Complexity of Small Silicon Self-Interstitial Defects

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The combination of long-time, tight-binding molecular dynamics and real-time multiresolution analysis techniques reveals the complexity of small silicon interstitial defects. The stability of identified structures is confirmed by *ab initio* relaxations. The majority of structures were previously unknown, demonstrating the effectiveness of the approach. A new, spatially extended tri-interstitial ground state structure is identified as a probable nucleation site for larger extended defects and may be key for the compact-to-extended transition.

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Silicon self-interstitial defects impact the fabrication of electronic devices [1,2]. Self-interstitial defects are created through ion implantation and associated with the transient enhanced diffusion of dopants, directly [2–4] or indirectly through the formation of larger, extended defects [5–7]. Experiments have revealed the presence of small self-interstitial clusters [8–10]. Theoretical investigations of the structure and dynamics of small self-interstitial clusters have produced a diversity of results and proven computationally challenging [11–13].

Theoretical studies of silicon interstitials have investigated a range of properties related to the structure and dynamics of small clusters [13–25]. Most efforts have relied upon *a priori* assumptions in proposing candidate geometries [13–19]. Molecular dynamics simulations with classical and quantum Hamiltonians [20–25] have identified stable structures and studied diffusion mechanisms. Deficiencies in the underlying classical potentials often lead to spurious results, and the ability to fit a classical potential sufficiently robust for such investigations remains open to debate [25]. Short, picosecond *ab initio* molecular dynamics simulations have been reported to provide greater accuracy, yet even "fast" diffusion mechanisms yield no more than a few transition events in each computationally expensive simulation [24]. The analysis of molecular dynamics simulations is challenging and has relied on visual inspection and the periodic relaxation of the system at predetermined intervals.

Extensive tight-binding molecular dynamics simulations [26] study the evolution of di-interstitial (I_2) and tri-interstitial (I_3) structures. A novel real-time multiresolution analysis (RTMRA) technique [27] extracts locally stable structures directly from the simulations. *Ab initio* relaxations refine the structures and determine the defect formation energies. The complexity revealed in this study is striking when compared to the picture uncovered in previous efforts. Three I_2 and three I_3 clusters are discovered with low formation energies. Two of the I_2 and two of the I_3 clusters have, to our knowledge, not been previously reported. Remarkable are the complex, extended geometries of some of the newly discovered clusters. Most interesting is the extended chainlike structure of the newly discovered I_3 ground state and its probable connection to the nucleation of large, extended defects. In addition, seven intermediate structures are identified in the diffusion of the I_3 that consist of a single-interstitial (I) and I_2 bound pair.

Simulation of defect dynamics.—Long, tight-binding molecular dynamics simulations using OHMMS [28] are performed for I, I_2, and I_3 defects at temperatures of 800, 900, 1000, and 1100 K. Each n-interstitial defect is modeled using a $64 + n$ atom unit cell with a lattice constant of 5.43 Å and Γ-point sampling of the Brillouin zone. A total of 20 ns of simulation time is accumulated at each temperature in 0.5 ns runs using a time step of 2 fs. Initial configurations for each run are chosen to be the compact structures *previously* assumed to be the respective defect ground state [13,15,22,23]. An analysis of the TB simulation data yields effective TB diffusion activation energy of 0.5 eV for both di- and tri-interstitial defects. Equivalent simulations of a single-interstitial find the effective TB diffusion activation energy of 0.8 eV.

Identifying stable structures.—The dynamics are recorded using a wavelet-based compression scheme reducing the stored data a hundredfold without compromising the fidelity of the fast dynamics during transition events. The algorithm is extended to perform RTMRA of the dynamics, enabling the detection of stable structures and transition events over multiple time scales [27] ranging from 4 fs to 8 ps. This allows the detection and tracking of stable defect structures against the background of thermal noise without the bias of a time-scale dependent definition of stability. From about 8000 structures extracted from the dynamics, three unique I_2 and 14 unique I_3 apparently locally stable structures are identified.

Refining the geometries.—The identified structures are carefully verified with tight-binding and *ab initio* calculations. When relaxed using the tight-binding potential, all identified structures remain locally stable. Structural relaxations typically yield a maximum atomic displacement of less than 0.1 Å, demonstrating the effectiveness of the RTMRA technique in identifying locally stable structures without costly structural relaxations. The geometries are further refined by *ab initio* calculations using VASP [29,30], a plane-wave based code using ultrasoft Vanderbilt-type pseudopotentials [31] as supplied by Kresse and Hafner [32]. The calculations are performed using the generalized gradient approximation of Perdew and Wang [33]. For each n-interstitial structure, the atomic positions are relaxed using a $64 + n$ and $216 + n$ atom unit cell. Convergence of the defect formation energies to within 0.01 eV is achieved using a plane-wave kinetic-energy cutoff of 250 eV and a $3 \times 3 \times 3$ k-point mesh for the $64 + n$ cell and a $2 \times 2 \times 2$ k-point mesh for the $216 + n$ and $512 + n$ cells. Formation energies per interstitial, E_f, are reported for the $216 + n$ atom calculations unless otherwise stated. They are defined as $E_f(n) = [E_{\text{tot}}(I_n) - (1 + n/N)E_{\text{bulk}}(N)]/n$, where N is the number of atoms in the bulk unit cell, $E_{\text{tot}}(I_n)$ is the energy of the I_n interstitial in the $N + n$ atom cell, and E_{bulk} is the energy of the N atom cell of crystalline silicon. When relaxed within density-functional-theory–generalized-gradient-approximation (DFT-GGA), all three I_2 structures remain stable. Of the fourteen I_3 structures, ten remain stable, and four collapse into the structure designated I_3^b shown in Fig. 3(a) (below).

The di-interstitials.—Figure 1 shows the three I_2 structures identified in the dynamics. The ground state structure (I_2^a) is the compact cluster with C_{1h} symmetry reported previously [15,23] with a formation energy of 2.83 eV. Two previously unreported, nearly degenerate local minimum structures (I_2^b and I_2^c) are found about 0.4 eV above the ground state. The I_2^b has C_{2h} symmetry and may be described as two dimers forming a chairlike structure in the [110] plane. The I_2^c has C_{1h} symmetry and is similar to the ground state with the exception of a single atom that is strongly displaced from a lattice site along the ⟨111⟩ direction. In the dynamics of the I_3, each I_2 reappears paired with an additional I.

The tri-interstitials.—Figure 2(a) emphasizes the C_2 symmetry and extended nature of the newly identified ground state (I_3^a) with a formation energy of 2.24 eV (2.11 eV) using a 216 + 3 (512 + 3) atom unit cell. All atoms are fourfold coordinated [34] with a bond length within 5% of crystalline silicon, explaining its low formation energy comparable to that of the I_4 compact cluster [14]. The extended, chainlike structure suggests a link to the nucleation of larger, extended defects.

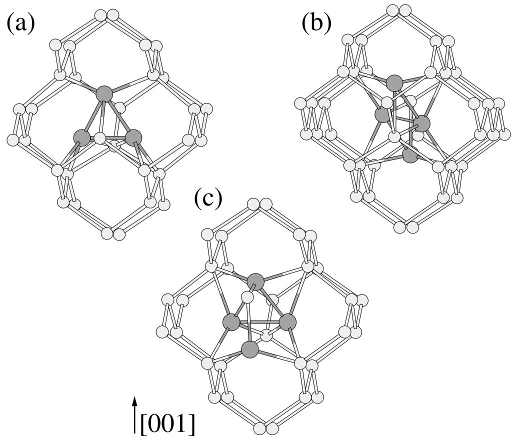

FIG. 1. Three di-interstitial clusters. The formation energy E_f of the ground state structure (a) I_2^a is found to be 2.8 eV using a 216 + 2 atom unit cell. Two nearly degenerate local minimum structures (b) I_2^b and (c) I_2^c are found 0.4 eV above the ground state. The I_2^a and I_2^c have C_{1h} symmetry, whereas the I_2^b has C_{2h} symmetry.

Figure 3 shows the I_3 local minimum structures. The (I_3^b) is the compact cluster with D_{2d} symmetry previously reported to be the ground state [13,22]. A 512 + 3 atom unit cell is used to confirm the true ground state, which increases the formation energy difference between the ground state I_3^a and the I_3^b from 0.13 eV (216 + 3 atom cell) to 0.21 eV (512 + 3 atom cell). Figure 3 also shows a previously unreported structure (I_3^c) with C_3 symmetry and a formation energy of 2.47 eV. Similar to the ground state, the I_3^c exhibits a complex, extended geometry and may be described as having three four-member rings forming three sides of a distorted cube in an otherwise nearly perfect lattice and with all atoms fourfold coordinated.

Our results are in contrast to the two I_3 structures reported in Refs. [17,24]. While Ref. [24] reports a C_{3v} symmetry structure as the ground state found in *ab initio* molecular dynamics simulations using a local orbital basis method, we find this structure to be unstable in both local density approximation and GGA. A second structure with the same symmetry being related by a 30° rotation about the [111] direction has been discussed as a W center in electron paramagnetic resonance (EPR) experiments [17]. We find the formation energy of this structure to be 0.5 eV higher than the I_3^a. We do not detect this structure in our simulations. A possible explanation might be the existence of a large transition barrier.

Nucleation of extended defects.—The most interesting discovery is the identification of the extended, chainlike ground state structure I_3^a suggesting a role in the

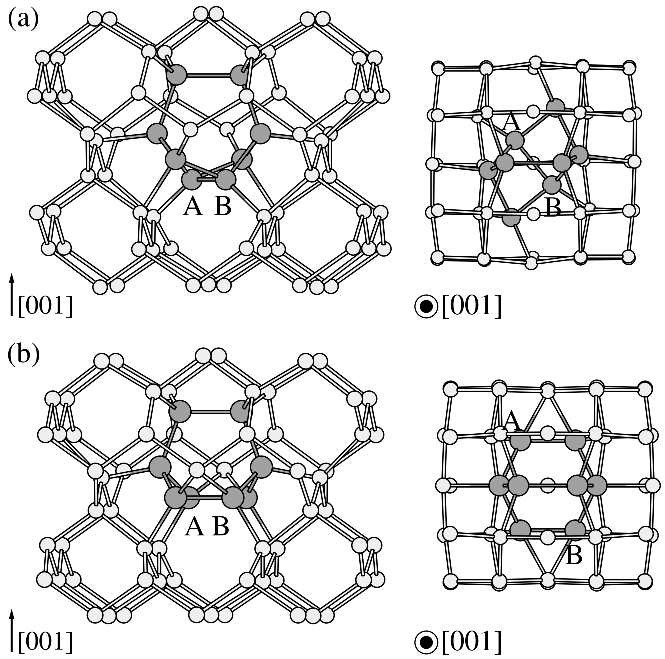

FIG. 2. (a) Two views of the tri-interstitial ground state structure I_3^a with DFT-GGA formation energy of 2.1 eV using a $512 + 3$ atom cell. The arrow denotes the C_2 rotation axis in the [001] direction. All atoms are fourfold coordinated [34]. (b) Equivalent views of an extended [110] tri-interstitial chain with a formation energy of 2.8 eV (using a $216 + 3$ atom cell) reflecting the core structure of larger extended [110] chains. The atoms have fourfold coordination with the exception of a single fivefold coordinated atom at each end. The two structures shown are connected by the displacement of the atoms designated *A* and *B*.

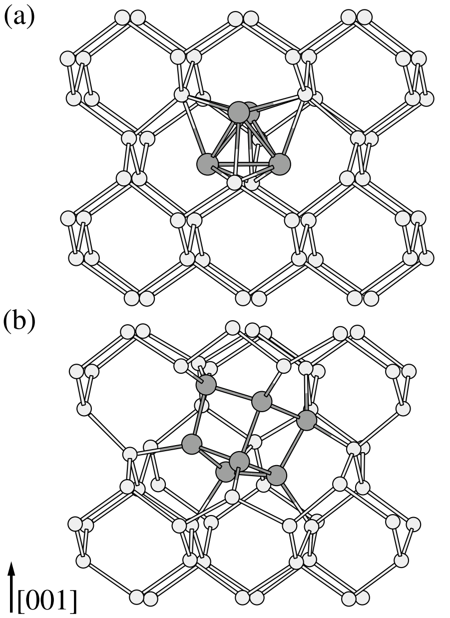

FIG. 3. Two energetically low-lying tri-interstitial local minimum structures. The formation energies of the (a) compact I_3^b and (b) extended I_3^c are found to be 0.13 and 0.23 eV higher than the ground state structure shown in Fig. 2(a), respectively. The I_3^b has D_{2d} symmetry. The I_3^c has C_3 symmetry with all atoms fourfold coordinated.

nucleation of large, extended {311} defects. Rodlike {311} defects are composed of extended [110] interstitial chains [13]. It has been shown [13] that the growth of these chains through the capture of an additional interstitial at either end is energetically favorable for chains of more than four interstitials. The energetics may be understood by observing that chains of any length have fourfold coordination with the exception of a single fivefold coordinated atom at each end. In contrast, structures containing less than five interstitials were shown to prefer a compact structure [12–14]. Moreover, the four-interstitial (I_4) compact ground state is shown [14] to be highly stable and immobile with no obvious transition path to an extended chain without global bond rearrangement. The compact-to-extended transition needed for the nucleation of larger extended defects has remained unclear.

Figure 2(b) shows two views of an extended tri-interstitial [110] chain (I_3^{chain}) referred to as an "elongated tri-interstitial cluster" [13] and found to have a formation energy of 2.70 eV within DFT-GGA. This structure reflects the core of longer chains. The connection between I_3^{chain} and the ground state structure I_3^a is readily apparent in Fig. 2. Specifically, I_3^a may be connected to I_3^{chain} through the displacement of the atoms designated *A* and *B*. This displacement breaks the bond between these atoms and each form a bond with the fivefold coordinated atoms at the ends of the chain. The energy barrier for this displacement is only 1.5 eV within DFT-GGA. An interpretation of the ground state I_3^a is seen by considering the systematic removal of interstitials from a larger extended chain; for three interstitials the ends of the extended chain (I_3^{chain}) are close enough to allow for a structural transformation that reduces the formation energy by eliminating the fivefold coordination. Atoms *A* and *B* are close enough to "reach across" and form a common bond with a simple displacement.

The close connection between I_3^a and I_3^{chain} strongly suggests a role for the former in the nucleation of larger extended defects. The capture by I_3^a of an additional interstitial to form a four-interstitial extended chain (I_4^{chain}) is energetically favorable with a reduction in formation energy of 0.18 eV. Although the I_4^{chain} is a local minimum structure lying 0.38 eV above the compact I_4 ground state cluster, the collapse into the latter requires a complex transformation. The key point is that the identification of an extended, chainlike I_3 ground state structure provides a mechanism for a compact-to-extended transition to bypass the compact I_4 cluster. The proposed mechanism relies only on the process by which extended [110] interstitial chains are believed to grow [13,25].

Intermediate structures.—In addition to the three I_3 clusters, we identify seven intermediate structures consisting of an I and I_2 pair. These intermediate structures are local energy minima and can be divided into two groups based on their energetics. Three structures are found with binding energies on the order of 1 eV and a (center-center) separation between constituents of between 4–6 Å. Four structures are found to be weakly bound with a (center-center) separation of about 7 Å.

The intermediate structures have implications for I_3 formation. Based on ground state energetics, the formation of I_3^a from single interstitials ($I + I + I \longrightarrow I_2 + I \longrightarrow I_3$) is energetically favorable with a binding energy of 4.7 eV, and the formation of the intermediate I_2^a is energetically favorable with a binding energy of 1.9 eV. The intermediate structures provide energetically favorable intermediate states from which formation mechanisms can be inferred. We emphasize that there are likely more intermediate structures in addition to the ones identified here. However, the identified intermediate structures indicate that the I_2 exhibits a "capture radius" of about 6 Å for single interstitials and that the energies of the bound intermediate states with a separation of between 4–6 Å already account for roughly half the binding energy of I_3^a (relative to an isolated I and I_2^a).

The complexity of small interstitial defect structures is revealed using an approach combining tight-binding molecular dynamics, real-time multiresolution analysis and *ab initio* calculations. The majority of structures have not been reported previously, indicating the limitations of studying the behavior of small interstitial clusters with more conventional methods. Three I_2 clusters are found; two of them were previously unknown. Three low-energy I_3 clusters are found; two of them were previously unknown and are spatially extended. Seven intermediate structures are identified in the dynamics of the I_3, consisting of I and I_2 pairs. A new I_3 ground state is identified with an extended, chainlike structure that may be connected to the compact-to-extended transition in the nucleation of large, extended defects.

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