Barrier to Migration of the Silicon Self-Interstitial

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The first total-energy calculations of barriers to interstitial migration have been used to study silicon self-interstitial migration. Migration occurs through the low–electron-density path. Relaxation was found to be important in determining the barrier for both $Si^{(0)}$ and $Si^{(++)}$. Electron-assisted migration has been demonstrated. $Si^{(++)}$ was found to have lower energy at the tetrahedral site while $Si^{(0)}$ has lower energy at the hexagonal site.

Silicon self-interstitials are defects in silicon crystals consisting of extra silicon atoms in an otherwise perfect silicon crystal. As an intrinsic defect, silicon self-interstitials exist in all real crystals and play an important role in the behavior of silicon-based devices. In particular, they are thought to determine migration rates of other impurities, and the time evolution of dislocations.[1] Nevertheless, self-interstitials are poorly understood in comparison to other defects (vacancies, for example).[2] At low temperatures (4.2 K) in irradiated silicon only vacancies are observed, though vacancies and interstitials should be created in equal numbers. However, impurities, which are normally substitutional, are observed to be located at interstitial sites. These experimental results have been explained by the suggestion that silicon self-interstitials can migrate very rapidly, kick the substitutional impurities into interstitial sites, and replace them in the lattice.[2] Rapid migration at low temperatures requires either an extremely low barrier to migration or an electron-assisted transport mechanism.[3] This mechanism suggests that Si interstitials have more than one charge state with different migration barriers and/or different minimum energy positions. Then the charge state can alternate over time and position through the capture of electrons and holes. In irradiated systems this is easy because of the profusion of athermal electrons and holes generated by irradiation.

In this paper we present results of total-energy calculations in an attempt to elucidate the nature and energetics of Si self-interstitials. Our results provide information on the migration path, barrier energies, relaxation energies, and the bonding nature of these defects. To our knowledge, these are the first total-energy migration barrier calculations.

There have been two paths suggested for the migration of silicon self-interstitials. The first path, suggested by Watkins et al.,[4] is roughly described as movement through the bonds. The second path,

supported recently by Pantelides et al.,[5] is a path through the low–electron-density regions of the crystal. We found from our total-energy calculations (using Geometry II configurations described below) that the first path is not realizable. Placement of the interstitial at high-density configurations such as the split interstitial or bond centered positions[4] is completely unstable to decay into the low–electron-density regions. Consequently, we will henceforth focus on the low–electron-density path.

The low–electron-density path passes through what are called the tetrahedral and hexagonal sites (Fig. 1). We calculated the total energy at and between these sites using the self-consistent total-energy approach of Ihm, Zunger, and Cohen,[6] with norm-conserving pseudopotentials.[7] In this momentum-space formulation supercells are used to model the interstitial. In our calculations a plane-wave basis set with an energy cutoff of 6 Ry was treated exactly with an additional set up to 11 Ry included in perturbation theory. Two different supercell geometries were considered to ensure that the details of the interdefect coupling do not crucially affect the results. Geometry I contains eight host atoms with an interstitial near the center and a nearest-neighbor interstitial distance of 5.4 Å.
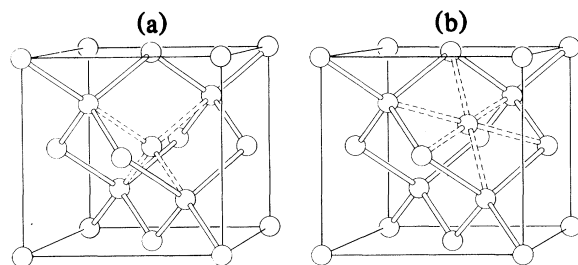

FIG. 1. Supercell geometry I with eight host atoms and an interstitial near the center. (a) Tetrahedral site. (b) Hexagonal site.
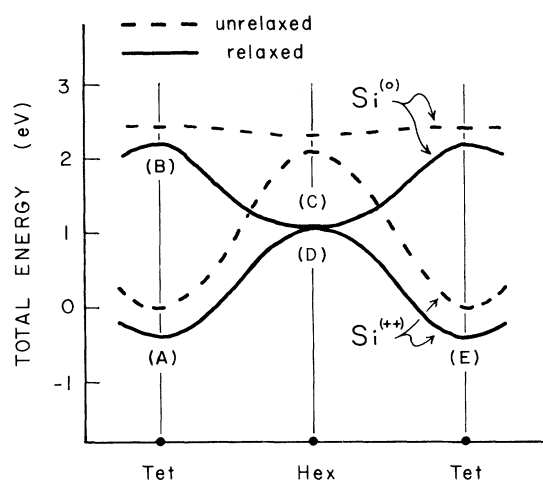
FIG. 2. Silicon self-interstitial migration barriers for unrelaxed and relaxed $Si^{(0)}$ and $Si^{(++)}$ along the (111) direction. The relative energy of $Si^{(0)}$ and $Si^{(++)}$ is chosen for p-type silicon. The zero of energy is arbitrarily set at the unrelaxed tetrahedral site.

Geometry II, not shown, contains sixteen host atoms and a nearest-neighbor interstitial distance of 7.6 Å. This doubling of the supercell assured convergence with deviations in barrier heights and relaxation energies of less than 0.1–0.3 eV. Specifically, the largest changes encountered between Geometry I and Geometry II were for the $Si^{(0)}$ unrelaxed barrier (0.3 eV) and the $Si^{(++)}$ hexagonal-site relaxation energy (0.2 eV). Both geometries were used for all calculated points.

Let us now proceed to the results. Figure 2 and Table I summarize the energy-barrier calculations. The results are for the barrier of $Si^{(0)}$ and $Si^{(++)}$ migration.[8] The relative locations of the $Si^{(0)}$ and $Si^{(++)}$ curves have been drawn for p-type silicon.

We consider first the hypothetical case of placing the interstitial in an ideal host environment without allowing the crystal atoms to distort. The total-energy migration curves are shown as dashed lines in Fig. 2. We observe that the energy curve for $Si^{(0)}$ is essentially flat with a very weak barrier to migration. The stable charge state, however, is $Si^{(++)}$ which has a large migration barrier of 2.1 ± 0.1 eV and a minimum-energy position at the tetrahedral site.

Recently, some very pretty results were obtained by Baraff, Schlüter, and Allan[9] who studied the low-density migration path using Green's function pseudopotential transition-state arguments. Even though they did not calculate the barrier itself they were able to predict an unrelaxed barrier lowering of $Si^{(++)} \rightarrow Si^{(0)}$ of 2.2 eV in agreement with our results. Our results, like theirs, indicate that the

TABLE I. Migration energy barriers in electronvolts.

	Unrelaxed	Relaxed
$Si^{(++)}$	2.1 ± 0.1	1.4 ± 0.2
$Si^{(0)}$	0.1 ± 0.3	1.0 ± 0.3

barrier lowering is driven by an electronic energy level which moves across the gap as the self-interstitial moves from the tetrahedral to hexagonal sites: starting as a hydrogenic state just below the conduction band at the tetrahedral site and moving to a state at the top of the valence band at the hexagonal site.

Let us now allow the host atoms surrounding the interstitial to relax. As a first approximation to the effects of relaxation on migration we studied the breathing-mode relaxation of interstitial nearest neighbors.[10] The size of the relaxation was determined by total-energy minimization. Results are summarized in Table II. Total-energy curves including relaxation are shown as solid lines in Fig. 2. Clearly, relaxation plays an important role in determining barrier heights for both $Si^{(0)}$ and $Si^{(++)}$. We note in particular that the relaxation energy at the hexagonal site is considerably larger than at the tetrahedral site. As a result, the $Si^{(0)}$ migration barrier is found to be 1.0 ± 0.3 eV and is stable at the hexagonal site. The migration barrier of $Si^{(++)}$ is now found to be reduced to 1.4 ± 0.2 eV and remains stable at the tetrahedral site. We emphasize that the minimum-energy configurations for $Si^{(0)}$ and $Si^{(++)}$ are the hexagonal and tetrahedral sites, respectively. This is crucial for the electron-assisted transport to be described shortly. Finally, we note in passing that at a given site, the relaxation energy for both charged states is essentially the same.

The calculations confirm that electron-assisted transport can occur through the low–electron-density path. This mechanism, the Bourgoin-Corbett mechanism,[3] proceeds as follows. Starting with $Si^{(++)}$ at the tetrahedral site (A) (see Fig. 2),

TABLE II. Relaxation of nearest neighbors in units of the nearest-neighbor distance.

	Tetragonal		Hexagonal	
$Si^{(++)}$	3.5%	-0.3 eV	5%	-1.0 eV
$Si^{(0)}$	3.5%	-0.2 eV	5%	-1.1 eV

it can capture two athermal electrons and become $Si^{(0)}$ at (B). Since it is unstable at (B) it will fall to the hexagonal site at (C). Then it can capture two holes and become $Si^{(++)}$ at (D) and then fall to either (A) or (E) providing a mechanism for transport even if thermal energy will not make possible the crossing of the barrier (A)-(D)-(E).

The energetics for self-interstitial migration in n-type silicon can be determined from Fig. 2 simply by rigidly shifting the $Si^{(0)}$ total-energy curves down by 2.4 eV. Electron-assisted transport by the Bourgoin-Corbett mechanism[3] will still occur, now proceeding from the hexagonal site $Si^{(0)}$ $\rightarrow Si^{(++)} \rightarrow Si^{(0)}$.

Though we did not perform total-energy calculations on $Si^{(+)}$, its migration barrier can be estimated to reasonable accuracy from Fig. 2 by averaging the $Si^{(0)}$ and $Si^{(++)}$ barriers. This indicates that the $Si^{(+)}$ barrier is low $(0.2 \pm 0.4$ eV) and may make possible thermal migration even at low temperatures. Our results are currently not sufficiently accurate to specify the minimum-energy position. The actual location of the $Si^{(+)}$ minimum will determine whether zero-temperature transport will occur for $Si^{(0)} \rightarrow Si^{(+)} \rightarrow Si^{(0)}$ or $Si^{(++)} \rightarrow Si^{(+)}$ $\rightarrow Si^{(++)}$. This one–electron-assisted transport could be important in determining the migration *rate* of Si self-interstitials because it can occur with greater frequency than the two–electron-capture mechanism. In particular, the migration rates in n- and p-type silicon can be different. It is likely that the most common charge state transitions in irradiated n- and p-type silicon are $Si^{(++)} \rightarrow Si^{(+)}$ $\rightarrow Si^{(++)}$ and $Si^{(0)} \rightarrow Si^{(+)} \rightarrow Si^{(0)}$, respectively. Therefore, if $Si^{(+)}$ is stable at the hexagonal site the migration in p-type silicon will occur for the one-electron process while for n-type silicon a two-electron process is necessary. If $Si^{(+)}$ is stable at the tetrahedral site the reverse is true. Indirect experimental evidence[2] seems to indicate that self-interstitials are somewhat more mobile in p-type silicon. On the other hand, the very rapid migration rates in both n- and p-type material might suggest that a one-electron migration process may be operative in both cases. This would be possible if the $Si^{(+)}$ barrier is very low, making possible thermal- or recoil-enhanced[3] migration at low temperatures. Under these circumstances, it is also conceivable that the $Si^{(+)}$ may migrate more than one step per electron capture. We thus find that several different electron-assisted transport mechanisms may be involved and additional work is necessary before the self-interstitial migration is completely understood.
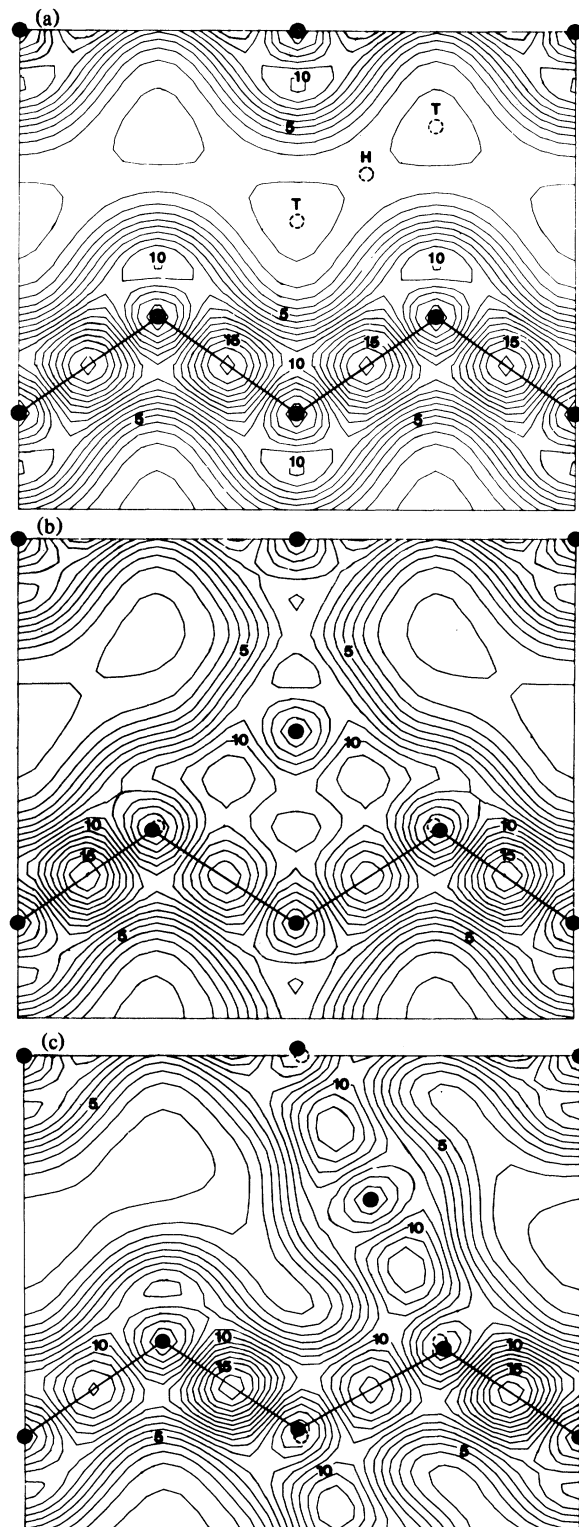

FIG. 3. Total valence charge densities (arbitrary units) in the (110) plane for (a) pure silicon, (b) Si self-interstitial at tetrahedral site, and (c) Si self-interstitial at hexagonal site. Dashed circles in (b) and (c) represent unrelaxed atomic positions.

Finally, in order to examine the nature of the self-interstitial–lattice bonding we show in Fig. 3 contour plots of the total valence charge density obtained from our calculations. The plane shown is the (110) plane containing a zigzag chain of atoms which can be seen in Fig. 1. The charge density of perfect Si crystal [Fig. 3(a)] shows the bonding charge along the chain and the low–charge-density path in which the tetrahedral and hexagonal sites are indicated.

The charge densities for an interstitial at the tetrahedral site and hexagonal site are shown in Figs. 3(b) and 3(c). These figures are for the relaxed configurations and the relaxed and unrelaxed atomic locations are indicated. Bonding between the interstitial and the lattice is evident and weakening of lattice bonds can be seen. In particular, the Si interstitial at the tetrahedral site bonds not only to its four nearest neighbors but also bonds strongly to its six second-nearest neighbors. This is important for the total energy and for energies of electron states.

[1]For example, see *Defects in Semiconductors*, edited by J. Narayan and T. Y. Tan (North-Holland, Amsterdam, 1981).

[2]For a review of the low-temperature experimental and theoretical background see G. D. Watkins, J. R. Troxell, and A. P. Chatterjee, in *Defects and Radiation Effects in Semiconductors—1978*, edited by J. H. Albany, IOP Conference Proceedings No. 46 (Institute of Physics, Bristol, 1979), p. 16; G. D. Watkins, in *Lattice Defects in Semiconductors—1974*, edited by F. A. Huntley, IOP Conference Proceedings No. 23 (Institute of Physics, Bristol, 1975), p. 1.

[3]J. C. Bourgoin and J. W. Corbett, in *Lattice Defects in Semiconductors—1974*, edited by F. A. Huntley, IOP Conference Proceedings No. 23 (Institute of Physics, Bristol, 1975), p. 149, and Phys. Lett. $\underline{38A}$, 135 (1972).

[4]G. D. Watkins, R. P. Messmer, C. Weizel, D. Peck, and J. W. Corbett, Phys. Rev. Lett. $\underline{27}$, 1573 (1971).

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[6]J. Ihm, Alex Zunger, and Marvin L. Cohen, J. Phys. C $\underline{12}$, 4409 (1979).

[7]D. Hamann, M. Schlüter, and C. Chiang, Phys. Rev. Lett. $\underline{43}$, 1494 (1979).

[8]The total-energy curves for $Si^{(0)}$ have been corrected by adding the energy difference between the correct highest occupied level and that obtained in this calculation. This entailed two corrections: (1) For hydrogenic levels a correction to the gap was necessary since current local-density–functional theory does not reproduce the gap and (2) an extrapolation to large supercells was made for this eigenvalue to enhance supercell size convergence. The error bars given include the estimated error from this procedure. For $Si^{(++)}$ this was unnecessary since the orbital sensitive to these corrections is unoccupied.

[9]G. A. Baraff, M. Schlüter, and G. Allan, Phys. Rev. Lett. $\underline{50}$, 739 (1983).

[10]Symmetry-breaking relaxations of neighboring atoms are not expected since the filled defect levels are nondegenerate.