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Identification of the migration path of interstitial carbon in silicon

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We have performed *ab initio* total-energy calculations of ground-state properties and migration paths of interstitial carbon in silicon. The ground state involves threefold-coordinated carbon and silicon atoms and its geometry suggests primarily p and sp bonding for carbon, rather than sp^2 one would naively expect. Examination of possible migration paths reveals that only three correspond to small "jumps" involving a single "bond breaking." Of these, we predict that only one has a barrier of considerably lower energy ($\sim$ 0.5 eV) and involves an intermediate "saddle-point" configuration of C_2 symmetry.

Carbon is a common and technologically important impurity in silicon,[1] occurring in concentrations as high as 10^{18} cm^{-3} in Czochralski-grown materials. In its most common form, carbon is a substitutional impurity (C_s), electrically inactive in the neutral charge state. However, radiation damage can generate carbon interstitials (C_i),[2,3] which have enough mobility at room temperature to migrate and form defect complexes. Measured activation energies for migration range from 0.73 eV (Ref. 4) to 0.87 eV (Ref. 5) and seem to be independent (within experimental precision) of the charge state of the defect. These barriers for migration are obtained by measuring the annealing rate of the defect (due to formation of complexes) as a function of temperature.

Experimental results[2,4] suggest a ⟨100⟩-oriented C-Si interstitialcy (also called "split interstitial") as the probable ground-state configuration. In this configuration, carbon and silicon share an atomic position of the original diamond lattice (see Fig. 1). The configuration displays C_{2v} symmetry. Reorientation measurements were also performed,[2,4] in which uniaxial stress is applied in order to induce preferential alignment of the defects, and then recovery from alignment (reorientation) is monitored as a function of time for several different temperatures. Measured activation energies for reorientation range from 0.77–0.80 eV (Ref. 4) to 0.88 eV (Ref. 2). Theoretical calculations, using either classical empirical potentials[6] or the "modified intermediate neglect of differential overlap" (MINDO) method,[7] have focused primarily on the ground state and possible metastable states of the interstitial. The migration problem has not been systematically investigated.

Because of the complexity of the interstitial geometry, a migration pathway is yet to be identified. Although activation energies for annealing and reorientation are similar, a slightly lower barrier for annealing with respect to reorientation (as found in Ref. 4) could well be explained by the existence of more than one pathway of similar barrier heights. In this work we address these issues through *ab initio* total-energy calculations for ground-state properties and possible migration pathways of interstitial carbon in silicon. Our results provide enough evidence to conclude that in fact only one "jump" mechanism is responsible for both annealing and reorientation phenomena. The identified pathway for interstitial carbon migration in silicon is predicted to possess a "saddle-point" configuration with C_2 symmetry.

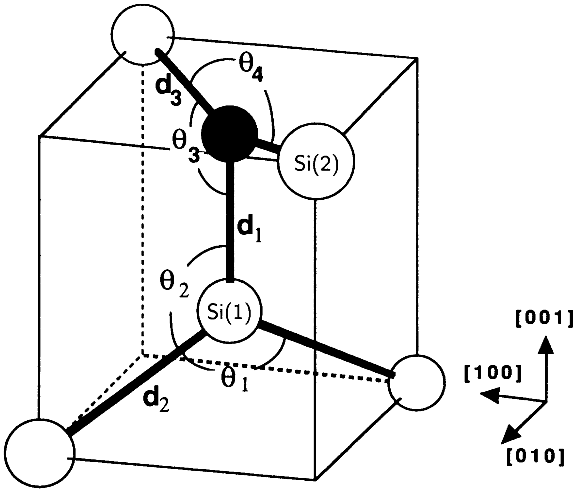

FIG. 1. Ground-state configuration of interstitial carbon in silicon. White spheres represent silicon atoms and the dark sphere represents the interstitial carbon. Bond lengths and angles defined in the figure have the values d_1 = 1.77 Å, d_2 = 2.22 Å, d_3 = 1.80 Å, θ_1 = 122°, θ_2 = 119°, θ_3 = 102°, and θ_4 = 157°.

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Our calculations are based on the local-density-functional theory,[8] with the exchange-correlation functional given by the Perdew-Zunger parametrization[9] of Ceperley-Alder results.[10] Electronic wave functions are obtained by conjugate-gradient minimization of the energy functional.[11] We have used separable norm-conserving nonlocal pseudopotentials with optimized convergence.[12] A 32-atom bcc supercell (33 atoms including the interstitial carbon) is used in order to treat the problem in the context of Bloch's theorem. Full relaxation of the 33 atomic positions is allowed for the ground-state calculation (saddle-point configurations are calculated by imposing the symmetry condition of the final configuration and relaxing the atomic coordinates subjected to this constraint). The cutoff energy for the plane-wave basis set was 40 Ry. Reciprocal space summations were restricted to the Γ point and two special $\vec{k}$ points in the irreducible part.[13] Recently, the method described above has been shown to account successfully for a variety of properties of other carbon-related defects in silicon.[14]

First, we present results for the structural and electronic properties of the ground-state configuration. The atomic arrangement obtained by fully relaxing the ionic coordinates is depicted in Fig. 1; it is indeed the $\langle 100 \rangle$ split-interstitial configuration, with threefold coordinated carbon and silicon atoms, and C_{2v} symmetry. Relevant geometrical parameters of the defect are defined in the figure. Note that the three bonds of the silicon interstitialcy make almost perfect 120° angles with each other, implying predominant sp^2 hybridization. The carbon atom, however, is pushed upwards so that it becomes almost collinear with the other two of its neighbors. Therefore the geometric configuration of the carbon atom implies a strong predominance of p and sp bonding, rather than the usual sp^2 hybridization one would have naively expected.

Two defect states were found in the gap, in agreement with experimental results.[4] Although density-functional theory does not provide a reliable estimate for the level positions with respect to the band edges, the charge density signatures of the two levels seem to be consistent with predictions from electron paramagnetic resonance (EPR) measurements,[2,4] as can be seen in Figs. 2(a) and 2(b). Figure 2(a) shows the lower defect state. Note that this state is a very localized p-like orbital in the carbon atom. The higher defect state is shown in Fig. 2(b), and also resembles a p-like charge distribution around the silicon atom of the interstitialcy. Note, however, that this state is not as localized as the lower one, and an electron associated with this state has a substantial probability to be found in some of the nearby bonds. This result was also noticed in EPR experiments.[4] The fact that the carbon-localized state is lower in energy and more localized than the silicon-localized state is consistent with the higher electronegativity of carbon with respect to silicon.

We now consider the problem of interstitial carbon migration in silicon. Our goal is to obtain the most likely migration path (or paths, if more than one) which can explain the annealing and reorientation measured activation energies. First of all, note that two of the three nearest neighbors of carbon are equivalent by 180° rotations about the defect axis. We denote the two nonequivalent silicon neighbors by Si(1) and Si(2) (see Fig. 1). In the analysis of all the possible migration "jumps" that take the carbon atom from the initial ground-state configuration to a different (but energetically equivalent) ground state configuration, a reasonable starting point is to consider those paths whose sole effect is the "breaking" of only one "bond." By this we mean that such paths preserve two of the three nearest neighbors of the carbon atom. Inspection shows that, for each initial configuration, only three nonequivalent final configurations fulfill this condition, and we will consider them in detail in the following discussion.

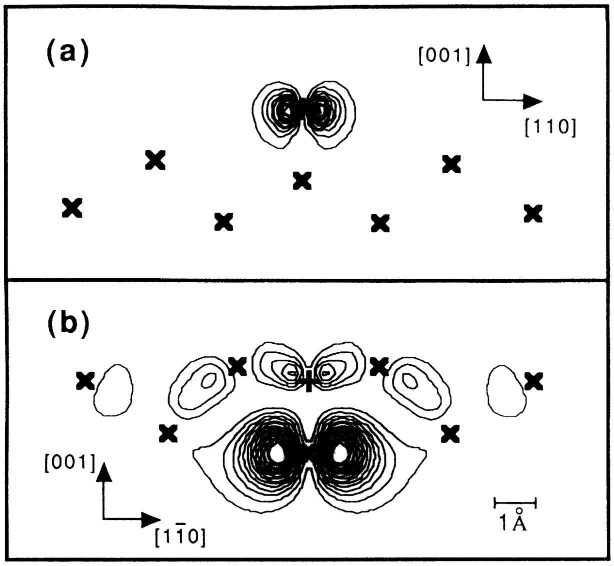

FIG. 2. Charge density contour plots of the gap states. We use ($\times$) to represent Si and (+) to represent C. Fifteen evenly spaced contours from zero to the maximum charge density were used in each case. (a) Lower defect state on the gap. Note the strongly localized p orbital on the carbon atom. (b) Higher defect state, primarily localized on the silicon atom and bonds nearby.

One of these migration pathways[6] involves an intermediate (saddle-point) configuration with a bond-centered geometry (C_{3v} symmetry). This path is shown in Figs. 3(a), 3(b), and 3(c), which illustrate, respectively, the initial (split), intermediate (bond-centered), and final (split) configurations. Note that the carbon atom remains in the (110) plane along the path, and the final configuration has an inverted orientation with respect to the initial one. A bond between the carbon and one of the Si(2) atoms is broken and another one is formed during the process. Note that the original Si(1) neighbor now plays the role of a Si(2) neighbor, and the Si(2) neighbor which is preserved becomes the Si(1) neighbor in the final configuration. We find an activation energy of 2.1 eV for this path,[15] which is much greater than the experimental values for either annealing or reorientation experiments. Therefore we can safely rule out this process as the migration path of interstitial carbon in silicon.

A second path is proposed in Figs. 3(d), 3(e), and

3(f). This migration jump is harder to visualize, since the trajectory of the carbon atom is not constrained to the (110) plane. The initial configuration is the [001]-oriented split interstitial, while the final configuration is [100] oriented. The intermediate configuration has C_2 symmetry (although this is difficult to discern from the figure), and the path also corresponds to the breaking of one Si(2) bond and the formation of another, with the Si(1) and Si(2) neighbors inverting their roles. Also note that this path can be viewed approximately as a rotation of the carbon atom with respect to an axis defined by the Si(1) and Si(2) neighbors which are preserved. This path has a much lower activation energy than the first one, namely 0.51 eV, which is much closer to the experimental values for both annealing (0.73 – 0.87 eV) and reorientation (0.77 – 0.88 eV) experiments. The discrepancy between theory and experiment can be due to the small supercell size. The defect state localized on the carbon atom was found to have an energy dispersion of $\sim$ 0.2 eV, indicating a non-negligible interaction between defects in the supercell scheme.[16] However, since the energy barrier for this second pathway is about four times lower than the energy barrier for the first pathway, it is clear that the second is a preferential path for migration.

Finally, a third path can also be regarded as a "one-bond-breaking" process, but corresponds to a much bigger hop of the carbon atom. In this process, the Si(1) neighbor remains Si(1)-type but the defect changes orientation from [001] to [010]. This process can also be viewed as a rotation of the same kind as in the second path, but with an angle of rotation that is essentially twice as large. Therefore this pathway is more likely to be composed of two consecutive steps of the second path. Indeed, the saddle-point symmetry for this path is C_{1h}, with the same mirror-symmetry operation as the C_{2v} ground state, and a constrained relaxation with this initial symmetry was found to lead to the ground-state configuration, indicating a two-step process. Hence we can also rule it out as an independent migration process of carbon in silicon.

Therefore although an entire phase space of possible carbon migration pathways has not been calculated, by focusing our analysis on the most likely paths we have been able to identify a migration path for the interstitial impurity which can explain both annealing and reorientation experiments, and possesses an activation energy in fair agreement with experiments. The path is the one shown in Figs. 3(d), 3(e), and 3(f) and corresponds approximately to a small rotation of the carbon atom with respect to an axis defined by two of its neighbors, breaking the original mirror symmetry of the initial configuration. The saddle-point configuration has C_2 symmetry. We claim that this is the only relevant migration path for interstitial carbon around room temperature, and we can conclude that the discrepancies in activation energies between annealing and reorientation experiments must be related to imprecisions in temperature determination or some sample dependence on the radiation dose,[4] since the underlying microscopic process in both cases is the same.

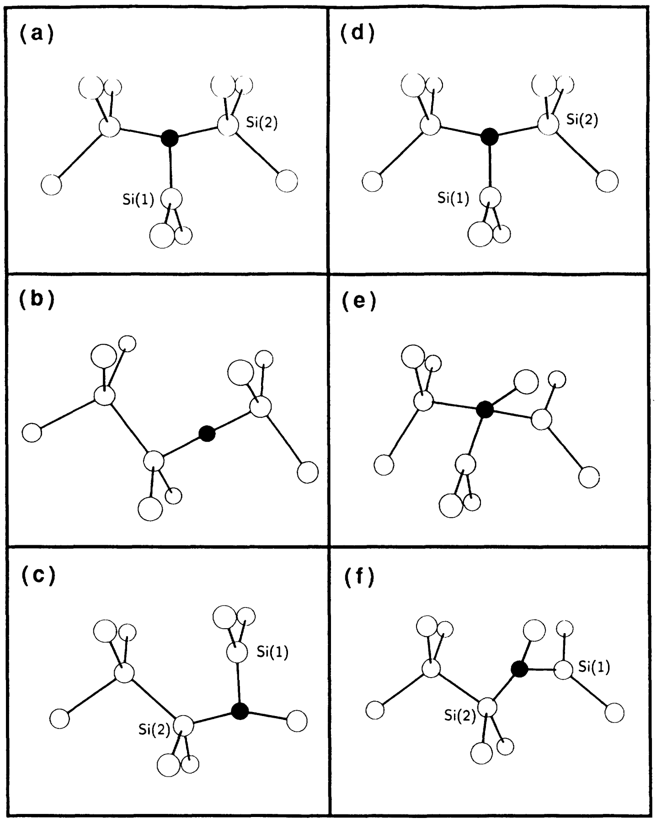

FIG. 3. Two migration paths for interstitial carbon in silicon. (a), (b), and (c) represent a migration path on which the intermediate configuration (b) is bond centered (C_{3v} symmetry). Note the inverted position of the final configuration with respect to the initial one. The activation energy for this path is 2.1 eV. (d), (e), and (f) represent migration with change of orientation from [001] to [100], breaking the original mirror symmetry. The intermediate configuration (e) has C_2 symmetry and the activation energy for this process is 0.51 eV, in reasonable agreement with experiments. The two kinds of nearest neighbors of the carbon atom, Si(1) and Si(2) (see text) are shown for each initial and final configuration.

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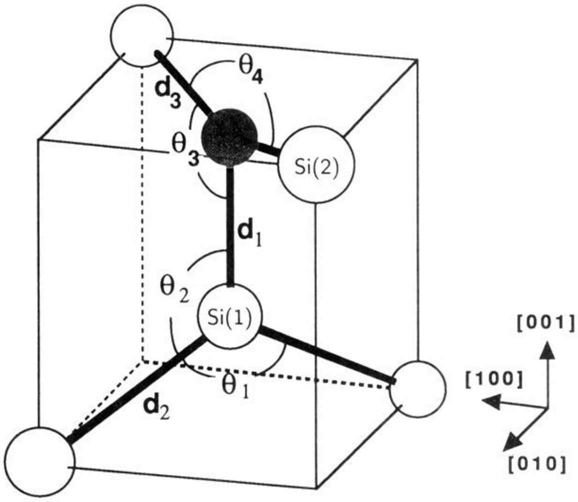
[15] The activation energy was computed by taking the energy difference between the split and bond-centered configurations. This is justifiable, since we found the bond-centered configuration to be indeed a saddle point, and not a metastable configuration. The same is true for the other migration path discussed. Interestingly, both the classical potential method employed by Ref. 6 and the MINDO method of Ref. 7 find the bond-centered configuration to be metastable. There is no experimental evidence for the metastability of the bond-centered configuration.

[16] The strain-mediated component of this interaction can be extracted by using a conventional valence force field model. Calculations of this type were performed in a 216-atom supercell and provided a strain correction for the energy barrier of the order of 0.01 eV only. This indicates that the ground-state and saddle-point configurations have similar long-range relaxations.



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