First-principles study of the self-interstitial diffusion mechanism in silicon

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Abstract.   We study the stability and migration mechanism of self-interstitials in Si through first-principles self-consistent pseudopotential calculations. The neutral Si interstitial is lowest in energy at a [110]-split site, with energy barriers of 0.15–0.18 eV for migrating into hexagonal and tetrahedral interstitial sites, while the migration barrier from a hexagonal site to a tetrahedral site is lower, 0.12 eV. These migration barriers are further reduced through successive changes in the charge state at different sites, which allow for the athermal diffusion of interstitials at very low temperatures. The [110]-split geometry is also the most stable structure for negatively charged states, while positively charged self-interstitials have the lowest energy at tetrahedral sites. Apart from the migration barrier, the formation energy of the [110]-split interstitial is estimated to be about 4.19 eV; thus, the resulting activation enthalpy of about 4.25 eV is in good agreement with high-temperature experimental data.

Self-interstitial diffusion in silicon has been studied for the last few decades because of its scientific and technological importance. One of the main issues in technological process simulations is the role of self-interstitials in describing the enhanced diffusion of dopants, such as transient-enhanced diffusion or oxidation-enhanced diffusion. Although the understanding of self-interstitial diffusion may provide a clue to the enhanced diffusion of dopants, the dominant mechanism for self-diffusion is still debated. Moreover, the difference between the low-temperature and high-temperature diffusion mechanisms is not well understood. In particular, at very low temperatures (4.2 K), Al-doped Si samples irradiated with 1.5–3.0 MeV electrons exhibit nearly equal concentrations of Al interstitials and isolated vacancies; there is no evidence for Si interstitials being produced [1]. Since Al interstitials are likely to be created by capturing Si interstitials, Si interstitials must be mobile at very low temperatures. In n-type, p-type, and high-purity Si, ac conductivity measurements also showed that Si interstitials migrate with almost no activation energies [2]. Many theoretical attempts have been made to explain the athermal diffusion of Si interstitials in Si, and only the Bourgoin–Corbett type of electron-assisted transport was shown to lower the energy barrier [3–5]. It is generally agreed that a neutral Si interstitial is lowest in energy at a [110]-split site, while there is no consensus for the equilibrium geometry of the 2+ state; hexagonal, tetrahedral, and [110]-split sites have been proposed [4, 6, 7].

At high temperatures not too far below the melting temperature ($T_m \sim 1685$ K), experiments [8–13] showed that the self-diffusion coefficient follows an Arrhenius relation:

$$D = D_0 \exp(-Q/kT). \tag{1}$$

In general, although description of non-equilibrium diffusion phenomena requires that the activation enthalpy (Q) and the pre-exponential factor (D_0) are known, these data are difficult to obtain from experiment alone. For self-diffusion, experimental estimates for Q vary over the wide range 4.1–5.1 eV and the pre-exponential factor D_0 of about 10^3 cm^2 s^{-1} is larger by two orders of magnitude than those for metals and other semiconductors; for example, Ge has the pre-exponential factor 10.8 cm^2 s^{-1} [14]. The large value of D_0 for Si was thought to be caused by a large entropy term, although its origin is not completely explained. Car and co-workers calculated formation and migration energies of Si interstitials in equilibrium and suggested that interstitials and vacancies contribute to self-diffusion at high temperatures [5]. Although they showed that the activation enthalpy is mostly due to the formation energy, their calculated migration barriers of 0.4–1.4 eV are still too high to explain the self-diffusion at very low temperatures.

In this paper, we present a comprehensive investigation of the equilibrium structure and diffusion mechanism of self-interstitials in Si. For both neutral and negatively charged states, a [110]-split interstitial is found to be the equilibrium configuration, and a tetrahedral site is the most stable for positively charged Si interstitials. A neutral Si interstitial is found to have an energy barrier of about 0.15 eV for migrating through hexagonal and [110]-split sites, while the barrier along the tetrahedral–hexagonal–tetrahedral path is slightly lower, 0.12 eV. We find that the Bourgoin–Corbett type of diffusion is possible, which allows for cyclic changes in the charge state during migration and consequently gives rise to almost no barriers. At high temperatures, the migration of a neutral [110]-split interstitial through the hexagonal site is found to play a major role in self-diffusion, and the calculated activation enthalpy of 4.25 eV is in good agreement with experiments.
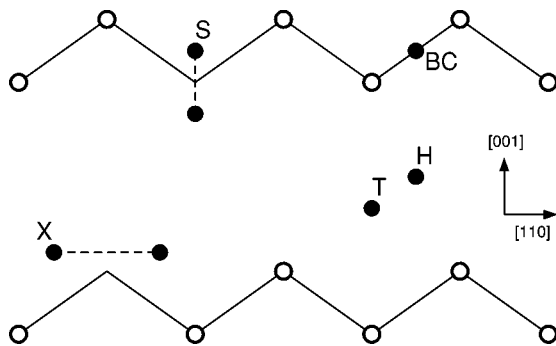

Figure 1. Various self-interstitial configurations are shown in the ($1\bar{1}0$) plane: tetrahedral (T), hexagonal (H), [110]-split (X), [001]-split (S), and bond-centred (BC) interstitials.

Our calculations are based on the first-principles pseudopotential method within the local-density-functional approximation (LDA) [15]. For the exchange and correlation potential, the Wigner interpolation formula is used. Norm-conserving pseudopotentials are generated by the scheme of Troullier and Martins [16], and then Kleinman–Bylander separable potentials are constructed [17]. We use a supercell containing 64 host atoms in which the distance between the interstitials is 10.91 Å, and find that this supercell size is large enough for us to ignore the elastic interaction between the interstitials. The wave functions are expanded in a plane-wave basis set with a kinetic energy cut-off of 12 Ryd, and the Brillouin zone summation of the charge density is performed over a uniform grid of k-points, which are generated by equal-n cuttings of the reciprocal-lattice vectors. Increasing the kinetic energy cut-off up to 16 Ryd and the number of k-points, we find that the relative

energies of the defects are sufficiently converged with the cut-off energy of 12 Ryd. The energy functional is fully minimized by the modified Jacobi relaxation method which has been employed successfully for a wide range of systems [18]. In calculating the energies of charged defects, we use a jellium background that neutralizes the charged unit cell and prevents the Coulomb interaction from being divergent [4]. To find the equilibrium geometry of a self-interstitial, we fully relax the coordinates of ions surrounding the interstitial until the Hellmann–Feynman forces acting are less than 0.01 eV Å^{-1}.

Table 1. The lowest-energy sites of a neutral self-interstitial for various kinetic energy cut-offs and different sets of k-points which are generated by equal-n cuttings of the reciprocal-lattice vectors. The numbers (in units of eV) in parentheses denote the total energy differences between the X and H sites. The calculations were performed with a supercell containing 64 host atoms.

n	6 Ryd	9 Ryd	12 Ryd	16 Ryd
1	X (0.07)	X (0.03)	H (0.03)	H (0.04)
2		X (0.16)	X (0.08)	X (0.08)
3		X (0.12)	X (0.04)	X (0.03)
4		X (0.11)	X (0.03)	

We consider various interstitial positions including five major configurations shown in figure 1: tetrahedral (T), hexagonal (H), bond-centred (BC), [001]-split (S), and [110]-split (X) interstitials. The migration barrier for each charge state is examined by calculating the total energies for many positions of Si interstitials along a migration path. In the case of self-diffusion at high temperatures, we assume that the diffusion is mediated dominantly by Si interstitials [8]. Then, the activation enthalpy Q in equation (1) is obtained by calculating the formation (E_F) and migration (E_M) energies of the defect:

$$Q = E_F + E_M. \tag{2}$$

The formation energy of a self-interstitial is expressed as a function of the atomic chemical potential (μ_{Si}) of Si and the electron chemical potential (μ_e):

$$E_F = E_D + q_D\mu_e - n_{Si}\mu_{Si} \tag{3}$$

where E_D is the total energy of a supercell containing a Si interstitial in charge state q_D and n_{Si} is the number of all Si atoms in the supercell. Here μ_{Si} is given by the total energy of bulk Si per atom, and the Fermi energy μ_e varies in the band gap. Although our LDA band gap is underestimated by about 40% for bulk Si, the total energies for different charge states of a defect are accurate and can be used to determine the migration and formation energies as well as the transition levels, with the measured gap value as bounds for the electron chemical potential. This approximation of using the measured gap value does not cause severe errors in estimating the transition levels, as previously addressed and employed in other calculations [19, 20].

(i) *The equilibrium configuration of self-interstitials.* We examine the energetics of the X and H sites using various kinetic energy cut-offs and different sets of k-points. As seen in table 1, the kinetic energy cut-off of 12 Ryd and the k-point set generated by $n = 3$ are sufficient for obtaining numerical convergence. The calculated total energies for various interstitial configurations are given in table 2. The results show that the equilibrium configuration of a self-interstitial depends on the charge state of the defect. Among the tetrahedral, hexagonal, bond-centred, [001]-split, and [110]-split interstitials considered here, we find that the [110]-split interstitial is lowest in energy for neutral and negatively charged

Table 2. Total energies of self-interstitials in a supercell containing 64 host atoms at the T, H, X, S, and BC sites for different charge states. The calculations were performed with a kinetic energy cut-off of 12 Ryd and a k-point set generated by three cuttings of the reciprocal-lattice vectors. All of the values are relative to the lowest one for each charge state (in units of eV).

Charge state	T	H	X	S	BC
2−	0.50	0.31	0.0	1.20	1.58
1−	0.38	0.19	0.0	1.12	1.54
0	0.16	0.04	0.0	1.12	1.43
1+	0.0	0.47	0.59	1.28	1.40
2+	0.0	1.15	1.32	1.60	1.65

states, in good agreement with previous theoretical calculations [6, 7]. For a single positively charged interstitial, the tetrahedral site is found to be the equilibrium geometry, whereas other calculations showed that the [110]-split site is the most stable [6, 7]. In the case of the 2+ state, the equilibrium site is also found to be the tetrahedral site, consistent with other *ab initio* pseudopotential calculations [4], while semi-empirical molecular orbital calculations suggested that the hexagonal site is more stable [7]. The [110]-split interstitial that has a pair of Si atoms at a substitutional site directed along the [110] axis is found to be shifted by 0.76 Å from its ideal-lattice site in the [001] direction. In fact, such a displacement minimizes the strain energy because it reduces the relaxations of the nearest atoms, and the interatomic distance (2.45 Å) of the pair almost recovers the bulk bond length. We find that the two fivefold-coordinated neighbours are bonded to the split interstitials with the bond lengths of 2.49 Å increased by 5.4%, while the bonds to the other two fourfold neighbours are nearly the same as the bulk value to within 1%. For the tetrahedral and hexagonal geometries, the relaxations of nearest-neighbour atoms are extremely small, about 0.1 Å. Regardless of the charge state, we find that the hexagonal site is the second lowest in energy. At the tetrahedral site, the neutral interstitial has four dangling bonds, so this geometry is stabilized when positively charged because of the reduced dangling bonds. In the case of the bond-centred geometry, since the two nearest-neighbour atoms undergo large outward relaxations of about 1.0 Å, this geometry is always unstable because of the large strain energy. In the [001]-split configuration, although the interstitials form a double bond with the bond length smaller by 8% than the bulk value, this geometry induces large relaxations for the neighbouring atoms, and thereby large strain energy. We also consider the puckered-bond and bridge-bond (twofold-coordinated) configurations [6], and find that both are unstable against the relaxations into the [110]-split or hexagonal geometry.

(ii) *Migration at low temperatures under electron irradiation.* Since the [001]-split and BC geometries are higher in energy, highly probable diffusion paths will pass through the X, T, and H sites. The total energies calculated along the T–H–T, X–T–X, and X–H–X paths are plotted for Si interstitials in neutral and singly and doubly positively charged states in figure 2. Among these diffusion paths, neutral interstitials are likely to move either along the X–T–X or X–H–X path because the [110]-split geometry is the most stable as discussed earlier. In this case, one of the split interstitials passes through a neighbouring tetrahedral or a hexagonal site and forms a [110]-split pair at the second-nearest neighbour. Because the X, T, and H sites are close to each other, the migration barriers are not very different from the total energy differences between these interstitial sites, so the energy barriers along the X–T–X and X–H–X paths are estimated to be 0.18 and 0.15 eV, respectively. Although a neutral interstitial that moves along the T–H–T path has a lower migration barrier of 0.12 eV than
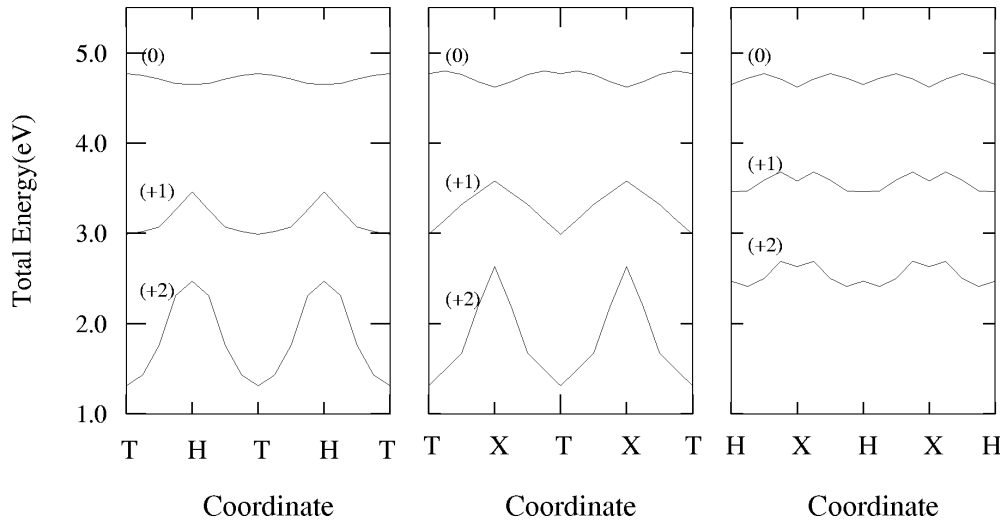
Figure 2. Total energy curves for Si interstitials for three different charge states (neutral, 1+, and 2+) along the T–H–T, T–X–T, and X–H–X paths. Calculations are performed using the kinetic energy cut-off of 12 Ryd and the k-point set generated by three cuttings of the reciprocal-lattice vectors.

for the X–T–X and X–H–X paths, this atom may rapidly fall into the [110]-split geometry during migration to follow either the X–T–X or X–H–X path, because the T–H–T path is energetically unstable. For both single- and double-positive states, the tetrahedral site was shown to be lowest in energy, so the X–T–X and T–H–T diffusion paths are highly probable. The migration barriers for the 1+ state are found to be 0.47 and 0.59 eV along the T–H–T and X–T–X paths, respectively, while these barriers are above 1.0 eV for the 2+ state. On the basis of our calculations, we suggest that the migration of self-interstitials at low temperatures is highly probable along the X–H–X path.

However, at very low temperatures, the migration barriers are still too high for Si interstitials to diffuse for all of the charge states considered here. Nevertheless, the Bourgoin–Corbett type of diffusion, which allows for cyclic changes in the charge state during interstitial migration, can lower the energy barrier, particularly along the T–H–T or X–T–X path, as illustrated in figure 2; these results are qualitatively consistent with previous calculations [4, 5]. For the T–H–T and X–T–X paths, a neutral Si interstitial at the H or X site will capture one or two holes; the ionized Si atom can then diffuse into the T site with no migration barrier, which corresponds to the equilibrium site for the 1+ and 2+ states. For further migration from the T site, the ionized interstitial should be in a neutral charge state, on capturing one or two electrons. The energy barriers in such carrier-assisted diffusion processes along the T–H–T and X–T–X paths are found to be less than 0.05 eV. In the case of the X–H–X path, when a neutral interstitial at the [110]-split site captures holes and moves to the hexagonal site, this atom is likely to fall into the more stable tetrahedral site. Thus, this diffusion path gives a higher barrier of about 0.25 eV, and the Bourgoin–Corbett type of migration may not exist. In thermal equilibrium, the Bourgoin–Corbett mechanism is unlikely to occur, because the frequency of electron or hole capture is not so high. However, under electron irradiations at low temperatures, the high-energy electron beam creates electron–hole pairs as well as native defects, so Si interstitials can easily migrate a long distance by means of cyclic changes in the charge state. We also consider possible

athermal migrations along the T–S–T or T–BC–T path, and find that these diffusion paths have higher energy barriers because interstitial atoms prefer to migrate into the [110]-split or hexagonal site rather than into the [001]-split or bond-centred site, when the charge states change from positive to neutral or negative.
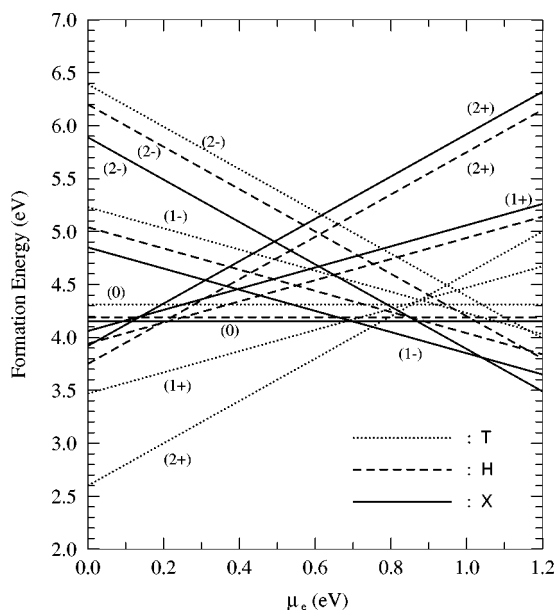

Figure 3. Formation energies of self-interstitials for different charge states as functions of the Fermi level. The calculations were performed using the kinetic energy cut-off of 12 Ryd and the *k*-point set generated by three cuttings of the reciprocal-lattice vectors.

   (iii) *Self-diffusion at high temperatures.* In high-temperature self-diffusion experiments, there is no electron irradiation, and interstitial atoms migrate thermally, with the diffusion coefficient following the Arrhenius behaviour. In this case, since the activation enthalpy in equation (2) is represented by the sum of the formation energy of the lowest-energy configuration and the migration barrier from that equilibrium site, self-diffusion has its greatest contribution from the path that gives the lowest activation enthalpy for a given temperature. Because the formation energy is calculated under the assumption of thermal equilibrium, our calculation should be adopted for such experimental situations. However, our results involve estimating the behaviour of the non-equilibrium cases indirectly, like other calculations [5, 8]. Figure 3 shows the formation energies of self-interstitials at the [110]-split, tetrahedral, and hexagonal positions for different charge states as a function of the Fermi level (μ_e). For μ_e less than 0.19 eV, diffusing self-interstitials are in a doubly positive charge state, with the activation enthalpies ranging from 3.75 to 4.13 eV along the T–H–T path, which are lower than those for neutral self-interstitials. This result indicates that the self-diffusion at relatively lower temperatures is enhanced in p-type samples. As μ_e increases up to about 0.25 eV, the self-interstitials in the 1+ state have lower activation enthalpies, of 4.13–4.19 eV, than for the 2+ state. For all values of the Fermi level in the gap, the formation energies of neutral interstitials are always higher than those for charged interstitials. However, we find that for 0.25 eV $< \mu_e <$ 0.85 eV, a neutral interstitial has the lowest activation enthalpy along the X–H–X path, which involves a site exchange of a Si interstitial with the host atom. In this case, the activation enthalpy is estimated to be 4.24 eV,

including the migration barrier between the H and X sites. At high temperatures, since the Fermi level normally lies in the midgap at any doping level, we believe that diffusing species are in a neutral charge state, with the activation enthalpy of about 4.24 eV, in good agreement with experimental values of 4.1–5.1 eV [8–13]. We also find similar activation enthalpies along the T–X–T and T–H–T paths.

Finally, to explain the pre-exponential factor D_0 in equation (1), we have to calculate the formation entropy for self-interstitials. In recent calculations [8], Blöchl and co-workers showed a large formation entropy of $\sim 6\,k_B$ for the [110]-split interstitial, while a formation entropy of about $10\,k_B$ is needed to explain the experimental data; however, they did not consider the X–H–X diffusion path. Here we point out, without considering extended interstitials or the participation of several kinds of interstitial, that the [110]-split interstitial can give rise to a larger entropy. If the [110]-split interstitial diffuses along the X–H–X path, this atom at a hexagonal site can migrate into one of six nearest neighbours to form a [110]-split configuration. Then, the interstitial atom increases the number of migration paths, giving an additional migration entropy to the total entropy term.

In conclusion, we have calculated the formation energies and migration barriers of Si interstitials for various charge states rigorously using the first-principles pseudopotential method. Although we find a diffusion path going through the [110]-split and hexagonal sites with a very low activation energy of about 0.15 eV, the Bourgoin–Corbett type of charge-assisted migration is more probable at extremely low temperatures under electron irradiations, in agreement with previous calculations. At very high temperatures, the migration of the neutral [110]-split interstitial into the hexagonal site is found to have an activation enthalpy of about 4.25 eV, which is in good agreement with experimental data, and this diffusion path is suggested to give rise to the additional migration entropy caused by the increased configurations.

Acknowledgments

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