Atomic and Electronic Structures of the 90° Partial Dislocation in Silicon

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Two reconstructions of the 90° partial dislocation core in silicon have been investigated using *ab initio* total-energy pseudopotential calculations. The asymmetric fourfold-coordinated configuration is shown to be stable and to be associated with only shallow states in the band gap. The symmetric quasi-fivefold-coordinated configuration is found to be metastable and to be associated with states that span the band gap. These results are reproduced with tight-binding Hamiltonians if the range of hopping integrals is restricted to include no more than four nearest neighbors.

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The 90° glide partial is one of the most common dislocations in plastically deformed silicon [1]. These dislocations lie on {111} planes along ⟨110⟩ directions separated from 30° partial dislocations by intrinsic stacking faults [2]. Their atomic and electronic structures have been the subject of intense experimental [3,4] and theoretical investigation [5-10] because of their occurrence in semiconductor devices and interfaces. In this Letter we report the first *ab initio* investigation of the atomic structure of the 90° partial dislocation using periodic boundary conditions.

The fundamental issues that must be addressed are the atomic structure of the dislocation core and the possible presence of localized electronic states. Images of the projected atomic structure along the dislocation line have been obtained [11] by electron microscopy. They indicate the presence of five- and seven-membered rings. However, no information is available from such micrographs about bonding along the dislocation line. There are two models for the reconstruction of the core in which five- and seven-membered rings appear in projection, but which involve different bonding *along* the dislocation line. Figure 1(a) shows the atomic structure in the slip plane of the dislocation prior to reconstruction. Each atom in the core is associated with a dangling hybrid. Figure 1(b) shows the reconstruction that was proposed by Hirsch [12] and Jones [5]. Each atom in this core is fourfold coordinated and the mirror plane along the dislocation line is broken. We call this structure the asymmetric reconstruction. The second reconstruction was found by Duesbery, Joos, and Michel [7] and ourselves [13] on the basis of calculations using certain empirical interatomic potentials, and is shown in Fig. 1(c). It is formed by the atoms with dangling hybrids in Fig. 1(a) moving closer together without breaking the mirror plane along the dislocation line. This reconstruction results in each atom along the core having three first neighbors and two further neighbors at a distance 17% greater than the equilibrium bond length: a situation described as "quasi-fivefold" coordination [7]. We call this the symmetric reconstruction. In this Letter we determine the relative stabilities of the reconstructions shown in Figs. 1(b) and 1(c).

The existence of localized states associated with the 90° dislocation core remains highly controversial [6,8-10]. Even among those authors who favor the asymmetric reconstruction, some report states in the band gap [8,9] and others do not [10]. The lack of agreement stems partially from the reliance on empirically constructed interatomic potentials to obtain the relaxed atomic structure, or the use of clusters of atoms to model the dislocation core. Cluster calculations suffer from (a) unrealistically large band gaps and (b) lack of coupling between the elastic field and the core structure of the dislocation. The electronic structure of the symmetric reconstruction has not been investigated. These considerations motivate the present *ab initio* study with periodic boundary conditions.

In order to apply periodic boundary conditions it is necessary to introduce a dislocation dipole in each unit cell [14]. We have identified a previously overlooked problem in applying periodic boundary conditions to a dislocation dipole, which accounts for some of the contro-

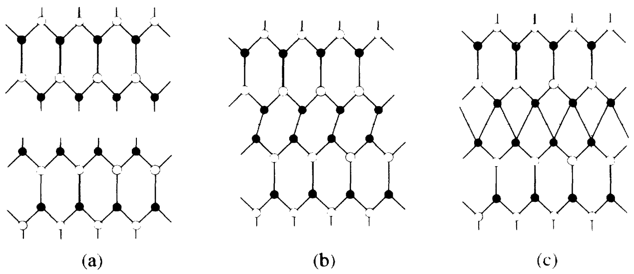
(a) (b) (c)

FIG. 1. Atomic structures within the core of a 90° partial dislocation (dotted line) on the (111) slip plane. (a) Unreconstructed core. (b) Asymmetric reconstruction. (c) Symmetric reconstruction with the dashed line showing the mirror plane.

versy over the existence of electronic states in the gap. Since this problem is geometrical in nature it calls into question all previous simulations of dislocations using periodic boundary conditions. In Fig. 2(a) we show the *dipolar* lattice that is generated by periodically repeating the dipole in a rectangular unit cell. Tilt grain boundaries (solid lines) of equal and opposite misorientations are generated. *Unless the height of the repeat cell, d, is commensurate with the periodicity of the grain boundaries, a misfit is introduced at the horizontal cell borders.* For 90° partial dislocations on (111) planes it is necessary to include six (or a multiple of six) dipoles in the unit cell to avoid any misfit [13]. For example, in the present *ab initio* simulations the spacing d of the partial dislocations is $4a/\sqrt{3}$, where a is the crystal lattice parameter. The tilt boundaries that are generated have a misorientation of 10.10° and they are parallel to (7,7, −17) in one crystal and (3,3, −5) in the other. The period of these boundaries is $a/2|[17,17,14]|=a/2|[15,15,18]|=a/2\sqrt{774}$ and contains *six* Shockley partial dislocations. Therefore, unless each rectangular computational cell contains six (or a multiple of six) dislocation dipoles it will not contain a full period of the grain boundary, and a misfit will be generated between the horizontal cell borders. With just one dipole in the unit cell the misfit causes a spurious shear strain. This spurious strain splits a band of states off the bulk valence band edge by as much as 0.2 eV in some cases [13] and it must, therefore, be eliminated.

The solution to this problem is to generate a *quadrupolar* lattice as shown in Fig. 2(b). Now there are no grain boundaries and hence no misfit at the horizontal cell borders. Although the lattice is quadrupolar it is still possible to find a unit cell containing only two dislocations by selecting the oblique unit cell shown in Fig. 2(b) [15]. The dislocations were introduced by imposing the anisotropic elastic fields of the quadrupolar array. Each unit cell contains 64 atoms and the two partials were separated by a stacking fault of length $a\sqrt{6}$ (13.3 Å). Calculations using a variety of empirical potentials indicate that the relaxed atomic structures obtained with 112, 128, and 224 atoms in the unit cell are the same as those obtained with 64 atoms to within 0.5% in bond length distortions and 1.1% in bond angle distortions. The electronic energy levels computed for these relaxed configurations within the tight-binding approximation differed by less than 0.05 eV. Thus, the 64-atom cell is sufficiently large to determine the stable reconstruction and whether there are electronic states in the gap.

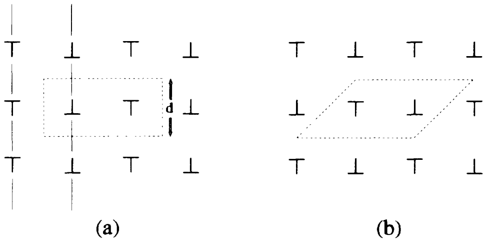

FIG. 2. (a) Dipolar lattice of dislocations formed by periodic repetition of rectangular cell (broken lines) resulting in parallel tilt grain boundaries (solid lines). (b) Quadrupolar lattice formed by periodic repetition of oblique unit cell avoids grain boundaries.

The *ab initio* calculations were carried out with the parallel total energy pseudopotential code CETEP [16] using 16 of the 64 nodes on the Meiko Computing Surface at Edinburgh University. This code is based on density functional theory and uses the Perdew-Zunger parametrization [17] of the exchange-correlation energy. The occupied valence orbitals are expanded in plane waves, and the total energy functional is minimized with respect to their expansion coefficients and the ionic degrees of freedom. Kerker pseudopotentials [18] were applied in the Kleinman-Bylander form [19], using a real-space projection technique [20], with the s-wave component treated as local, retaining three p and five d projectors. Two k points along the dislocation line were used (i.e., $[0,0,\frac{1}{8}]$ and $[0,0,\frac{3}{8}]$), because the length of the real-space cell in this direction was only $a/\sqrt{2}$. An energy cutoff of 120 eV was used for the plane-wave expansion. All atoms in the cell were allowed to relax and the relaxation was stopped when the force on any atom was less than 0.1 eV/Å. The size and shape of the unit cell were kept fixed throughout the relaxation.

Our main result is that, contrary to calculations [7,13] based on certain empirical interatomic potentials [21,22], we find that the asymmetric reconstruction shown in Fig. 1(b) is the most stable configuration. The reconstructed bond across the core is stretched by 2.6% and the maximum bond stretch of 5.4% occurs in the seven-membered ring, whereas the maximum bond compression of 3.2% occurs in the five-membered ring. The maximum and minimum bond angles are 138° and 96°. The initial configuration for the symmetric structure was generated by a relaxation with the Stillinger-Weber potential [21]. After the ionic and electronic degrees of freedom were optimized with CETEP it was found that the symmetric configuration was higher in energy by 0.23 eV/Å per dislocation. More significantly, it was found that the symmetric configuration was metastable and it transforms spontaneously to the asymmetric configuration if the mirror plane normal to the dislocation line is broken by a small distortion.

The projected band structures are shown in Fig. 3. Since the local-density approximation does not yield a satisfactory band gap we have used a tight-binding Hamiltonian to display the band structures for the atomic configurations produced by CETEP. The tight-binding Hamiltonian we use is that of Vogl, Hjalmarson, and Dow [23] for silicon, which uses an sp^3s^* basis. This Hamiltonian is fitted to the experimental band gap, and it provides an excellent description of electronic states in the energy range spanning the band gap. We assumed a

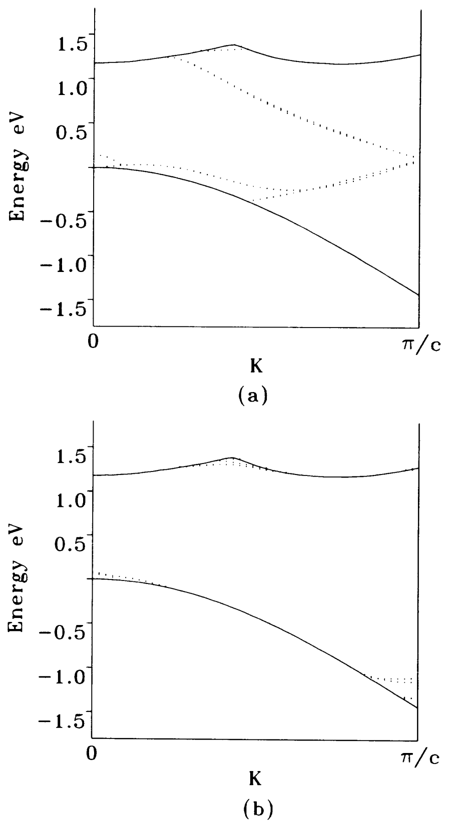

FIG. 3. Band structures projected along the dislocation. Solid lines show the bulk valence and conduction band edges. $c = a/\sqrt{2}$ is the period along the dislocation. (a) Symmetric reconstruction. (b) Asymmetric reconstruction.

$1/r^2$ scaling relation for the hopping integrals in the Hamiltonian with a smooth cutoff radius of $0.55a$.

For the symmetric configuration [Fig. 3(a)] two bands split away from the valence and conduction bands and nearly meet at the Brillouin-zone boundary. Analysis of the eigenvectors shows that these states are concentrated on the quasi-fivefold-coordinated atoms in each dislocation core, and that the states are *sp* hybrids oriented almost normal to the dislocation line rather than towards each other. Each line of weakly interacting hybrids gives rise to a band spanning the gap. But one period of the dislocation contains *two* inequivalent quasi-fivefold atoms, and therefore a small gap is opened at the zone boundary. The gap is small because the environments of the two atoms differ only slightly. The bands would be degenerate if the dislocations were sufficiently far apart. The splitting of the degeneracy is small except just above the valence band edge.

For the asymmetric configuration the band gap is almost cleared of states. The displacement along the dislocation line shown in Fig. 1(b) opens the small gap at the Brillouin-zone boundary of Fig. 3(a) to such an extent that the upper pair of bands moves into the bulk conduction band and the lower pair into the bulk valence band. Thus the sum of the occupied one-electron energy is lowered. The *sp* hybrids on the atoms that were quasi-fivefold-coordinated pair up and form directed bonds to each other, as originally envisaged by Hirsch [12] and Jones [5]. Therefore, we can conclude that the electronic contribution to the total energy stabilizes the asymmetric reconstruction, and that it is associated with only shallow electronic states.

Having established that the asymmetric reconstruction is the correct structure of the core it is very useful to see whether this result can be reproduced by more approximate models of interatomic forces, such as tight-binding Hamiltonians and other empirical interatomic potentials. Evidently, the Stillinger-Weber potential fails in this regard (see Ref. [24] for examples of the failure of this potential at modeling surface reconstructions). The advantage of much greater computational speed of more approximate models is always tempered by uncertainty in their accuracy. This point is particularly relevant here as the vast majority of simulations of the 90° partial have not used *ab initio* methods to relax the atomic structure of the core. In the following we shall use our *ab initio* results for the 90° partial as a benchmark for testing the efficacy of four widely used simple models, and we identify specific restrictions and/or limitations in their applicability. The tight-binding Hamiltonians for silicon of Chadi [25] and Goodwin, Skinner, and Pettifor (GSP) [26] were tested. Two empirical potentials for silicon due to Tersoff [27,28] were also tested.

The tight-binding total energy minimizations were performed for the same supercell geometry and k-point sampling used for the *ab initio* calculations, and tests established that the energy is converged to within 0.06% with this k-point sampling. For Chadi's Hamiltonian the repulsive pair potential was taken as A/r^4, with A determined by the equilibrium condition for the bulk Si crystal at the experimentally observed lattice parameter ($A = 4.0655$ eV Å^4). To avoid discontinuities in the forces we ensured that the radial variation of the hopping integrals and the repulsive pair potential and their derivatives in both Hamiltonians fell smoothly to zero at a chosen cutoff radius r_t. The choice of r_t is arbitrary and we have investigated $r_t = 0.51a$, $0.54a$, $0.60a$, and $0.63a$ for the Chadi Hamiltonian and $r_t = 0.55a$ and $0.68a$ for the GSP Hamiltonian. The atomic relaxation was terminated when the force on any atom was less than 10^{-6} eV/Å. For the Tersoff potentials we have used the recommended cutoff radii, except for the Tersoff 1988b [28] potential where we also investigated the larger cutoff radius of $0.69a$ suggested in [7].

The lowest energy structures for both tight-binding Hamiltonians, and the Tersoff 1988b potential [28], were in reasonable agreement with the *ab initio* result *provided* that the value of r_t was restricted to ensure only four interacting neighbors per atom. The reconstructed bond undergoes the maximum stretch of between 3.4% and 5.6%, in contrast to the *ab initio* case where the stretch of the reconstructed bond is less than some of the adjoining back bonds. Accordingly, bond angles differed from corresponding *ab initio* values by up to 5°.

Using the same Tersoff potential, but with a larger cutoff of $0.69a$, Duesbery, Joos, and Michel [7] obtained a relaxed structure for the asymmetric core in which the reconstructed bond is approximately 11% stretched. We have reproduced this result and have obtained a similar opening of the dislocation core, where the reconstructed bond is 8% stretched, using the same cutoff for the hopping integrals in the GSP Hamiltonian. With a cutoff of $0.69a$ second-neighbor interactions are included in the dislocation core, in addition to the four nearest neighbors. This weakens the first-neighbor bond order and the repulsive pair potential contribution to the bond energy dominates. Thus the bond is longer than when hopping is restricted to four nearest neighbors. Using either of these wide core configurations as starting points in CETEP the reconstructed bond was returned to a stretch of 3%. Since the GSP Hamiltonian was designed to extend to second neighbors and beyond we conclude that it attaches too much weight to interactions beyond first neighbors. We also conclude that extending the range of the Tersoff 1988b potential [28] beyond its recommended value, as in Ref. [7], is not advisable.

Finally, we have used the Tersoff 1988a potential [27] to model the asymmetric dislocation core. In agreement with a calculation on a single 90° partial dislocation in a large cluster [6], all bonds in the unit cell are stretched by less than 2%, but the spread of bond angles is greater (90°-146°). The structure leads to greater penetration of states into the gap than structures we have considered with 11% stretched bonds. This indicates the importance of bond angle deviations in affecting the electronic structure of the dislocation core. Therefore, we conclude the the Tersoff 1988a potential [27] is not as accurate as the Tersoff 1988b [28] potential for describing the relative importance of bond stretching and bond bending energies.

In conclusion, we have shown that the asymmetric dislocation core structure has a lower energy than the symmetric quasi-fivefold-coordinated configuration and that the relative stabilities can be directly attributed to the electronic structures of the dislocations. The stable core structure is associated with only shallow electronic states. Tight-binding Hamiltonians [25,26] and the Tersoff 1988b [28] potential reproduce the *ab initio* structure reasonably well, provided the range of hopping integrals is restricted to no more than the four first nearest neighbors. The potentials of [21,22,27] are unable to describe the energetics of the reconstruction of this dislocation core.

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