

***Ab Initio* Determination of the Structure of a Grain Boundary by Simulated Quenching**

M. C. Payne,^(a) P. D. Bristowe, and J. D. Joannopoulos

Massachusetts Institute of Technology, Cambridge, Massachusetts 02139

(Received 5 January 1987)

Results of the first completely *ab initio* investigation of the microscopic structure of a grain boundary in a semiconductor are presented. By use of the molecular-dynamics-simulated annealing method for performing total-energy calculations within the local-density-functional and pseudopotential approximations, the $\Sigma=5$ (001) twist boundary is germanium is studied. A number of rotation-and-translation states are investigated leading to a prediction for the structure of this geometry. Evidence for the possible presence of novel defects and glasslike tunneling-mode states at grain boundaries is presented.

PACS numbers: 61.70.Ng, 68.35.Ja, 68.35.Md

Internal interfaces in a solid, such as grain boundaries, often control the mechanical, chemical, and electrical properties of the material. It is essential, therefore, to have an understanding of their structure at an atomic level. Unfortunately, the structural complexity of grain boundaries makes their study a formidable task both experimentally and theoretically. Recently, experimentally, new electron-diffraction and imaging techniques have begun to yield detailed structural information about a number of grain boundaries in special tilt and twist orientations.¹⁻⁵ On the theoretical side, first-principles approaches to calculating the total energy of solids have begun to be applied to interfaces.⁶⁻¹⁰ These studies have provided important information on the distribution of charge density at the boundary, the local density of states, the atomic structure, and the boundary energy. However, the methods employed so far have not been entirely *ab initio* in the sense that a starting atomic configuration has been assumed based on geometric models or experimental observations.

In this paper we present a completely *ab initio* investigation of the structure of a twist grain boundary in germanium where nothing is known about its microscopic structure. A method is employed which provides for the self-consistent and simultaneous relaxation of the atomic and electronic coordinates. The only input data are the atomic number and mass of germanium.

Specifically, we consider the $\Sigma=5$ (001) twist boundary in the diamond structure, where Σ is the inverse density of coincidence sites. Two distinct $\Sigma=5$ boundary structures with the same coincidence site lattice (CSL) can be formed by rotating one diamond half-crystal with respect to another about the [001] direction by 36.9° or its complementary angle, -53.1° .¹¹ Both structural variants are studied in the present work and are designated $\Sigma 5$ and $\Sigma 5^*$. As an example, in Fig. 1(a) we illustrate the atomic positions of two layers on either side of an *ideal, unrelaxed* $\Sigma 5$ boundary. In this case, the axis of rotation passes through the atom at the center of the indicated unit cell. Experimentally, it is not possible to constrain the position of this axis to any specific translation state and a given rotation state will adopt the

translation state of the lowest energy. Since the position of this rotation axis is *a priori* unknown to within a "displacement-shift-complete" vector¹² of $\frac{1}{10}\langle 310 \rangle$,¹³ it becomes a challenge to theory to predict the appropriate lowest-energy translation state.

It is not possible, however, to calculate the energies of all the translation states within a displacement-shift-complete lattice unit cell. In this work we study the CSL configurations for both rotation states, the $\frac{1}{20}\langle 210 \rangle$ translation state of $\Sigma 5$ and the $\frac{1}{10}\langle 210 \rangle$ translation state of $\Sigma 5^*$. These particular states were chosen because the structures have higher symmetry than boundaries produced by arbitrary translation states. Moreover, in the pair-potential simulation¹⁴ of fcc twist boundaries in metals, such states appear to have the lowest energies. Whether this is true for semiconductors is certainly not clear. Nevertheless, for simplicity, we restrict ourselves to these four rotation-and-translation states.

The grain-boundary structures were modeled within the supercell approximation which imposes periodicity *normal* to the interface boundary. Experimentally, it is found that grain-boundary "widths" in semiconductors are extremely narrow ($\leq 10 \text{ \AA}$)^{5,15} so that a relatively small number of atomic layers on either side of the interface can accurately model the system. Our supercell contains twelve layers of atoms representing two six-layer crystal slabs rotated relative to each other by either 36.9° or -53.1° . All the atoms in the supercell were allowed to relax except for the atoms in the central two layers of each crystal slab which were confined to their crystallographic positions. In addition, the distance between these fixed layers was allowed to vary as the local grain-boundary volume changed. The atomic positions and local grain-boundary volume were assumed to have reached their equilibrium values when the forces had become smaller than $0.1 \text{ eV/\AA}$.

The calculations were performed with use of the molecular-dynamics simulated quenching method for total-energy calculations.^{16,17} The exchange-correlation potential was calculated within local-density-functional theory with use of the Perdew and Zunger parametrization.¹⁸ The electron-ion interaction was determined with

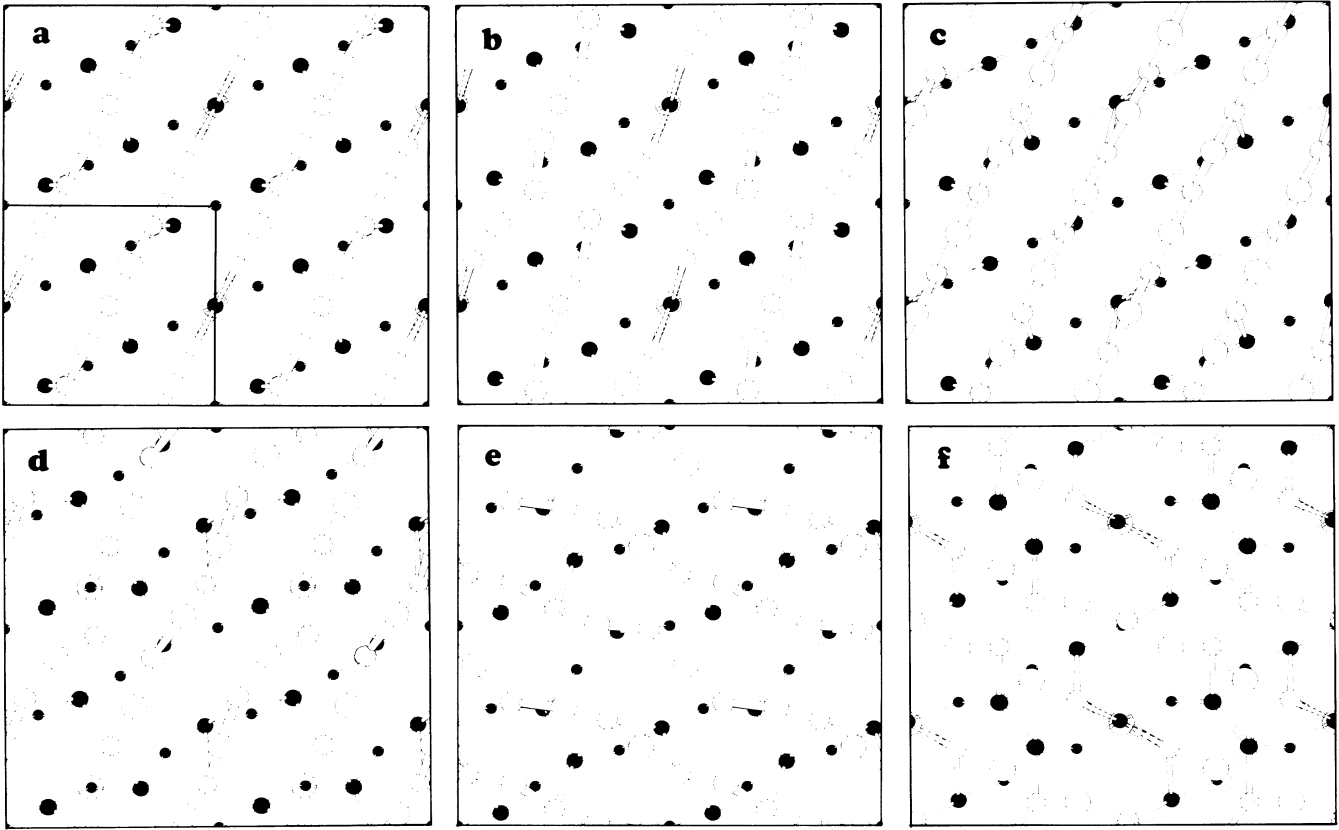


FIG. 1. Atomic positions in planes normal to the (001) direction for two layers above (open circles) and below (filled circles) a twist-grain boundary in germanium. (a) Unrelaxed $\Sigma 5$ CSL; a typical unit cell is indicated. (b) Relaxed $\Sigma 5$ CSL. (c) Unrelaxed $\Sigma 5 \frac{1}{20} \langle 210 \rangle$ state. (d) Relaxed $\Sigma 5 \frac{1}{20} \langle 210 \rangle$ state. (e) Relaxed $\Sigma 5^*$ CSL. (f) Relaxed $\Sigma 5^* \frac{1}{10} \langle 210 \rangle$ state.

use of the Starkloff-Joannopoulos *ab initio* local pseudopotential approach.¹⁹ The molecular-dynamics scheme is particularly suited to the relaxing of systems with many degrees of freedom. Briefly, conventional matrix diagonalization is avoided and replaced by simple integration of classical equations of motion for the electrons, ions, and unit-cell volume. This method allows the use of a large number of basis functions and our calculations were performed with an energy cutoff of 10 Ry, which corresponds to about 4300 plane waves. Two Monkhorst-Pack²⁰ k points were used for Brillouin-zone averaging. No symmetry was imposed on the system and the symmetry-breaking element in the molecular-dynamics method allowed the systems to explore regions of phase space with lower symmetry than the initial configurations.

The results of all our calculations are presented in Table I and Fig. 1. The table lists the total energies for the four twist boundaries considered and the change in grain-boundary volume after relaxation. The geometric structures of the relaxed boundaries are shown in Figs. 1(b), 1(d), 1(e), and 1(f). In the figures, we have arbitrarily chosen to draw bonds between all pairs of atoms

that are separated by distances less than 1.15 times the bond length in the bulk. In the extremely distorted environment of the grain boundary, it is possible that atoms separated by this distance could still be bonded although a detailed investigation of the electronic charge density is required to test this. We shall present a detailed study of the bonding in the grain boundaries in a forthcoming publication.

Figure 1(b) shows the structure obtained after allowing the ($\Sigma 5$ CSL) grain boundary in Fig. 1(a) to relax. The relaxation basically involves the formation of a di-

TABLE I. Grain-boundary energies (E) and local volume changes ($\Delta\Omega$).

Rotation	Translation	Energy (E)		$\Delta\Omega$ (Å)
		(mJ m ⁻²)	(eV)	
36.9° ($\Sigma 5$)	CSL	1288	5.87	+0.07
36.9° ($\Sigma 5$)	$\frac{1}{20} \langle 210 \rangle$	851	3.88	-0.05
-53.1 ($\Sigma 5^*$)	CSL	1415	6.45	+0.07
-53.1 ($\Sigma 5^*$)	$\frac{1}{10} \langle 210 \rangle$	937	4.27	-0.22

mer bond between a pair of atoms in the layer above the interface. We note that it appears to be energetically *unfavorable* for new bonds to form on *both* sides of the interface. The distortion leaves six atoms per unit cell with only three near neighbors and the structure contains one four-membered ring per unit cell. Fourfold rings of bonds are very unusual in germanium or silicon structures and to our knowledge have never been observed before. They are, however, an intrinsic structural element of this type of twist boundary.

In Figs. 1(c) and 1(d) we show respectively the unrelaxed and relaxed geometries of the $\Sigma 5 \frac{1}{20} \langle 210 \rangle$ grain boundary. The relaxation in this boundary is much larger than in the previous case and some atoms move distances greater than 40% of the bond length during the relaxation. All the atoms have four near neighbors after distortion and the relaxed structure contains two four-membered rings per unit cell. If the pairs of near-neighbor atoms are assumed to be bonded, all the atoms have fourfold coordination with maximum bond length 13% greater than the bulk value. Unlike the $\Sigma 5$ CSL state, this translation state *does* allow new bonds to form on both sides of the interface.

Figures 1(e) and 1(f) illustrate the geometric structures obtained after the relaxing of two $\Sigma 5^*$ boundaries. Figure 1(e) shows the CSL after relaxation. We find that the distortion has produced three atoms per unit cell which have only three near neighbors and the structure contains four four-membered rings per unit cell. The coincidence-site atom in this structure has five near neighbors as a result of formation of a dimer bond with an atom in the same layer which becomes fourfold coordinated. The occurrence of a fivefold-coordinated atom in this structure is particularly interesting in the context of recent suggestions that such defects may dominate over threefold-coordinated atoms in amorphous silicon.²¹ Finally, Fig. 1(f) shows the relaxed $\Sigma 5^* \frac{1}{10} \langle 210 \rangle$ state. This boundary relaxes by forming dimer bonds between atoms in the layers above and below the interface. The dimers bond across the interface to form continuous chains of fourfold-coordinated atoms lying along $\langle 310 \rangle$ as can be deduced from the figure. However, after reconstruction, there are still two atoms per unit cell that have only three near neighbors and only one weak four-membered ring. We note in particular from Table I that the boundary undergoes a marked contraction in width during relaxation.

For both the $\Sigma 5$ and $\Sigma 5^*$ boundaries, the nonzero-translation states studied had the lowest total energies. It has often been assumed that the presence of the coincidence atom in a site belonging to both crystals would lead to a low-energy boundary. Previous experimental and theoretical results^{4,22} for tilt boundaries in semiconductors have shown that this is not necessarily the case and the results of our calculations for twist boundaries in germanium support this. In addition, whereas the CSL

states both involve a slight expansion of the local grain-boundary volume, the translated states both undergo a contraction. Previous theoretical studies of grain boundaries in metals and ionic materials have always predicted an expansion at the grain boundary. However, small contractions have been calculated for tilt boundaries in semiconductors with use of simple valence force-field calculations²² and a possible small contraction in a 22° (001) twist boundary in germanium has been detected experimentally by use of electron diffraction.⁵ The magnitude of this contraction is very similar to that reported here.

In any simulated quench or stimulated anneal performed at finite cooling rate there is a possibility that the system will not reach the ground state but will instead remain in a metastable state of higher energy. To test whether our lowest-energy boundary was a metastable state we made a large perturbation to the structure. The perturbation consisted of moving all the atoms in the four layers around the interface by distances of 10% of the bulk bond length. The perturbed configuration was then allowed to relax to equilibrium. Of the twenty ions that were displaced, eighteen moved closer to their positions in the original boundary; but two atoms in the layer immediately below the interface moved further from their original positions in a direction away from the interface, so that the lengths of their bonds across the interface were increased but the bonds to the atoms two layers from the interface were reduced in length. The connectivities of the two relaxed structures were identical and the boundary formed after the perturbation was only 0.1 eV higher in energy than the original boundary. This then leads to a very interesting and unexpected result. The structures with the connectivity of the original boundary lie in an "attractive" region of phase space since the connectivity is not destroyed by a significant perturbation to the system. Moreover, within this region of phase space there are at least two known local energy minima and possibly many more. Tunneling transitions between configurations in the energy minima should then give a range of effects similar to those produced by two-level systems in glasses.²³ Further investigation of the energies of metastable minima and tunneling barriers in this region of phase space is currently underway. Finally, the energy difference between the two local energy minima is smaller than the energy differences between different translation states and this suggests that the $\Sigma 5 \frac{1}{20} \langle 210 \rangle$ translation state is the lowest-energy boundary of the four studied here. Without calculating the energies of many other translation states, it is not certain that the $\frac{1}{20} \langle 210 \rangle$ translation state is the minimum-energy boundary. However, the complete fourfold coordination present in the relaxed structure of this boundary must make it a good candidate.

Finally, we note that the $\Sigma 5$ and $\Sigma 5^*$ grain boundaries are related to one another by the removal or insertion of

an odd number of atomic layers normal to the interface. To fabricate a $\Sigma 5$ boundary experimentally, two oriented crystals with (001) surfaces would be rotated through 36.9° and then sintered together (see, e.g., Ref. 5). In general, the resulting boundary will be a mixture of 36.9° and -53.1° rotations unless the original crystals had monolayer-smooth (001) surfaces. Consequently, a fabricated grain boundary would normally contain *both* $\Sigma 5$ and $\Sigma 5^*$ interfaces.

This work was supported in part by U.S. Air Force Office of Scientific Research Contract No. 87-0098 and by Department of Energy Grant No. DE-FG02-84EF-45116.

^(a)Present address: Cavendish Laboratory, Madingley Road, Cambridge, CB3 0HE, United Kingdom.

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¹³The standard crystallographic notation $\langle n, l, m \rangle$ indicates the full set of equivalent vectors $[n, l, m]$.

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²³See, e.g., articles in *Amorphous Solids: Low Temperature Properties*, edited by W. A. Phillips (Springer-Verlag, Berlin, Vienna, 1981).