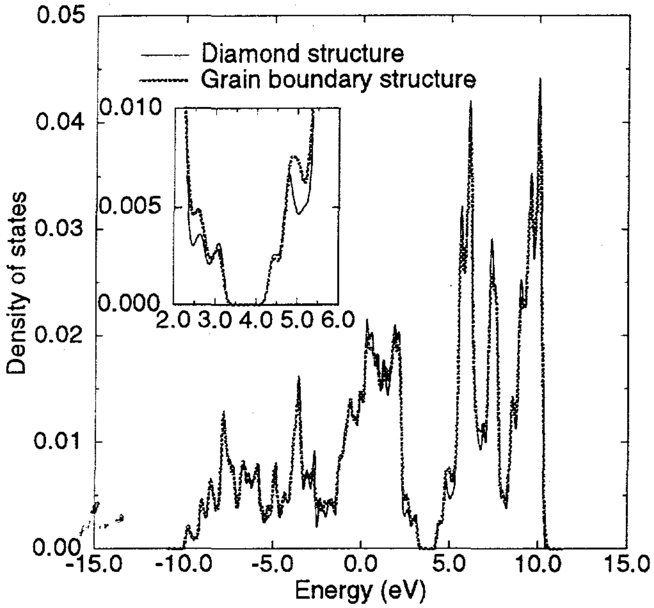
One of the interests in grain boundaries in semiconductors is their electronic properties. In particular, the possibility of gap states would affect the properties of polycrystalline semiconductors. While electronic activity of such boundaries has been noted experimentally [2, 25], calculations of pure Si and Ge systems [3, 11, 26] have not shown any states in the gap, although edge states localized to grain boundaries have been predicted.

We have begun analyzing the electronic structure using our tight-binding model. While these calculations are still underway, we have been able to show that the presence of the grain boundary shown in fig. 1a does not significantly affect the density of states, when compared to a perfect system. In particular, the density of states (DOS), shown in fig. 3, shows no evidence of mid-gap states. Although there is some increase in the DOS near the band gap (see inset), this is not a strong effect. Preliminary analysis of states near the gap using inverse participation ratios do not show strong localization of the states.

CONCLUSION

We have used first-principles calculations to examine eight different structures for the {510} symmetric tilt boundary in Si, and have found that the experimentally observed structure is lowest in energy. Despite the fact that all of the structures are four-fold bonded,

Figure 3: Electronic density of states, calculated using the tight-binding model. Comparing the system with the boundaries shown in fig. 1a with the perfect diamond lattice, we see that there are no mid-gap states introduced by the boundary. The inset shows the region near the gap.



there is a considerable variation in energy between the structures. Results based upon a recently developed tight-binding Si potential compare very well with the ab-initio results. Electronic density of states calculations, made with this tight-binding model, suggest that the lowest energy grain boundary has little effect on the band structure, and no states strongly localized near the boundary.

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