Fast Diffusion Mechanism of Silicon Tri-interstitial Defects

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Molecular dynamics combined with the nudged elastic band method reveals the microscopic self-diffusion process of compact silicon tri-interstitials. Tight-binding molecular dynamics paired with ab initio density functional calculations speed the identification of diffusion mechanisms. The diffusion pathway can be visualized as a five defect-atom object both translating and rotating in a screw-like motion along ⟨111⟩ directions. Density functional theory yields a diffusion constant of $4 \times 10^{-5} \text{ exp}(-0.49 \text{ eV}/k_B T) \text{ cm}^2/\text{s}$. The low-diffusion barrier of the compact tri-interstitial may be important in the growth of ion-implantation-induced extended interstitial defects.

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Following high-energy ion implantation, strongly supersaturated silicon self-interstitials can agglomerate to form macroscopic planar interstitial structures, {311} defects 1. High-temperature annealing is necessary to remove lattice damage following ion implantation. However during the annealing process the {311} defects comprise a large reservoir of interstitials 2 3 4, which are released upon annealing and hence drive boron transient enhanced diffusion 3 6 7, an undesirable process which causes spatial broadening of boron concentration profiles. On the other hand, following low-energy implantation, significant boron TED is still observed, even though no visible {311} defects are developed 6.

It is crucial to understand the diffusion of various point defects in order to have a quantitative understanding of boron TED. Measurements of the diffusion rate of defects in silicon have been reported in experiments 8 9 10 11 12 13 14. Current experimental techniques cannot cleanly resolve the diffusion rates of more complex defect species, and due to the atomic-scale size of point defects, defect diffusion pathways cannot be resolved at all 11. Thus, numerical simulations provide a unique way to study the technologically-important dynamics of point defects in crystalline silicon.

Previously, such simulations have studied numerous defect species using both classical and quantum Hamiltonians 11 12 13 14 15. Using nudged elastic band methods (NEB) 21 within density functional theory (DFT) code, Lopez et al. compute an activation energy of 0.28 eV for a neutral single interstitial diffusing along the X-T-X path 22. Kim et al. estimates the self-diffusion barrier of a particular di-interstitial performing a reorientation to be 0.5 eV 17. Recent DFT-NEB calculations done in our group confirm this pathway but give a somewhat lower barrier of 0.3 eV 38.

Cogoni et al. 23 use temperature-accelerated molecular-dynamics 24 with the Kwon et al. 25 tight-binding (TB) potential to systematically study the diffusion of low-lying single-, di- and tri-interstitials. In particular they find all are fast diffusers with diffusion barriers of 0.94, 0.89 and 1.71 eV, respectively. We extend that work both with a more accurate tight-binding potential and with density-functional theory to further refine the diffusion pathway and the diffusion constant. Here we concentrate on the tri-interstitial finding an activation energy of 0.4-0.5 eV in DFT (and 0.6 eV in TB).

Which tri-interstitial to study? In a previous work from our research group 26, the three lowest-energy...
tri-interstitial geometries, denoted \( I_3^b, I_3^h, \) and \( I_3^c \), were identified by analysis of tight-binding molecular dynamics (MD) simulations followed by density functional relaxations. The TB calculations use the Lenosky et al. \[27\] potential. \( I_3^b \) is the ground state and \( I_3^b \) and \( I_3^c \) are excited states \[39\]; the density functional energies for the three defects in \( 216+3 \) atom supercells were 2.24 eV/atom, 2.37 eV/atom, and 2.47 eV/atom respectively. The tight-binding MD simulations show only \( I_3^b \) is a rapid diffuser, while \( I_3^b \) and \( I_3^c \) can be formed by interconversion of \( I_3^b \), but are themselves immobile within the 5 ns time scale of the simulations \[26\]. Hence, we focus on elucidating the microscopic diffusion process of the compact tri-interstitial \( I_3^b, I_3^b \) has a compact defect geometry in which a perfect tetrahedron of four atoms replaces a single atom in the silicon lattice, with the faces oriented along the four symmetry related \( 111 \) directions.

Tight-binding molecular dynamics determines an initial \( I_3^b \) diffusion path. Density-functional theory uses the nudged-elastic-band method to refine the diffusion path and determines the accurate diffusion barrier. The self-diffusion of \( I_3^b \) can be visualized in terms of the atoms most distorted during the process. In particular a five-atom object translates while rotating to avoid adjacent atoms. NDB finds four equivalent paths along \( (111) \) with a diffusion constant of \( D = 4 \times 10^{-5} \exp(-0.49 \text{ eV}/k_B T) \text{ cm}^2/\text{s} \).

**Minimum energy path / nudged elastic band.** Figure 1 shows two \( I_3^b \) defects in neighboring sites that correspond to initial and final configurations along the diffusion path, the \( [111] \) direction. We obtain the initial pathway from analysis of molecular dynamics trajectories \[26\]. The climbing-image NEB (CI-NEB) method \[28\] refines an accurate pathway and finds the diffusion barrier between these two \( I_3^b \) minima. The CI-NEB scheme guarantees that the image with the highest energy converges to the saddle point. All NEB calculations are performed with the VASP density functional code \[29, 30\] employing the Perdew-Wang GGA functional \[31\], and ultra-soft Vanderbilt-type pseudopotentials \[32\] as provided by G. Kresse and J. Hafner \[33\]. An initial relaxation of the two end points initiates a full relaxation of seven images along the path, keeping the volume of the cell fixed. Energy and atomic position convergence of 3 meV and 0.005 Å, respectively, is confirmed for \( 64+3 \) atom supercell by comparing the results for 250 eV energy cutoff and a \( 3 \times 3 \times 3 \) k-point mesh with a 300 eV cutoff and a \( 4 \times 4 \times 4 \) mesh. The seven images are initialized by linear interpolation between the two relaxed end points. Each of the images is relaxed until the atomic and spring forces are less than 10 meV/Å.

Figure 2 shows the diffusion path with an activation energy of 0.49 eV. Harmonic transition state theory \[34\] calculates the defect jump rate \( \Gamma \) from the phonon frequencies at the minimum \( \nu_{i}^{min} \) and at the saddle point \( \nu_{i}^{sadd} \) and the activation energy \( \Delta E \)

\[
\Gamma = \Gamma_0 \exp(-\Delta E/k_BT),
\]

where the prefactor \( \Gamma_0 \) is given by:

\[
\Gamma_0 = \prod_i \nu_{i}^{min} / \prod_i \nu_{i}^{sadd}.
\]

The dynamical matrix method within \textit{ab initio} GGA density functional theory determines the phonon frequencies. Each atom is displaced in the \( x, y, z \) direction by 0.03 Å and the calculated forces are used to construct the Hessian matrix for the system, which is diagonalized to find the phonon frequencies. This yields a jump rate \( \Gamma = 0.2 \text{ THz} \exp(-0.49/k_BT) \). Calculations for a larger cell of \( 216+3 \) atoms provide a diffusion barrier of 0.43 eV estimating a finite size error of about 0.1 eV.

**Collective motion of atoms.** In the diffusion event, the five most-displaced atoms move collectively, with a screw-like motion. The insets in Figure 2 showing the atomic configurations for initial, saddle and final states, indicate significant displacement of the five solid-colored atoms. All other atoms relax only slightly during the diffusion with a maximum displacement of 0.18 Å.

In order to illustrate the screw-like collective motion, we highlight the five highly-displaced atoms in Figure 3.

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**Figure 3:** Five most displaced atoms during the diffusion. These five atoms move collectively. Atom D and E define an axis of rotation \((111)\), around which atom A, B and C are rotating.
At the saddle point. The insets show images 3, 5 (saddle point), and 7 viewed from the [111] direction and illustrate that three-fold symmetry persists during the diffusion. The diffusion event is approximated by a uniform energy is 0.6 eV, only 20% higher than the fully relaxed value.

Figure 4 shows the translation and rotation of the double-tetrahedron during the diffusion. Translation occurs before the structure rotates. The double-tetrahedron is displaced half way and rotated 30 degrees at the saddle point. The insets show images 3, 5 (saddle point) and 7 viewed from the [111] direction and illustrate that three-fold symmetry persists during the diffusion.

**Discussion.** Table II summarizes the *ab initio* density functional theory results for formation and activation energy of the neutral single-interstitials. We also perform the NEB calculation to examine the diffusion paths of single- and di-interstitials will be published elsewhere. We also perform the NEB calculation to examine the diffusion paths of single- and di-interstitials will be published elsewhere [38].

| Formation energy /atom (eV) | Activation energy (eV) |
|----------------------------|-----------------------|
| $I_1$                      | 3.810                 |
| $I_2$                      | 2.827                 |
| $I_3$                      | 2.368                 |

$^{a}$NEB result from Ref. [22] is calculated using $216 + 1$ atom supercell.

Our pathway for $I_3$ diffusion is the same as that found by Cogoni et al. [23] in the $64 + n$ atom supercell. On the other hand, our DFT barriers for $I_1$, $I_2$, and $I_3$ of 0.3, 0.3 and 0.4-0.5 eV are much smaller than the tight-binding results by Cogoni et al. [23] of 0.9, 0.9 and 1.7 eV. We also perform the NEB calculation to examine the diffusion path of the compact tri-interstitial within Kwon’s potential [23], and obtain a diffusion barrier of

**Table I:** The translation and rotation of five atoms along the [111] direction with respect to the initial state for all seven images in Fig 4

| image | Translation (Å) | Rotation (degree) |
|-------|-----------------|-------------------|
| 1     | 0.18            | 0.4               |
| 2     | 0.42            | 4.6               |
| 3     | 0.57            | 16.4              |
| 4     | 0.66            | 30.0              |
| 5     | 0.75            | 43.6              |
| 6     | 0.89            | 55.4              |
| 7     | 1.13            | 59.6              |

For instance, rotating the double-tetrahedron of the initial configuration (image 1) by 16.4 degrees, and translating it by 0.57 Å while keeping its geometry fixed and relaxing the other atoms provides an approximation to image 3. Applying this procedure to each of the images along the diffusion path, we obtain the approximate diffusion path in Figure 4. The approximate activation energy is 0.6 eV, only 20% higher than the fully relaxed value.

**Table II:** Formation and activation energy of the neutral single-interstitials. The formation energy varies along the transition path, we obtain the approximate diffusion path in Figure 4. The approximate activation energy is 0.6 eV, only 20% higher than the fully relaxed value.

The diffusion event is approximated by a uniform translation and rotation of a fixed double-tetrahedron. For instance, rotating the double-tetrahedron of the initial configuration (image 1) by 16.4 degrees, and translating it by 0.57 Å while keeping its geometry fixed and relaxing the other atoms provides an approximation to image 3. Applying this procedure to each of the images along the diffusion path, we obtain the approximate diffusion path in Figure 4. The approximate activation energy is 0.6 eV, only 20% higher than the fully relaxed value.

**FIG. 4:** Transition path with seven images projected onto two-dimensional reduced coordinates. The inset shows images 3, 5 (saddle point), and 7 along the transition path.

Atom A, B, and C are located in a (111) plane, forming an equilateral triangle, and translate along and rotate about the [111] axis defined by atom D and E. Meanwhile, atoms D and E translate along the same [111] direction. Atoms D, A and B form an equilateral triangle, whose normal vector indicates another diffusion direction, and all five atoms form a double-tetrahedron. The bond between A and B is 2.49 Å at the minimum, 6% longer than the perfect silicon-silicon bulk bond distance. During the diffusion event this bond length varies by less than 4.5%. During defect migration the double-tetrahedron translates 1.31 Å and rotates 60 degrees as shown in Figure 1 and the insets of Figure 2. Table I lists the values for the translation and rotation of the seven relaxed NEB images.

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1.2 eV in contrast to 0.6 eV barrier within Lenosky’s TB potential [27]. The Kwon’s potential overestimates the phonon frequencies [27], which makes a local minimum steeper. This suggests that Kwon’s potential will consequently overestimate the barrier for the interstitial diffusion, which is characterized by the small displacements of several atoms deviating from the equilibrium sites.

We perform density of states (DOS) calculations for the interstitial defect along the diffusion path within a 216 + 3 atom supercell. The DOS is calculated for the minimum, the saddle point and an intermediate structure. The DOS shows a band gap of 0.71-0.74 eV for all three configurations along the diffusion pathway. There are no states in the gap. The size of the gap is close to the band gap of pure Si in GGA of 0.72 eV. The lack of gap states indicates that charge transfer may not play a significant role for the diffusion of a compact tri-interstitial.

During the self-diffusion event, five atoms move collectively in a screw-like motion along one of four symmetry-related (111) directions. Our DFT result shows a low activation energy of 0.49 eV and a diffusion constant of $4 \times 10^{-5} \exp(-0.49 \text{ eV} / k_B T) \text{ cm}^2/\text{s}$. Under conditions such as ion implantation that creates excess interstitials and hence favor cluster formation, $I_3^0$ diffusion may be an important process due to the low activation energy.

**Conclusions.** We have elucidated the pathway for the diffusion of the compact tri-interstitial, $I_3^0$, the only fast-diffusing tri-interstitial species in crystalline silicon. During the self-diffusion event, five atoms move collectively in a screw-like motion along one of four symmetry-related (111) directions. Our DFT result shows a low activation energy of 0.49 eV and a diffusion constant of $4 \times 10^{-5} \exp(-0.49 \text{ eV} / k_B T) \text{ cm}^2/\text{s}$. Under conditions such as ion implantation that creates excess interstitials and hence favor cluster formation, $I_3^0$ diffusion may be an important process due to the low activation energy.

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their $I^a_3$. 