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New physics of the 30° partial dislocation in silicon revealed through *ab initio* calculation

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Abstract. On the basis of *ab initio* calculation, 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 centre of plastically deformed silicon. We present the first *ab initio* determination of the free energy of the soliton, which is also in agreement with the experimental observation. 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.

Dislocations are central to the understanding of the mechanical response of materials. The mechanical behaviour 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° dislocations, which belong to the glide set. They dissociate into partial dislocations bounding stacking faults. The mobility of dislocations in high-Peierls-barrier materials such as silicon is effected by the motion of kinks, zero-dimensional defects. The 30° degree partial is less mobile than the 90° degree partial, so the motion of both types of dislocation in the glide set is controlled by the 30° degree partial. The low-energy kinks along the 30° partial have been shown to also involve a composite structure where kinks bind with soliton excitations in the reconstructed ground state of the dislocation core. The solitons arise because the reconstruction involves pairing of the core atoms, which leads to two degenerate ground-state configurations. The domains of the two configurations are separated by the soliton. These soliton excitations are also known as ‘anti-phase defects’ (APDs) [1] or ‘phase-switching defects’. For a general review on dislocations in semiconductors, see [2, 3], or more recently [4, 5].

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 behaviour of the solid. Using a special multiscale sampling technique, we are able to present, for the first time, an *ab initio* calculation for the free energy of formation for this defect. 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’) only has three bonds and therefore an unpaired electron. This simple model, however, does not lead to predictions consistent with any of the observed ESR signals associated with plastically deformed silicon.

We propose a new theory for the 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 centre in plastically deformed silicon, the only one which remains after careful annealing. The reason that the natural connection between this centre and the lowest-energy excitation of the dislocation core has not been made previously is that the observed ESR centre 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 signal strength could be used to determine experimentally the soliton density in plastically deformed silicon, a parameter which is important for understanding the plastic response of the material.

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. The dislocation undergoes a reconstruction whereby the core atoms pair up in dimers forming intra-core 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 that we expect for such an excitation leads us to expect a relatively large equilibrium population at silicon

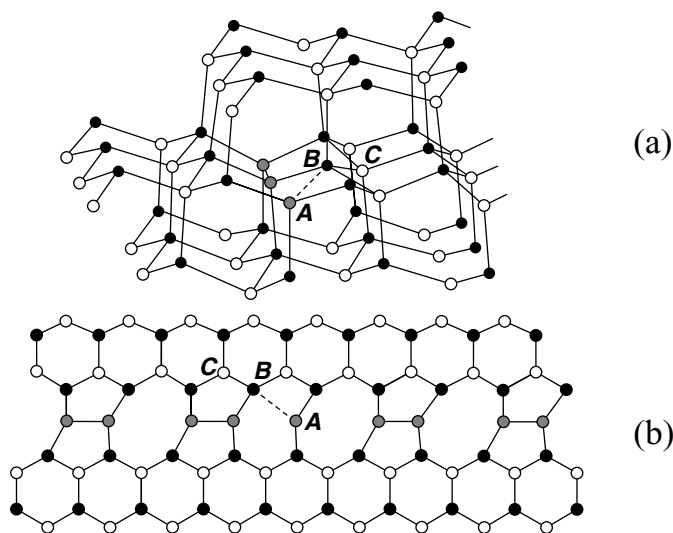


Figure 1. (a) A three-dimensional view of a 30° partial dislocation, with a soliton domain wall; (b) a schematic drawing of the same in the (111) plane. The grey circles represent the atoms in the central core of the dislocation.

annealing temperatures (~ 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 thirty years ago that plastically deformed silicon gives a wide variety of ESR signals [6–11]. Out of the dozens of ESR centres, four have been identified as associated with the 30° dislocation core. The literature refers to these centres as Si-K1, Si-K2, Si-Y and Si-R. The K2 and K1 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) timescale of about an hour [2]. Only one signal remains, the one labelled R [10, 12, 13]. This centre 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 centre was shown to be very similar to Y in its near isotropy and large width and also similar to the ESR signals obtained from amorphous silicon [12]. Kisielowski-Kemmerich *et al* [12] mentioned the possibility that R is the residue of Y after annealing. However, there is no direct evidence that the Y centre and the R centre are due to the same structural defect. The intensities for both centres are proportional to the dislocation density, but the Y intensity is also proportional to the area swept out by the glide of the dislocations during the deformation.

The nature of the ESR centres and the soliton excitation energy of the 30° partial dislocation have yet to be addressed with modern *ab initio* techniques. The APD was studied previously by Heggie and Jones [14–16]. Nunes *et al* [17] reported results of a tight-binding study including the energetics of kinks and solitons for the 90° partial dislocation. More recently, Bennetto *et al* [18] proposed a new kind of period-doubling reconstruction for the 90° partial using calculations based on density functional theory. Spence *et al* [19] investigated kink motion. Bulatov *et al* [1] have carried out a comprehensive study of the 30° partial dislocation and its defects but using only the Stillinger–Weber (SW) inter-atomic potential [20], which provides no electronic structure information. 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 SW potential. While doing this, we discovered that the soliton atom moves out of line with respect to the dislocation core. To probe this interesting feature further, we carried out calculations within the plane-wave total-energy density functional approach [21]. To describe the electron–electron interactions we used the Perdew–Zunger [22] parametrization of the Ceperley–Alder [23] exchange–correlation energy of the uniform electron gas. To describe the electron–ion interactions we used a non-local pseudopotential of the Kleinmann–Bylander form [24]. The electronic wave functions were expanded in a plane-wave basis up to a cut-off of 8 Ryd.

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* [25], the lattice vectors are arranged so that the periodic dislocation array has a quadrupolar arrangement. Each cell contains forty-eight atoms per core atom in the dislocation core. 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 (in total, 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 numerical errors, including those from k -point sampling, basis-set truncation and supercell effects, we compute differences of energy differences. 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 simulate the strain field which widely separated solitons would experience along a reconstructed dislocation line.

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 144-atom cell and $\{(0, 0, \pm 1/6), (0, 0, 1/2)\}$ for the 96-atom cell. To find relaxed structures, we moved the ions along the Hellmann–Feynman forces until the ionic forces were less than 0.02 eV \AA^{-1} . 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 [26].

Figure 2 shows the projection in the (110) plane of our *ab initio* results for the structure of the soliton. 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 neighbouring row of the dislocation core. Its new, fifth neighbour 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.

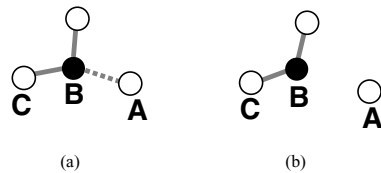


Figure 2. Coplanar atoms near the soliton: (a) in the proposed ground state for the soliton; (b) the conventional structure with the soliton atom in line with the remaining atoms in the dislocation core. The notation for the atoms is the same as in figure 1: atom A is the soliton atom; B is the fivefold-coordinated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

The *ab initio* excitation energy of the soliton is $0.65 \pm (\approx 0.2) \text{ eV}$, where we attribute most of the uncertainty to the uncontrolled local density approximation and supercell effects. If we are to estimate the equilibrium density of the APDs at 900 K, the entropy of the system must be taken into account. Specifically, we need the change in entropy associated with the creation of an APD.

To determine this, we used a new technique to carry out *ab initio* free-energy calculations for the fully reconstructed dislocation, and the completely unreconstructed dislocation, whose core can be viewed as a row of APDs. The entropy change between these two states gives an estimate of the entropy change of creating a pair of APDs on the dislocation core. Traditional techniques for *ab initio* evaluation of the entropy are at present infeasible; hence we applied, for the first time in an *ab initio* calculation, the multiscale sampling approach [27]. The change in free energy is given by the adiabatic work of a single degree of freedom in going from the

reconstructed state ($\lambda = 0$) to the unreconstructed state ($\lambda = 1$):

$$\Delta F = \int_0^1 d\lambda \langle \partial E / \partial \lambda \rangle.$$

The essence of multiscale sampling is that the phase space of the integral is explored in a crude, simple model (in this case, the Stillinger–Weber one) using a very large number of samples, resulting in a much smaller number of statistically independent points. These are evaluated within an accurate model (*ab initio*) and a corrective Boltzmann factor is used to establish the true Boltzmann distribution of the accurate model. This method is related to correlated sampling, or biased sampling. The key here is that the samples are obtained from an atomistic, higher-level description of the same physical system, but the exact *ab initio* thermal ensemble average is obtained at a dramatically accelerated rate (see [27] for details). The sampling was carried out with the standard Monte Carlo method using the Metropolis algorithm.

Figure 3 shows the free energy as a function of λ for the SW model, a tight-binding model and the *ab initio* model, the latter two obtained using multiscale sampling from the SW model. Table 1 shows the entropy calculated from the free energy. Although the free-energy values are quite different for the three models (due to the subtleties of the quantum mechanics of the bond being broken), the entropy variation (mostly changes in the vibrational modes of the surrounding lattice) is much smaller. Taking $T \Delta S$ to be about 0.1–0.2 eV, the free-energy difference associated with creating an APD can be estimated to be about 0.3–0.6 eV. This corresponds to a density

$$\rho = \frac{1}{2} e^{-\Delta F/kT}$$

in the range of 4×10^{-4} to 10^{-2} solitons per core atom at 900 K, which is consistent with the observed ESR signal strengths; the R centre is estimated to have a density of about 0.001 per core atom [13,28]. (The factor of one half in ρ comes from the fact that in a particular 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, with the caveat

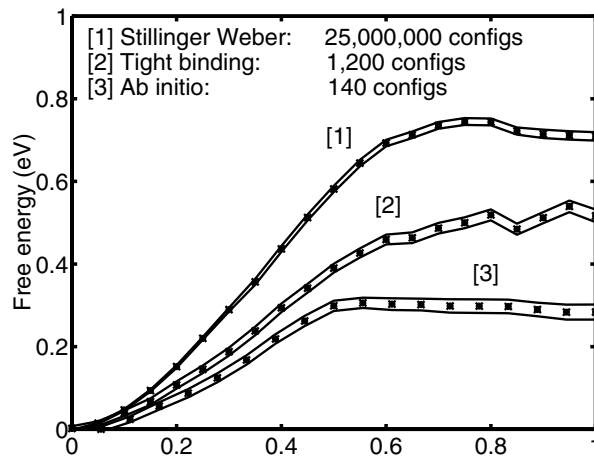


Figure 3. The free energy of reconstruction in three different models using the multiscale sampling approach (see the text). The free energy is evaluated by integrating the work done in moving the system along the coordinate λ from the reconstructed state to the completely unreconstructed state. The lines above and below the data points represent statistical error bars resulting from the sampling.

Table 1. The free energy and entropy of reconstruction. The statistical uncertainty from the multiscale sampling method is shown. The reconstruction energy is displayed in the first column for information.

| Model | ΔE (eV) | ΔF (eV) | $T \Delta S$ (eV) |
|------------------|-----------------|-----------------|-------------------|
| SW | 0.81 | 0.71 ± 0.01 | 0.10 ± 0.01 |
| Tight binding | 0.71 | 0.53 ± 0.02 | 0.18 ± 0.02 |
| <i>Ab initio</i> | 0.42 | 0.27 ± 0.03 | 0.15 ± 0.03 |

that the exact temperature at which the density of solitons is frozen during the quenching after the annealing is at present unclear.

A great advantage of the *ab initio* calculations, beyond their accuracy, is that they also yield the electronic states, in particular giving information about their spatial symmetry. In figure 4 we plot the angular momentum decomposition of the local density of states as obtained from the Kleinmann–Bylander projections of the electronic eigenstates. Part (a) shows, for an atom far from the core, the familiar concentration of s-like states at the bottom of the valence band and p-like states at the top. To explore the nature of the soliton state, we compare this to the local densities of states for the soliton atom in the proposed (figure 4(b)) and conventional (figure 4(c)) configurations. We also plot the local density of states for the quasi-fivefold-coordinated atom (figure 4(d)). The appearance of the peak near the top of the valence band in the s channel of the soliton atom in its ground state (figure 4(b)) shows that the state associated with the soliton is much less anisotropic than the simple dangling p-like bond on the soliton atom in the conventional picture (figure 4(c)). Note also that the density in the p channel of

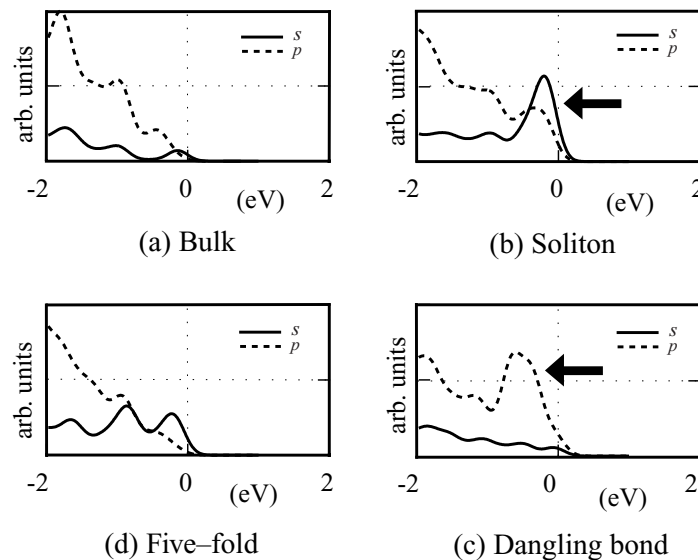


Figure 4. The local density of states, calculated by acting on the filled bands with the Kleinmann–Bylander projectors centred at (a) an atom deep in the bulk, (b) the soliton atom in its proposed ground state, (c) a conventional soliton atom with a dangling bond, (d) the quasi-fivefold-coordinated atom. The horizontal axis is the energy (eV); the scale of the vertical axis is arbitrary but the same for all four panels. Solid and dashed lines represent densities in the s and p channels respectively.

the soliton atom is also correspondingly diminished relative to that in the conventional state. We further note an enhancement at the same energy in the s channel of the quasi-fivefold-coordinated atom (figure 4(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 centres. Similar mechanisms can plausibly play a role in the decrease in anisotropy of other point defects.

The connection between the symmetry of the electronic state and the corresponding ESR signal is via the effective g -tensor:

$$g_{ij} = g_0\delta_{ij} - 2\Lambda \sum_n \frac{\langle \phi_0 | \mathbf{L}_i | \phi_e \rangle \langle \phi_e | \mathbf{L}_j | \phi_0 \rangle}{E_e - E_0}$$

where ϕ_0 is the unpaired state and ϕ_e are the excited states and Λ is the atomic spin-orbit coupling constant. In general ϕ_0 can be broken into angular momentum components (as in figure 4), of which the s-wave component makes no contribution to the off-diagonal matrix elements, so 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 two as the soliton moves from its symmetrical dangling-bond configuration (figure 4(c)) to our proposed state (figure 4(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 presumed to be the residual after annealing. In [4], this anisotropy is compared directly with that of the K1, 2 centres, which have typical dangling bonds, and is shown to be less by about a factor of two, 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 figure 5, which shows that the soliton atom (A) makes a weak bond with the neighbouring 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 [29] and more recently by Duesbery *et al* [30]. 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 [31]. In amorphous silicon, however, the shift from the p channel to the s channel is more pronounced with the peak in the p channel disappearing completely.

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 that we calculate with the first *ab initio* application of the multiscale approach for this new defect corresponds to a thermal equilibrium density which is compatible with the observed signal strength of the R centre, which is the only thermally stable paramagnetic centre 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 centre is observed independently of the method of deformation and in proportion to the dislocation density. Our calculations show that the soliton has an enhanced isotropy compared to that of a simple dangling bond, which correlates well with the puzzling, nearly isotropic signal of the R centre. In the ground-state structure which we propose, the soliton atom makes a weak bond with a neighbouring bulk atom and thus gives rise to an amorphous-like bonding arrangement. This could explain in part the similarity of the ESR signature of the R centre to that of amorphous silicon. On the basis of the above arguments and results, we propose that the

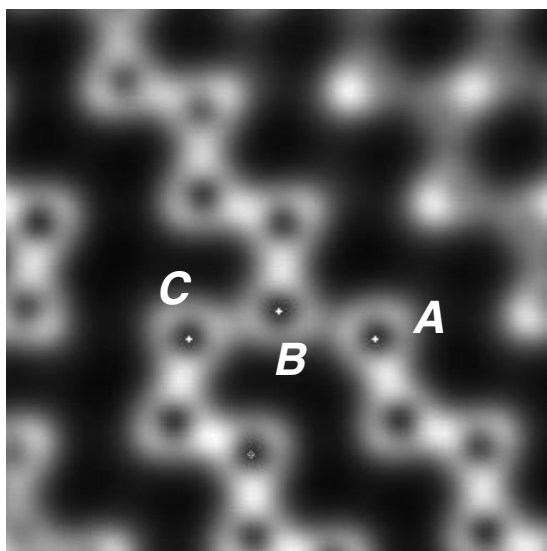


Figure 5. A two-dimensional slice of the total charge density from our *ab initio* calculation, through the plane containing the atoms A, B, C, as labelled in the previous figures. The new A–B bond is nearly as pronounced as the bulk B–C bond, which is clearly weakened compared to the other (vertical) bulk bond of atom B seen in the figure.

domain walls in the reconstruction of the 30° partial dislocation and the R centres 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 microscopic structure for the R centre and explain why the unpaired electron of the low-energy soliton does not exhibit an ESR signal.

It must re-emphasized that the above results and identification relate to thermally equilibrated paramagnetic centres. It is not clear at present what the precise connection is between the solitons and the Y centre. Furthermore, in the light of this new proposal for the native defect of the system, it might be time to re-examine the problem of the C line in the DLTS experiments on plastically deformed silicon. This, so far unidentified defect is also thermally stable, so it would be natural to investigate its relationship to the soliton of the 30° degree partial.

Acknowledgments

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