Paramagnetic Structure of the Soliton of the 30° Partial Dislocation in Silicon

Gábor Csányi, Sohrab Ismail-Beigi, and T. A. Arias
Department of Physics, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139
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Based on *ab initio* calculations, we propose a new structure for the fundamental excitation of the reconstructed 30° partial dislocation in silicon. This soliton has a rare structure involving a fivefold coordinated atom near the dislocation core. The unique electronic structure of this defect is consistent with the electron spin resonance signature of the hitherto enigmatic thermally stable *R* center of plastically deformed silicon. This identification suggests the possibility of an experimental determination of the density of solitons, a key defect in understanding the plastic flow of the material. [S0031-9007(98)05971-7]

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Dislocations are central to the understanding of the mechanical response of materials. The mechanical behavior of any crystalline material is determined by a hierarchy of crystalline defects of successively lower dimension. Grain boundaries are two-dimensional defects that control the evolution of the microstructure of the material. The creation and motion of dislocations, which are one-dimensional extended topological defects of the lattice, mediate the plastic response of a crystal to external stress. In silicon, which has a bipartite lattice, the primary mobile dislocations are the screw and the 60° dislocation, which dissociate into more primitive one-dimensional partial dislocations bounding stacking faults. The mobility of dislocations in high Peierls barrier materials such as silicon is effected by the motion of complex zero-dimensional local defects known as *kinks,* where the dislocation center skips from one row of atoms to a neighboring row. The low energy kinks along the 30° partial dislocation in silicon have been shown to also involve a composite structure where kinks bind with zero-dimensional soliton excitations in the reconstructed ground state of the dislocation core. These soliton excitations are also known as "antiphase defects" (APDs) [1].

Here we report the results of an *ab initio* study exploring the lattice and electronic structures, excitation energy, and the density of these APDs which are the simplest, lowest energy, fundamental excitations of the dislocations in the hierarchy ultimately leading to the macroscopic mechanical behavior of the solid. The soliton is associated with an atom in the dislocation core which is not part of a reconstructed dimer. In the simple, conventional picture, this atom (henceforth to be referred to as the "soliton atom") has only three bonds and therefore an unpaired electron. This simple model, however, does not lead to predictions consistent with any of the observed electron spin resonance (ESR) signals associated with plastically deformed silicon.

We propose a new structure of the soliton. We find that the ground state of the soliton has an unexpected structure with electronic states which *are* consistent with the most stable ESR center in plastically deformed silicon, the only one which remains after careful annealing. The reason why the natural connection between this center and the lowest energy excitation of the dislocation core has not been made previously is that the observed ESR center has a highly unusual symmetry. In support of our theory for the structure of the soliton, we gather here several pieces of evidence from both reports of ESR results and our own *ab initio* calculations. The final combined *ab initio* experimental identification which we make allows for the possibility that future more precise measurements of the ESR center density could be used to determine experimentally the soliton density, a key physical quantity in the process of deformation.

Figure 1 reviews the basic geometry of the 30° partial dislocation studied in this work. The dislocation is the one-dimensional boundary defining the edge of a half-planar (111) stacking fault. Atoms in the central core of the dislocation (shaded grey in the figure) are connected to the bulk with only three bonds per atom.

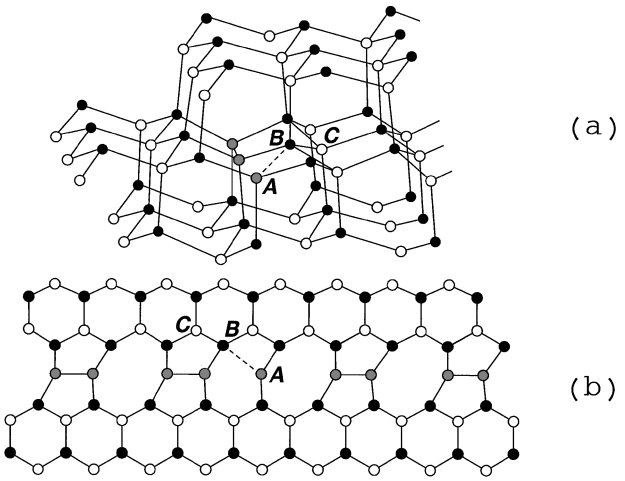

FIG. 1. (a) Three-dimensional view of a 30° partial dislocation, with a soliton domain wall, and (b) schematic drawing of the same in the (111) plane. The grey circles represent the atoms in the central core of the dislocation.

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The dislocation undergoes a reconstruction whereby the core atoms pair up in dimers forming intracore bonds and thus become fourfold coordinated. This reconstruction breaks the original translational symmetry along the core and doubles the primitive repeat distance along the core axis. Associated with this broken translational symmetry is a low energy soliton defect where, by creating a single unpaired core atom, the system may change along the line from one of the two symmetry related degenerate ground state phases to the other. Because the soliton atom is expected to have a dangling bond, it is natural to look for an ESR signal for this defect. The relatively low energy we expect for such an excitation leads us to expect a relatively large equilibrium population at silicon annealing temperatures ($\sim$900 K) and therefore that the ESR signal would not anneal out as quickly as other signals associated with the formation and motion of dislocations. We further would expect this signal to be detected in all systems which contain 30° partial dislocations.

Indeed, it was discovered over 30 years ago that plastically deformed silicon gives a wide variety of ESR signals [2]. (For an excellent review, see [3].) Out of the dozens of ESR centers, four have been identified as associated with the 30° dislocation core. The literature refers to these centers as Si-$K1$, Si-$K2$, Si-Y, and Si-R. The $K1$ and $K2$ defects have been identified to be electronic excitations of the same structural defect. Kisielowski-Kemmerich [4] made the currently accepted identification of the K and Y defects. It is well known that the first three of the aforementioned ESR signals anneal out over the (temperature dependent) time scale of about an hour [3]. Only one signal remains, the one labeled R [5,6]. This center is "thermally stable" (it does not anneal out) and is observed even at high deformation temperatures ($>$900 K) where the other signals anneal out too quickly to be observed. The R signal is the residue of Y after annealing, and is very similar to Y in its diminished anisotropy and large width [5].

Many authors have studied excitations of dislocations in silicon [1,7–9]. The nature of the ESR centers and the soliton excitation energy of the 30° partial dislocation, however, have yet to be addressed with modern *ab initio* techniques. In order to investigate the electronic structure of low energy excitations of the 30° partial dislocation core, we embarked upon a density functional study of the system.

To prepare approximately relaxed initial ionic configurations with the correct bonding topology, we first relaxed lattices containing dislocation cores using the Stillinger-Weber (SW) interatomic potential [10]. While doing this, we discovered that the soliton atom moves out of line with respect to the dislocation core. To probe this interesting possibility further, we carried out calculations within the plane wave total energy density functional approach [11]. To describe the electron-electron interactions we used the Perdew-Zunger [12] parametrization of the Ceperly-Alder [13] exchange-correlation energy of the uniform electron gas. To describe the electron-ion interactions we used a nonlocal pseudopotential of the Kleinmann-Bylander form [14]. The electronic wave functions were expanded in a plane-wave basis up to a cutoff of 8 Ry.

All supercells used in this study have the same size in the plane perpendicular to the (110) dislocation axis. Two partial dislocations of equal but opposite Burgers vectors at a separation of 14 Å cut through this plane. Following Bigger *et al.* [15], the lattice vectors are arranged so that the periodic dislocation array has a quadrupolar arrangement. Each cell contains forty-eight atoms per bilayer stacked along the dislocation core direction. To calculate the excitation energy of the soliton, it is also necessary to calculate the energy of the perfectly reconstructed dislocation. However, the smallest supercell which is commensurate with both structures contains six bilayers (288 atoms). It is possible, however, to reduce the computational time by using two different supercells. For the reconstructed case, the supercell contains two bilayers along the dislocation line, while the soliton structure contains three (96 and 144 atoms, respectively). The lattice vectors were obtained by relaxing a completely reconstructed dislocation within the SW model in the 96 atom cell. The three bilayer cell was then obtained from this by multiplying the lattice vector that points along the dislocation axis by $\frac{3}{2}$.

To minimize errors from k-point sampling, basis set truncation, and supercell effects, we compute differences of energy differences, as follows: For each supercell, we generated a completely unreconstructed configuration where all the core atoms have only three bonds. These structures can be realized in both supercells, and thus serve as the reference point. The final excitation energy is the difference between the deviations in the energy from the unreconstructed structure in each cell. By keeping the lattice vectors fixed throughout the calculations, we more closely simulate the environment which widely separated solitons would experience along a reconstructed dislocation line. To test for the impact of strain effects, we repeated all calculations using the corresponding lattice vectors of a bulk silicon system at the *ab initio* lattice constant. Our results did not change significantly.

To ensure maximum transferability of results between the two cells, the calculations employed k-point sets which give identical sampling of the Brillouin zone for the two supercells: $\{(0, 0, \pm 1/4)\}$ for the three bilayer cell and $\{(0, 0, \pm 1/6), (0, 0, 1/2)\}$ for the two bilayer cell. To find relaxed structures, we moved all ions along the Hellmann-Feynman forces until the ionic forces were less than 0.02 eV/Å. Typically, this was accomplished in 40 ionic steps, where between ionic steps we made 10–15 electronic relaxation steps using the analytically continued functional approach [16].

Figure 2 shows the projection in the (110) plane of our *ab initio* results for the structure of the soliton. (The

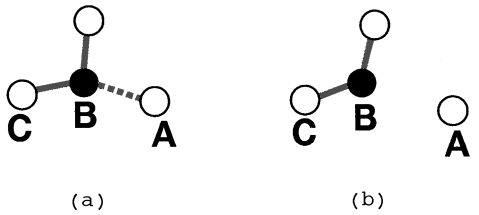

FIG. 2. Coplanar atoms near the soliton: (a) in the proposed ground state for the soliton; (b) conventional structure with the soliton atom in line with the remaining atoms in the dislocation core. The notation for the atoms is the same as in Fig. 1: atom A is the soliton atom, B is the fivefold coordinated bulk atom (see text), and C is a bulk atom bonded to B opposite from A.

same atoms are shown in Fig. 1 in full structural context.) The structure on the left is our prediction for the ground state. In this configuration, there is a fivefold coordinated bulk atom (B) in the immediate neighboring row to the dislocation core. Its new, fifth neighbor is the soliton atom (A). Our *ab initio* results show that the conventional structure on the right (generated by keeping the soliton atom collinear with the dislocation core) is not only higher in energy but also spontaneously decays into the ground state on the left.

The *ab initio* excitation energy of the soliton is $0.65 \pm (\approx 0.2)$ eV, where we attribute most of the uncertainty to the uncontrolled local density approximation and supercell effects. This energy corresponds to a density $\rho = \frac{1}{2}e^{-E/kT}$ in the range of 10^{-5} to 2×10^{-3} solitons per core atom at 900 K, which is consistent with the observed densities of the ESR centers: The R center represents a "fraction" of the density of the Y center, which is estimated in the experimental literature to be about 0.01 per core atom (Table II in [6], Table 2 in [17], and [3]). (The factor of $\frac{1}{2}$ in ρ comes from the fact that in a given phase of the ground state, only half of the core atoms represent possible soliton sites.) Given the exponential sensitivity of the density, we find this agreement encouraging, particularly as the energy of soliton is very low compared to typical point defects in silicon.

A great advantage of *ab initio* calculations, beyond their reliability, is that they also yield the electronic states, in particular giving information about their spatial symmetry. In Fig. 3, we plot the angular momentum decomposition of the local density of states as obtained from the Kleinmann-Bylander projections of the electronic eigenstates. Panel (a) shows, for an atom far from the core, the familiar concentration of p-like states at the top of the valence band. To explore the nature of the soliton state, we compare this to the local densities of states for the soliton atom in the proposed [3(b)] and conventional [3(c)] configurations. We also plot the local density of states for the quasi-fivefold coordinated atom [3(d)]. The appearance of the peak near the top of the valence band in the s channel of the soliton atom (and the corresponding diminution in the p channel) in its ground state [3(b)] shows that the state

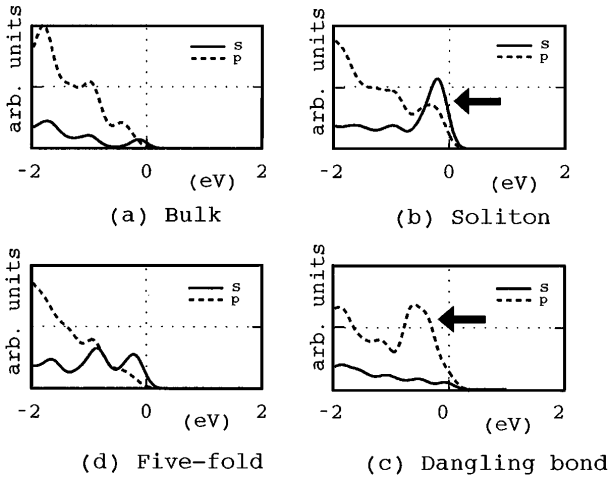

FIG. 3. Local density of states, calculated by acting on the filled bands with the Kleinmann-Bylander projectors centered at (a) an atom deep in the bulk, (b) the soliton atom in its proposed ground state, (c) a conventional soliton atom with a dangling bond, and (d) the quasi-fivefold coordinated atom. The horizontal axis is the energy (eV), the scale of the vertical axis is arbitrary but the same for all four plots. Solid and dashed lines represent densities in the s and p channels, respectively.

associated with the soliton is much less anisotropic than the simple dangling p-like bond on the soliton atom in the conventional picture [3(c)]. We further note an enhancement at the same energy in the s channel of the quasi-fivefold coordinated atom [3(d)], which indicates that the unpaired electron is shared between this atom and the soliton atom. Defects in the dislocation core therefore need not be associated with strongly directional electronic states, as has been previously assumed in identifications of ESR centers.

There is a direct connection between the symmetry of the electronic state of an unpaired spin and the symmetry of the corresponding ESR signal as described by its effective g tensor. The off-diagonal elements of this tensor involve a sum over matrix elements of the form $\langle\phi_0|\mathbf{L}_i|\phi_e\rangle\langle\phi_e|\mathbf{L}_j|\phi_0\rangle$, where ϕ_0 is the unpaired state and ϕ_e are the excited states [18]. In general, ϕ_0 can be broken into angular momentum components (as in Fig. 3), of which the s wave component makes no contribution to the preceding matrix elements. In general, then, we expect the anisotropy of g to be proportional to the population of the p channel. (Higher angular momentum components are negligible for filled states in silicon.) This population, the area under the peak associated with the unpaired electron in the p channel, drops by about a factor of 2 as the soliton moves from its symmetrical dangling bond configuration [3(c) to our proposed state 3(b)]. The literature contains qualitative observations of the decreased anisotropy of the R signal and one quantitative comparison which comes from measurements of the Y signal, of which the R is the residual after annealing. In [4], this anisotropy is compared directly

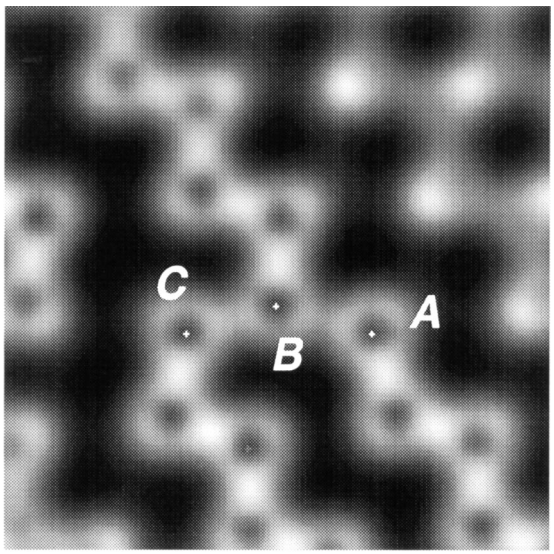

FIG. 4. Two-dimensional slice of the total charge density from our *ab initio* calculation, through the plane containing the atoms *A*, *B*, *C*, as labeled in the previous figures. The new *A*-*B* bond is nearly as pronounced as the bulk *B*-*C* bond, which is clearly weakened compared to the other (vertical) bulk bond of atom *B* seen in the figure.

with that of the $K1, 2$ centers, which have typical dangling bonds, and is shown to be less by about a factor of 2, in agreement with our electronic structure results.

To explore the nature of the bonding near the soliton atom, we plot the total valence charge density in Fig. 4, which shows that the soliton atom (*A*) makes a weak bond with the neighboring fivefold coordinated atom in the bulk (*B*). The new bond (*A*-*B*) of the bulk atom is very similar to a now weakened but previously existing bond in the spatially opposite direction (*B*-*C*). Such fivefold coordinated structures have been considered previously in silicon by Pantelides [19] and more recently by Duesbery *et al.* [20]. Through *ab initio* studies it was demonstrated that such fivefold defects in amorphous silicon should show similar anomalies in the angular momentum decomposition of the local density of states [21].

In conclusion, we have presented *ab initio* results indicating that the ground state of the soliton has an unusual structure involving a fivefold coordinated atom and a correspondingly unusual electronic structure. The excitation energy we calculate for this new defect corresponds to a thermal equilibrium density which is compatible with the observed density of the *R* center, which is the only thermally stable paramagnetic center associated with the 30° partial dislocation. In line with our notion of the soliton being the fundamental excitation of the reconstructed dislocation core, the *R* center is observed independent of the method of deformation and in proportion to the dislocation density. Our calculations show that the electron state of the soliton has a reduced anisotropy compared to that of a simple dangling bond which corresponds in magnitude to the puzzling reduction in anisotropy of the ESR signal of the *R* center. In the ground state structure which we propose, the soliton atom makes a weak bond with a neighboring bulk atom and thus gives rise to an amorphouslike bonding arrangement. This could explain in part the oft noted similarity of the ESR signature of the *R* center to that of amorphous silicon. Based on the above arguments and results, we propose that the domain walls in the reconstruction of the 30° partial dislocation and the *R* centers observed in ESR experiments are one and the same. Any viable competing theory which does not identify the *R* signal with the soliton must both predict a more plausible intrinsic excitation corresponding to the *R* center, and explain why the unpaired electron of the low energy soliton is not detected in ESR experiments.

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