Electrically Inactive Poly-Silicon Grain Boundaries

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ELECTRICALLY INACTIVE POLY-SILICON GRAIN BOUNDARIES

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Abstract

Structures, energies, and electronic properties of symmetric [001] tilt grain boundaries in Si have been studied using Stillinger-Weber and Tersoff classical potentials, and semi-empirical (tight-binding) electronic structure methods. The calculated lowest energy (310) grain boundary structure and electronic properties are consistent with previous TEM measurement and calculations. For the controversial (710) grain boundaries, our tight-binding calculations do not show any electronic energy levels in the band gap. This indicates that with every atom fully fourfold coordinated, the (710) grain boundary should be electrically inactive. Some high-energy metastable grain boundaries were found to be electrically active by the presence of the levels introduced in the band gap. Also, the vacancy concentration at the (310) GB was found to be enhanced by many orders of magnitude relative to bulk. The dangling bond states of the vacancies should be electrically active.
INTRODUCTION

Polycrystalline Si is an important electronic material because of its role as a self-aligned gate material in integrated circuits (IC) as well as its use for thin-film transistors (TFT) in flat panel displays, etc. [1]. Grain-boundary (GB) properties of Si are crucial for understanding the overall electronic, mechanical, and dynamical behavior of polycrystalline Si. Previous work in this area has focused on the [011] and [001] tilt GB [2-4], although some twist grain boundaries in Ge have also been studied [5]. In these studies, the calculated (310) GB structure in Si, which was confirmed to be not electrically active, was found to be in good agreement with many experiments [6]. But the other GBs have not been studied extensively. In the last few years, the Si (710) GB has been very controversial because two independent, contradictory experiments indicated that the (710) GB was electrically active [7] and inactive [8], respectively. There is no clear indication why these two experiments should differ and no theoretical work on (710) GB has been done [9]. In this paper we present calculations on a series of GBs with a [001] tilt axis, and explore the role of defects on the GB structural, energetic, and electronic properties.

METHODS OF CALCULATION

Our starting geometry was generated from a coincidence site lattice model [10] of the symmetric [001] tilt grain boundaries of various indices with varying misorientation angles $\theta$. We used the empirical Stillinger-Weber (SW) [11] and Tersoff (T) potentials [12] to relax the grain-boundary structures to their lowest energy state by a steepest descent method. The calculational cell was chosen to be periodic in $x$ and $y$ directions, and with a distance of 20 $a_0$ deep in the $z$-direction (where $a_0=5.43$ Å is the lattice parameter). The $z$-direction was left free. Both rigid shifts of the top and bottom grain as well as individual atomic motions were allowed. The relaxation was stopped when the maximum force on any given atom was smaller than $5\times10^{-3}$ eV/Å$^3$. This cutoff was chosen because relaxation to $5\times10^{-4}$ eV/Å$^3$ did not cause any appreciable motion of
the atoms for a few test examples. We used many different relative shifts of top and bottom grains to find the global minimum in energy. For angles other than 0° and 90° (these two structures correspond to perfect crystals), many metastable structures exist. The number of these metastable states (on the order of 10) are much larger than the corresponding number of metastable grain boundaries (about four) that is found for the metals Ni, Al, or Ni₃Al [13]. Both the structure and energies of the GBs and surfaces are calculated.

The total-energy, tight-binding (TB) method [14, 15] was employed to calculate the energy and the electronic structure of the grain boundaries. Two sets of tight-binding parameters for Si were considered, the Chadi parameters [16] (as specified in Ref. 15) and the Goodwin, Skinner and Pettifor (GSP) parameters [17]. The basis set consists of one s and three p atomic orbitals on each atom. The starting GB structure for the electronic calculation is taken from the previously relaxed GB using SW or T potentials. The calculation cell consists of 508 Si atoms for the (310) GB and 572 atoms for the (710) GB. Periodic boundary conditions are used in the x and y directions and free surfaces are used in the z direction. The total and local electronic density of states (DOS) are calculated by a full diagonalization of the tight-binding Hamiltonian. The local DOS is calculated by projecting the total DOS onto the basis functions of the atoms in the GB region. For the projection on (310), atoms with z-coordinates between -1.5 and 1.5 Å relative to the midplane of the GB are used. For (710), atoms with z-coordinates between -1.1 and 1.7 Å are used. All atoms with dangling bonds at the GB have been included. This simplifies the analysis, for example, by suppressing the electronic levels in the band gap due to the dangling bonds on the surface atoms. Calculations are then performed on cells with the same number of atoms, but with no GB (bulk Si with two free surfaces). The local DOS calculated by projecting onto the same number of atoms near the midplane in the cell provides a DOS that is nearly bulk-like, but which is also capable of indicating the (artifactual) effects of the free surfaces on the electronic structure of the GB. The local DOS constructed in this way is designated "bulk". The GSP parameters are very good for studying total energies of various Si clusters and crystal structures, but it introduces a spurious electronic state in the middle of the band gap for bulk Si. Therefore, interpretation and understanding of the GSP results for GBs is
difficult and not included in the following discussion. However, the
generic features of the electronic structure of the Si GB's are the
same as that obtained from the Chadi parameters. The Chadi
parameters are based on a nearest-neighbor diamond structure
model of the electronic band-structure of bulk Si. The radial
dependence $r$ of the TB hopping elements (Hamiltonian matrix
elements) falls off as $r^{-2}$. In the present work, these overlaps are
cut off at $3.1 \AA$, the mid-point between the first and second nearest
neighbors in bulk Si. Even though the difference in energy between
the $s$ and $p$ self energies [$\varepsilon_s$ and $\varepsilon_p$] is unique, the absolute position is
arbitrary. In the present work, $\varepsilon_s = -3\varepsilon_p = -4.8$ eV for the Chadi
parameters. The calculations are done using the $k=0$ point in
reciprocal space. This is typically adequate for calculational cells of
the size employed here. This assumption was tested by performing
extended Huckel calculations (EH) [18, 19]. Although the EH bandgap
for bulk Si is much too large (about 5 eV), the qualitative features
(apparition or lack of states in the band gap) in the GB local
$DOS$ for $k=0$ agreed with those observed with tight-binding. An EH
calculation with four $k$ points did not change the DOS qualitatively
with respect to the $k=0$ EH case.

RESULTS

The relaxed lowest-energy Si (310) and (710) GB structures
calculated with the Tersoff potential are shown in Figs. 1a and 1b,
respectively. The structure of the (310) GB is consistent with the
observed TEM (310) GB in Si (or Ge) [6, 20] and other TB calculations
[21, 22]. This structure is stable with respect to further relaxation
using tight-binding total energy calculations with the GSP TB
parameters. An interesting dependence of the GB expansion on the
misorientation angle $\theta$ between $<100>$ of the top grain and $<100>$ of
the bottom grain was observed (Fig. 2a). The total expansion of the
GB in the $z$ direction, $dz$, which is measured using atom positions far
from the GB region, was in the range of 0.02 to 0.04 $a_0$, or about 1/4
to 1/3 of what is found for fcc metal GBs [13]. The expansion of the
GB calculated with SW and Tersoff potentials are nearly the same for
the (310) GB. Our calculated (for SW and T potentials) (310) GB
expansion of 0.022 to 0.025 $a_0$ is in good agreement with TEM
measurement [20], but differs greatly from that for the (210) GB. This discrepancy in the (210) GB expansion may be an interesting opportunity for future TB studies and careful experiments. The local expansion near the GB is oscillatory, similar to that observed in metals [13]. The local and total expansions at the GB suggest that defect or impurity diffusion at the GB will be easier and that the defect concentration at the GB will be higher than the concentration of defects in the bulk.

The relaxed GB energy as a function of $\theta$ is shown in Fig. 2b. The GB energies show some non-smooth behavior; the (310) GB has the lowest energy for the high-angle GBs ($15^\circ < \theta < 75^\circ$). Surprisingly, calculations using either the SW or the Tersoff potentials give roughly the same GB energies over the whole range of $\theta$. How this disparity in the $dz$ and energy dependence on $\theta$ arises may be related to the fact that defect geometries are not fitted with these empirical potentials. The (210) GB needs to be treated with special care. The absolute $dz$ magnitude may be a good way to differentiate those potentials that are best suited for GB structural calculations. The high-angle GB energy is about 1.2 J/m$^2$ while the surface energy is about 2.1 J/m$^2$. This indicates that GBs in Si are well bonded, with a cohesive energy of about 3 J/m$^2$.

The TB electronic density of states near the bulk band gap for the (310) GB with the lowest energy of 0.63 J/m2 (which we will call A, shown in Fig. 1a) and with a higher energy of 1.53 J/m2 (which we will call B) are shown in Figs. 3a and 3b, respectively. For perspective, the local density of states for the whole range of energies for the geometry A is shown in Fig. 4. The band gap in bulk Si is between 0.4 and 1.6 eV for this set of Chadi's TB parameters. The rigid shift for these GBs are $[0.0003, 0.1407, 0.0350]$ a$_0$ and $[0.8068, 0.0, 0.0614]$ a$_0$, respectively. The A geometry has no dangling bonds at the GB, while the B geometry has a dangling bond density of 0.086 dangling bonds/Å$^2$. This shows up especially clearly in the density of states (DOS), since the A geometry has no energy levels within the conduction-valence band gap (which has a total width of about 1.2 eV). The B geometry has many electronic energy levels in the gap due to the GB dangling bonds. This suggests that the lowest energy (310) Si GB, which is the most likely GB in a properly
annealed sample, will be electrically inactive. This conclusion is consistent with the Electron Beam Induced Current (EBIC) experiments [2, 3, 9] and previous TB calculations [21, 22].

For the (710) GB, the lowest energy configuration (Fig. 1b), which we will call geometry C (see Fig. 3c), has a GB energy of 0.95 J/m², whereas the higher-energy geometry D (Fig. 3d) has a GB energy of 2.23 J/m². They have a relative GB shifts of [0.0150, 0.7069, 0.0149] a₀ and [3.1223, 0.4330, 0.1292] a₀, respectively. There are no dangling bonds in the C geometry, while the D geometry has 0.115 dangling bonds/A². The C geometry has a very small electronic DOS right below the valance band. This small DOS is not likely to cause the GB to be electrically active at room temperature (with a thermal energy of 0.025 eV), because the Fermi level (at the middle of the gap) is about 0.6 eV below the valance band. In contrast, the metastable D geometry is full of energy levels in the middle of the gap, and this will be electrically active. Comparing to experiment, Peterman and Haasen [7] showed that the (710) GB for a fairly pure GB in a float-zone refined Si was electrically active. In contrast, Maurice and Colliex [8], using a Czochralski-grown crystal, indicated that their (710) GB was not electrically active without further annealing (segregation). There is no satisfactory explanation for this discrepancy and the intrinsic nature of the electronic properties of the (710) GB are not known. The calculations presented here show that the (710) GB in its pure and lowest energy state is electrically inactive. The electrical activity could be caused by the trapping of the metastable GB structures, impurities and defects, as discussed next.

To explore the possibility of defect-induced electrical activity, we have performed Tersoff (as well as SW) calculations on the vacancy formation energy as a function of the distance from the GB. Because of its structural simplicity, we have chosen to study these effects for the (310) GB. The same qualitative behavior should also hold for the (710) GB as well. The bulk Si vacancy formation energy is 3.7 eV, in good agreement with recent ab initio band-structure calculations (3.7 ± 0.1 eV) of Wills [23] and with experimentally inferred data [24]. As shown in Fig. 5, the vacancy formation energy follows an oscillatory pattern around the GB midplane (with a z at 0.2 a₀). The effects of the GB start to show up about 1 a₀ away from the
GB midplane, and oscillate twice before hitting a minimum of 2.6 eV at the midplane of the GB. This significant reduction of the vacancy formation energy indicates that vacancies will almost surely segregate to the GB with some finite concentration and thickness about the GB. Because of the oscillatory formation energies, one would not expect the vacancies to distribute monotonically near the GB plane. At room temperature, the enhancement factor relative to bulk (without taking into account the entropy term) for the vacancy concentration at the GB center should be around $2.4 \times 10^{17}$, and about $4.4 \times 10^{5}$ at 900 K ($627^\circ$C). We conclude that vacancies will strongly segregate to the GB, creating dangling bonds that make the GB more electrically active, similar to the situation for the metastable GBs (B or D geometry in Fig. 3b and 3d). These defect-induced electric activities are likely to hold for all the GBs.

**CONCLUSIONS**

We have studied the structure and energies of the [001] tilt GB in Si. The GB expansions are smaller than for metals, and the GB energies have distinct dependence on the misorientation angle. The variation of the GB energy is about 20% for the high-angle boundaries. The (210) GB could be an ideal case for comparing first-principles calculations and TEM studies to pin down the exact value of the GB expansion and to differentiate which is the best potential for GB and defect studies. Using atomistic calculations, we found that the symmetric GBs in Si, at least in the [001] tilt GB series we tested, do not have dangling bonds. These GBs reconstruct to have full 4-fold coordination; consequently, these low-energy GBs do not have electronic energy levels in the middle of the conduction-valence band gap and should be intrinsically inactive. Any electrical activity of these GBs may derive from metastable GB structures that have not been fully annealed out, or due to impurities or defects. For example, we have shown that the vacancy concentration at the GB is enhanced by many orders of magnitude relative to the bulk, due to the large energy difference (about 1 eV) between the GB and bulk vacancy formation energy.
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Fig. 1. The relaxed, lowest-energy structure of (a) the Si (310) grain boundary and (b) the (710) grain boundary using Tersoff potential. Two repeated units are shown. All the atoms are fourfold coordinated.
Fig. 1 continued (Fig. 1(b)).
Fig. 2. (a) The grain boundary displacement and (b) the grain boundary energy plotted as a function of misorientation angle for the [001] tilt grain boundaries. The solid and dashed lines are only guides to the eyes.
Fig. 3. The local electronic density of states of (a) lowest energy geometry A and (b) metastable geometry B, for (310) GB, and (c) lowest energy geometry C and (d) metastable geometry D for (710) GB. Only the region around the bulk band gap is shown.
Fig. 3 continued (Fig. 3 (c) and (d)).
Fig. 4. The local electronic density of states for the lowest energy geometry A. The full energy range is shown; the bulk gap is between 0.4 and 1.6 eV.

Fig. 5. The relaxed vacancy formation energy (using the Tersoff potential) for (310) GB as a function of the z coordinate in units of the lattice constant $a_0$. The midplane of the GB is located at 0.2 $a_0$. 