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## Are the Structures of Twist Grain Boundaries in Silicon Ordered at 0 K?

S. von Althaus,<sup>1</sup> P. D. Haynes,<sup>2</sup> K. Kaski,<sup>1</sup> and A. P. Sutton<sup>3</sup>

<sup>1</sup>Laboratory of Computational Engineering, Helsinki University of Technology, P.O. Box 9203, FIN 02015 HUT, Finland

<sup>2</sup>TCM Group, Cavendish Laboratory, University of Cambridge, J. J. Thomson Avenue, Cambridge CB3 0HE, United Kingdom

<sup>3</sup>Department of Physics, Imperial College London, Exhibition Road, London SW7 2AZ, United Kingdom

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Contrary to previous simulation results on the existence of amorphous intergranular films at high-angle twist grain boundaries (GBs) in elemental solids such as silicon, recent experimental results imply structural order in some high-angle boundaries. With a novel protocol for simulating twist GBs, which allows the number of atoms at the boundary to vary, we have found new low-energy ordered structures. We give a detailed exposition of the results for the simplest boundary. The validity of our results is confirmed by first-principles calculations.

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The possible existence of amorphous intergranular films at grain boundaries (GBs) in elemental solids, especially network solids such as Si, impacts on their thermodynamic, mechanical, and electrical properties. Earlier simulations suggested [1,2] that some high-angle twist GBs in Si lower their energies by forming disordered amorphous intergranular films even at 0 K. Recent careful experimental measurements of the energies of (001) twist GBs in Si [3] found cusps at misorientations of  $\approx 16^\circ$ ,  $23^\circ$ ,  $28^\circ$ , and  $37^\circ$ . These are known as  $\Sigma = 25$ , 13, 17, and 5 (001) twist boundaries, respectively. The observations [3] indicate there must be structural order at least at these misorientations. In this Letter, we show that earlier simulations of twist boundaries [1,2,4–8] did not sample configurational phase space adequately. We address the question of structural order at an interface both geometrically and physically. We find *ordered* configurations for these four boundaries at 0 K, consistent with experimental observations [3]. We also obtain a new configuration for the (001) boundary with a misorientation of  $\approx 44^\circ$ , known as  $\Sigma = 29$ . Our configuration has a significantly lower energy and more order than published configurations [1,2], but it is less ordered and has a higher energy than the structures we obtain for the other 4 misorientations. These results are also consistent with the observations of Ref. [3].

We present a detailed study of the simplest (001) twist GB, i.e.,  $\Sigma = 5$  (001), using the Tersoff III (TS) potential [9]. We obtain new relaxed configurations, some of which have much lower energies than those obtained before. We confirm the accuracy of our relaxed configurations and their relative energies with a first-principles method. Thus, we demonstrate the robustness of our protocol for sampling the configurational phase space of twist boundaries in Si and that the TS potential is well-suited to this task. Our results for the other boundary misorientations were obtained with the same protocol and are, therefore, equally reliable.

A key aspect of our new protocol is the systematic removal of atoms from the GB. Removal of atoms from twist boundaries generates structures which are not acces-

sible in a molecular dynamics (MD) simulation with a constant number of atoms. Let the number of atoms in each layer parallel to the GB contained in one primitive cell of the GB be  $\nu$ . Suppose the ground-state configuration does not comprise an integer multiple of  $\nu$ . In reality, this could be achieved by removing atoms from the GB and placing them on the surface. There is no mechanism for doing this in a MD simulation with a constant number of atoms, because atoms removed from the boundary would become interstitials in the crystals.

First, we create an ideal  $\Sigma = 5$  GB by rotating two Si grains with respect to each other by  $\tan^{-1}(3/4) \approx 37^\circ$  about [001]. We cut out a supercell containing one primitive cell ( $\nu = 5$ ) in the GB plane and 30 Å thick slabs of crystalline Si on either side. The supercell is periodic parallel to the GB and has free surfaces normal to the GB. This defines our reference configuration. One grain can translate rigidly with respect to the other both parallel and perpendicular to the GB plane. We have confirmed that our results are unaffected by increasing the sizes of the adjoining regions of perfect crystal and that the initial translation state does not influence the relaxed structures. Let  $\Delta N$  denote the number of atoms removed from this reference configuration. For  $1 \leq \Delta N \leq 4$ , atoms are removed randomly from locations within a 6 Å slab centered on the GB. For  $\Delta N = 5$ , we remove an entire (004) atomic layer and translate one grain rigidly by  $\frac{1}{4}[001]$  to reinstate the density of the bulk crystal. This configuration is widely referred to as  $\Sigma = 5^*$ . For  $6 \leq \Delta N \leq 9$ , we remove 1–4 atoms from the  $\Sigma = 5^*$  configuration. For each value of  $\Delta N$ , alternative initial configurations are generated by making different random selections of atoms to be removed. After sufficient annealing,  $\Delta N = 10$  is equivalent to removing two entire (004) layers, which recreates the relaxed structure of the reference configuration. Hence, removing ten or more atoms should not, in principle, create any new configurations.

Second, we melt the material close to the GB to destroy all memory of the initial configuration by carrying out a 100 ps MD run at 3000 K. During this anneal, we clamp

atoms farther than  $10 \text{ \AA}$  from the GB. The equations of motion are integrated using the VERLET leap-frog algorithm [10] with a time step of 1 fs. The temperature is controlled by a Berendsen thermostat [11].

Third, we quench immediately to 1800 K and carry out simulated quenches of 50 ns duration with a time step of 2 fs, during which the temperature is linearly scaled from 1800 to 600 K. During these quenches, all atoms are free. Configurations generated throughout each quench are sampled every 100 ps and made the starting point of an energy minimization to 0 K using conjugate gradients. Each relaxation is deemed to be complete when the fractional change in the total potential energy is less than  $10^{-9}$ . During each quench, the structure visits several (typically up to five) metastable states with higher energies. These results indicate clearly the need for lengthy MD quenches to sample adequately the configurational phase space of the interfaces. For each value of  $\Delta N$ , we discuss only the minimum energy configuration.

The relaxed configurations for the 10 structures corresponding to  $0 \leq \Delta N \leq 9$  obtained with the TS potential were made the starting configurations of further conjugate gradient relaxations and energy evaluations using the Stillinger-Weber (SW) potential [12]. We did this to compare our results with earlier work using the SW potential [1,2].

In Fig. 1, the relaxed structures corresponding to  $0 \leq \Delta N \leq 9$  obtained with the TS potential are shown. In Table I, we present the relaxed energies for  $0 \leq \Delta N \leq 9$  and characterizations of the structural disorder.

To calculate the energy of each relaxed GB, we include as many layers from the GB as required to reach layers where the additional contribution is negligible. This is always significantly less than  $20 \text{ \AA}$  on either side of the GB, which is how we know our  $30 \text{ \AA}$  perfect crystal regions are sufficiently large.

We have used a bond orientational order parameter per atom [13] to identify atoms in the GB. This criterion is used to evaluate the GB width  $W$  and the standard deviations of bond lengths and angles. Atoms within  $2.7 \text{ \AA}$  from each other are considered to be bonded. For each atom, we calculate a set of complex numbers

$$\bar{q}_{lm}(i) = \frac{1}{N_b(i)} \sum_{j=1}^{N_b(i)} Y_{lm}(\hat{\mathbf{r}}_{ij}), \quad (1)$$

where  $N_b(i)$  is the number of neighbors of atom  $i$ ,  $Y_{lm}(\hat{\mathbf{r}}_{ij})$  are spherical harmonics, and  $\hat{\mathbf{r}}_{ij}$  is a unit vector from atom  $i$  to a neighbor  $j$ . From this, we construct a normalized complex vector  $\vec{q}_l(i)$  which has  $2l + 1$  components proportional to  $\bar{q}_{lm}(i)$ . For atom  $i$ , we then define the following order parameter:

$$q(i) = \frac{1}{N_b(i)} \sum_{j=1}^{N_b(i)} \vec{q}_6(i) \cdot \vec{q}_6^*(j). \quad (2)$$

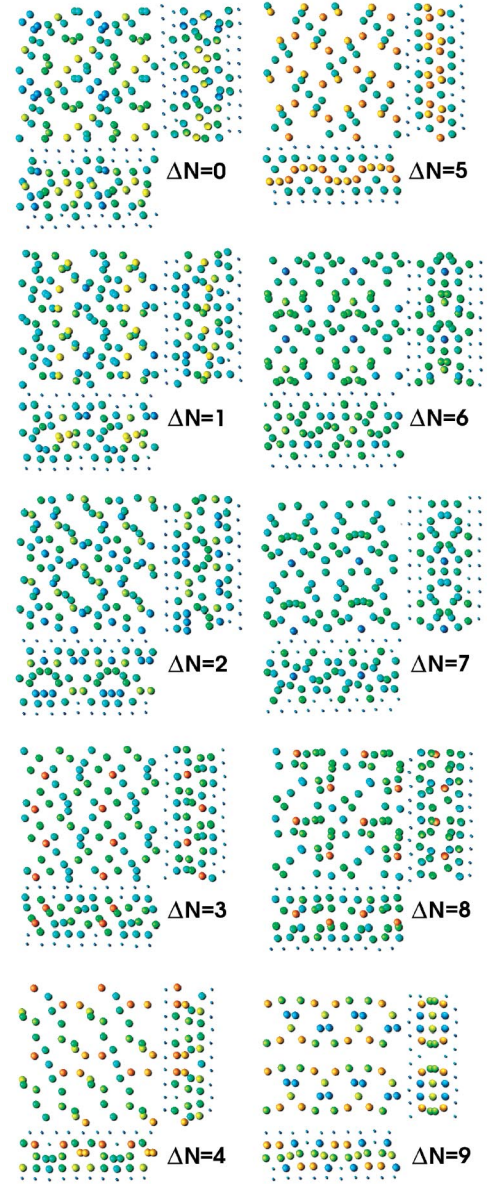


FIG. 1 (color). Minimum energy relaxed structures corresponding to  $0 \leq \Delta N \leq 9$  as obtained with the TS potential. For each value of  $\Delta N$ , there is a montage of three views: A patch of  $2 \times 2$  primitive cells is viewed along the boundary normal (top left) and from the two  $\langle 310 \rangle$  sides (bottom and top right). Left column:  $0 \leq \Delta N \leq 4$ ; right column:  $5 \leq \Delta N \leq 9$ . Atoms with an order parameter of less (more) than 0.7 are shown as large (small) spheres. The same color scale for all  $\Delta N$  from blue to red signifies low to high potential energy of the atom.

It can be shown that  $q(i)$  is always real. It is a measure of the correlation between the angular distribution of the bonds to atom  $i$  and the angular distribution of the bonds to atom  $i$ 's neighbors.  $q(i)$  is unity in a crystal and tends to zero in a completely disordered solid. In Fig. 2, we show values of  $q(i)$  for the  $\Delta N = 7$  relaxed structure. It is seen that  $q(i)$  rapidly approaches unity outside the GB region and that it has a mean value of about 0.4 within the GB.

TABLE I. Energies in (mJ/m<sup>2</sup>) of relaxed configurations for  $0 \leq \Delta N \leq 9$  obtained with the TS and SW potentials. Also given are the width ( $W$ ) in Å of the GB and the number of undercoordinated and overcoordinated atoms (3, 5) per primitive cell.  $\sigma_b$  and  $\sigma_\theta$  are the standard deviations of the bond lengths and bond angles, respectively, in the GB (see text).  $\theta_{\min}$  and  $\theta_{\max}$ , respectively, are the minimum and maximum bond angles in the GB.

$\Delta N$	TS	SW	$W(\text{Å})$	(3, 5)	$\sigma_b$ (%)	$\sigma_\theta$ (°)	$\theta_{\min}$ (°)	$\theta_{\max}$ (°)
0	1244	1190	7.2	0, 2	3.5	12.7	70.7	157.4
1	1295	1265	6.9	0, 2	2.4	12.6	73.6	169.2
2	1104	1049	6.7	0, 0	1.7	9.2	92.1	138.6
3	1189	1186	4.6	0, 4	2.7	16.2	73.6	169.2
4	1232	1249	3.3	0, 2	2.8	17.8	76.8	175.8
5	1369	1193	4.2	4, 0	3.0	17.4	74.3	173.2
6	1312	1299	6.5	0, 2	2.1	13.3	74.6	159.7
7	1070	1101	6.1	0, 0	1.4	9.4	85.0	134.7
8	1267	1301	5.2	0, 4	3.0	15.7	58.3	153.8
9	1169	1257	3.2	0, 0	2.3	14.4	81.5	143.9

This is typical for other relaxed structures. We define atoms in the GB as those having values of  $q(i)$  less than 0.7. This region can be seen in Fig. 2 to capture the transitional zone well.

We define the GB width  $W$  as the maximum separation normal to the boundary plane between atoms in the GB. To calculate  $\sigma_b$ , we consider all bonds to atoms in the GB, while to calculate  $\sigma_\theta$  we consider angles between all bonds to atoms in the GB.

To verify the results of the TS potential, we used the relaxed  $\Delta N = 0, 2, 5, 7$  structures as initial configurations for first-principles simulations within a plane-wave pseudopotential formulation of density-functional theory (DFT) [14,15]. Periodic boundary conditions were applied, and each supercell contained two symmetry-related GBs with approximately 160 atoms. A norm-conserving pseudopotential [16] was used with an energy cutoff of 300 eV, and a finite basis set correction [17] was applied to

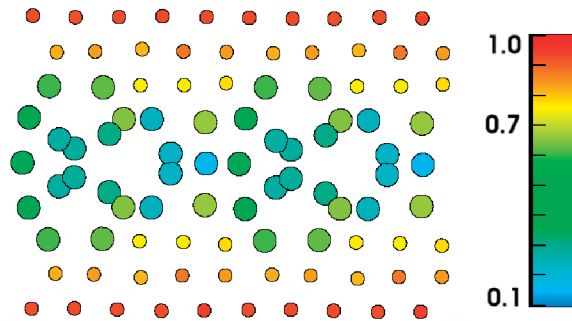


FIG. 2 (color). The variation of the order parameter  $q(i)$  across the relaxed GB structure with  $\Delta N = 7$ , viewed sideways along  $\langle 310 \rangle$ . Large (small) circles show atoms with  $q(i) < 0.7$  [ $q(i) > 0.7$ ]. Atoms are colored according to the value of  $q(i)$  as indicated by the color bar.

ensure accurate GB energies were obtained from the difference between total energies of different supercells. Two special  $\mathbf{k}$  points at  $(\pm \frac{1}{4}, \frac{1}{4}, 0)$  were used to sample the Brillouin zone [5]. The local density approximation [18] was used to describe exchange and correlation.

The results of the DFT simulations are presented in Table II. It is seen that the two lowest energy TS relaxed configurations ( $\Delta N = 7, 2$ ) undergo small further relaxations that lower the energies by 35 and 24 mJ/m<sup>2</sup>, respectively. The corresponding maximum atomic displacements from the TS generated configurations are 0.051 and 0.045 Å. The two higher energy structures ( $\Delta N = 0, 5$ ) undergo larger energy reductions and similar maximum atomic displacements. These results confirm that the relaxed configurations obtained with the TS potential do not change significantly. The order of the energies of the TS configurations is maintained. These results give us confidence in our results for the TS potential.

Only the  $\Delta N = 0, 5$  structures were studied previously, and we see in Table I that they are not the lowest energy configurations. By considering other values of  $\Delta N$ , we have accessed new configurations, some of which are significantly lower in energy (notably  $\Delta N = 7, 2$ ). As seen in Table II, this is not only confirmed by the DFT simulations but the energies for the  $\Delta N = 7, 2$  configurations are more than 30% lower than those of the  $\Delta N = 0, 5$  configurations.

In addition to the periodicity imposed on the boundary plane, there is further structural order which can be seen in other ways. In Table I, we see that the  $\Delta N = 2, 7, 9$  configurations have no coordination defects. In addition, the two lowest energy configurations also have the smallest values of  $\sigma_b$ , both of which are significantly less than 2%. They are also characterized by the smallest values of  $\sigma_\theta$ , which are about 9°, reflected by the smallest ranges of bond angles. The highest energy configuration ( $\Delta N = 5$ ) has the largest number (4) of undercoordinated atoms in each primitive cell and among the highest values of  $\sigma_b$  and  $\sigma_\theta$ . These correlations between boundary energy, on the one hand, and coordination defects and bond length and angle distortions, on the other, are a clear signature of local order in the low-energy configurations. There are point

TABLE II. GB energies (GBE) in (mJ/m<sup>2</sup>) obtained by DFT calculations before and after relaxation ( $r$ ) of the configurations relaxed with the TS potential. We also give the maximum force ( $F_{\max}$ ) in eV/Å acting on an atom before and after DFT relaxation.  $\Delta_{\max}$  is the maximum displacement of an atom during the DFT relaxation.

$\Delta N$	GBE	GBE ( $r$ )	$F_{\max}$	$F_{\max} (r)$	$\Delta_{\max}$ (Å)
0	1102	1040	0.33	0.008	0.028
2	805	781	0.24	0.006	0.045
5	1214	1135	0.38	0.031	0.133
7	732	697	0.28	0.016	0.051



group symmetries present in many of the configurations shown in Table I; e.g., the  $\Delta N = 2, 7, 9$  structures have space groups  $p222$ ,  $p2$ , and  $p2_122$ , respectively. Such point group symmetry is incompatible with structural disorder. The increase of the  $\Delta N = 7$  GB energy is  $\approx 0.9$  eV per primitive cell when one atom is added ( $\Delta N = 6$ ) or removed ( $\Delta N = 8$ ). This is a further indication that the  $\Delta N = 7$  structure is not disordered.

We find that  $\sigma_\theta$  and  $\sigma_b$  in the  $\Delta N = 2, 7$  configurations are smaller than those for well-equilibrated amorphous Si. Using the TS potential with a 20 ns quench from the melt, we find  $\sigma_\theta = 11^\circ$  and  $\sigma_b = 2.2\%$  for amorphous Si. This is another indication that the two lowest energy configurations may not be described as amorphous layers.

Our lowest energy structure obtained with the SW potential is for the  $\Delta N = 2$  configuration, with an energy of  $1049$  mJ/m<sup>2</sup>. We believe this is significantly less than any energy obtained before for this GB with the SW potential. To make a direct comparison with an earlier published result, our lowest energy relaxed structure for the  $\Sigma = 17$  (001) twist boundary in Si is  $1027$  mJ/m<sup>2</sup>. It was obtained with  $\Delta N = 0$  and a simulated quench from the melt of 10 ns duration. This is 25% lower than the value of  $1370$  mJ/m<sup>2</sup> obtained in Ref. [2], where the quench was 2 orders of magnitude shorter in duration. The boundary plane is microfaceted in our lowest energy configuration, which is inaccessible with such a high quench rate. Thus, in contrast to Ref. [2], we find this boundary structure displays a degree of order.

Using our new protocol, we have found [19] ordered low-energy configurations for  $\Sigma = 5, 13, 17$ , and  $25$  (001) twist boundaries. We have also obtained a new relaxed configuration of the  $\Sigma = 29$  (001) boundary using the SW potential, which has an energy of  $1149$  mJ/m<sup>2</sup>. This is 13% lower than that published in Ref. [2]. It is higher than the energies of the other 4 boundaries we have considered, which is consistent with the experiments of Ref. [3]. Although this boundary structure is significantly wider than the other 4, and hence appears more disordered, it is faceted and, therefore, displays a degree of order.

Our results indicate that earlier simulations [1,2,4–8] of this and most likely other twist boundaries in covalent semiconductors have failed to locate the global energy minima. There are two principal reasons. First, only  $\Delta N = 0, 5$  were considered prior to this work. We have shown that new configurations are obtained by removing this restriction. Some authors [5] have noted this restriction but, for reasons of computing resources, were unable to remove it. Second, MD quenches from the melt are required to be at least 20 ns duration to sample adequately the configurational phase space, such as the translational state, local relaxations, and the propensity for the GB to facet. A further but unnecessary assumption is that the boundary maintains the primitive periodicity. For the  $\Sigma = 5$  (001)

boundary, we have considered repeat cells comprising up to  $4 \times 4$  primitive cells. Although new metastable configurations were found, none was lower in energy than the  $\Delta N = 7$  structure. However, in general, the primitive  $1 \times 1$  configuration cannot be assumed to be the ground state at GBs any more than it can at surfaces.

In conclusion, we have used the simplest (001) twist boundary in Si to show that new relaxed configurations are accessed by removing atoms from the initial configuration and by carrying out simulated quenches from the melt that are orders of magnitude longer than have been performed before. Some of these configurations have much lower energies than the ground-state configurations generated before. Using our new protocol, we have already obtained [19] new ordered, low-energy configurations for four (001) twist boundaries consistent with experimental observations [3]. We have confirmed our principal results using first-principles methods. Earlier simulations to obtain ground-state configurations of twist, asymmetric tilt, and mixed tilt and twist boundaries in Si should now be reassessed in the light of these findings.

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