Stability of Si-Interstitial Defects: From Point to Extended Defects

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Trends in the growth of extended interstitial defects are extracted from extensive tight-binding and *ab inito* local density approximation simulations. With an increasing number of interstitials, the stable defect shape evolves from compact to chainlike to rodlike. The rodlike {311} defect, formed from (011) interstitial chains, is stabilized as it grows, elongating in the chain direction. Accurate parametrization of the defect-formation energy on the number of interstitials and interstitial chains, together with the anisotropy of the interstitial capture radius, enables macroscopic defect-growth simulations.

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Rodlike {311} defects are commonly observed in ion-implanted silicon and are believed to play important roles in boron transient enhanced diffusion (TED) by providing interstitials during annealing processes [1,2]. However, even under the implantation conditions to suppress the formation of extended defects, TED has been observed, suggesting that microscopic interstitial defects exist [3]. While the structural properties of rodlike {311} defects are well characterized by experiments, e.g., via high-resolution transmission electron microscopy (HRTEM) [4,5], the existence and properties of small clusters are not well understood. Only recently, the presence of interstitial clusters has been evidenced by deep-level transition spectroscopy [6].

The energetics of interstitial clusters with respect to the size, i.e., the number of interstitials n contained in a cluster, determines the temporal evolution of the mean size $\bar{n}$ of interstitial clusters and their density. The growth and decay of cluster-related deep-level states indicated Ostwald ripening of interstitial clusters [6,7]: bigger and more stable clusters are formed when the concentration of free interstitials exceeds the thermal equilibrium value as in implanted samples [2]. Kinetic Monte Carlo simulations [8] predict Ostwald ripening of interstitial clusters consistent with the experiments.

Recently, Cowern *et al.* reported the formation energy of interstitial clusters determined directly from TED measurements using B-doped makers by "inverse modeling of the ripening process" [9]. In contrast to the earlier assumption of the monotonous decrease in the formation energy of interstitial defects with increasing size [8], they reported that the formation energy for a given size has local minima at $n \simeq 4$ and $n \simeq 8$ and converges to an almost constant energy for larger clusters $n > 15$. The compact 4-interstitial cluster model of Arai *et al.* [10] was proposed by Cowern *et al.* to constitute building blocks for such stable interstitial clusters.

On the other hand, HRTEM images of large {311} defects indicate that rodlike {311} defects can grow by condensation of interstitial chains [5]. Figure 1 shows three possible stable configurations composed of interstitial chains. This observation is supported by tight-binding (TB) simulations [11] that also found isolated interstitial chains and smaller interstitial clusters to be stable against isolated interstitials. Furthermore, interstitial chains and small clusters share the same building blocks, namely, $\langle 110 \rangle$ dumbbell interstitials.

In this Letter, we present trends in the formation energies of n-interstitial defects. Using first-principles calculations within the local density approximation (LDA) [12,13], we consider relevant interstitial defects—small clusters ($n = 2$–5), chains, and planar {311} defects—and we relate them to the growth of interstitial defects in interstitial supersaturated silicon as achieved in ion-implanted samples. In general, the stability of interstitial clusters

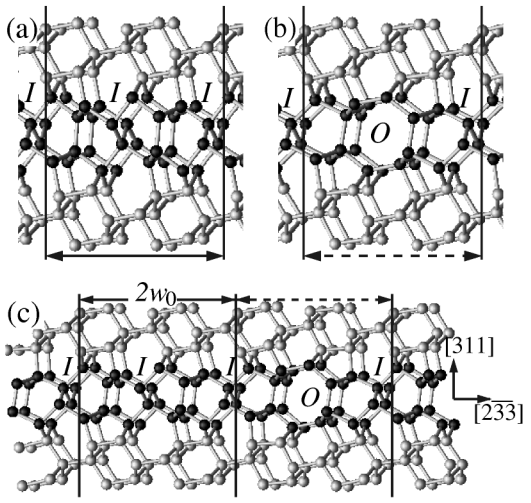

FIG. 1. Atomic configuration of planar {311} defects composed of I interstitial chains and O rows of 8-member rings: (a) $/II/$ (b) $/IO/$, and (c) $/IIIO/$ according to the convention in Ref. [5]. For the bulk lattice constant $a = 5.43$ Å, the unit length in the $[01\bar{1}]$ direction is $2l_0 = a/\sqrt{2}$ and that in the $[2\bar{3}\bar{3}]$ direction is $2w_0 = a\sqrt{11}/\sqrt{2}$. The unit cell of (c) $/IIIO/$ can be decomposed into II and IO as indicated by the arrows. We define M as the number of w_0 units n_c-interstitial chains occupy: (a) $M/n_c = 1$, (b) $M/n_c = 2$, and (c) $M/n_c = 4/3$.

increases as the size n increases. The formation energy per interstitial ranges from $E_f(n = 2) = 2.46$ eV for di-interstitials [14] to $E_f(\infty) = 0.7$ eV for rodlike {311} defects. Preferred elongation of rodlike defects in the [011] direction is predicted in accordance with experiments. We find that the stable configuration for a given size can be (a) *compact* for small clusters, (b) *elongated* for medium clusters, and (c) *planar* for large clusters.

Optimized initial guesses for the interstitial defects were obtained by extensive tight-binding molecular dynamics simulations using optimized parameters by Lenosky *et al.* [15]. The structures were further relaxed by conjugate gradient minimizations within first-principles LDA with a plane-wave energy cutoff of 140 eV. The convergence of the structural properties and formation energies with respect to the supercell size was monitored by large-supercell tight-binding total-energy calculations. The number of k points chosen was based on the dimension of the defects. For example, eight irreducible k points on a 2D grid are used for the planar $/IO/$ defect calculations, whereas four k points on a 1D grid are used for an isolated interstitial chain.

Rodlike {311} defects are *elongated planar defects*: the length in the [011] direction can reach a few μ, and the width in the [233] direction ranges 1–100 nm [4,5]. Atomistic simulations using classical potentials and tight-binding potentials [5,11] have shown that rodlike {311} defects can be modeled by coalescence of interstitial chains on the {311} plane. Figure 1 presents the atomic structure of the defect cores of three planar {311} defects projected on the {011} plane. The notations introduced by Takeda [5] are used to denote planar {311} defects: interstitial chains I and eight-member rings O. The minimum separation of two interstitial chains for stable {311} defects is $w_0 = a\sqrt{11}/(2\sqrt{2})$ for the bulk lattice constant $a = 5.43$ A.

A finite-size rodlike {311} defect containing n interstitials can be modeled as a collection of n_c-interstitial chains on the {311} plane. Each interstitial chain contains n/n_c interstitials. We simplify the model by ignoring roughness at the boundaries and assume a perfect rectangular shape for the defect. Then, the formation energy of a {311} defect can be expressed as

$$nE_f(n) = n_c E_f^{\text{end}} + n_c(n/n_c - 2)E_f^{\{311\}}(n_c), \qquad (1)$$

where E_f^{end} is the two-end formation energy for an interstitial chain and $E_f^{\{311\}}$ is the "average" formation energy per interstitial of a rodlike {311} defect. Note that $n/n_c - 2$ is the number of *inner* interstitials per chain and $E_f^{\{311\}}(n_c)$ depends on the number of interstitial chains n_c.

The two formation energies, E_f^{end} and $E_f^{\{311\}}$, are determined by calculations of constituting structures: (i) elongated n-interstitial clusters for $n = 3$–5, (ii) an isolated interstitial chain, and (iii) planar {311} defects.

Elongated interstitial clusters and an interstitial chain contain the same building blocks, namely, ⟨110⟩ dumbbells. Figure 2(a) shows the core structure of an elongated $n = 3$ interstitial cluster. Indeed, any finite-size elongated interstitial cluster can be viewed as a truncated interstitial chain with two ends [16]. Figure 3 shows the formation energies of such elongated clusters' monotonous decrease with an increasing number of interstitials. The formation energy of an elongated interstitial cluster converges to that of an infinite interstitial chain $E_f^c \equiv E_f^{\{311\}}(n_c = 1)$. Within first-principles LDA, $E_f^c = 1.02$ eV. We find that $E_f^{\text{end}} = 5.92$ eV gives a good fit to the formation energies for small elongated clusters. Considering only elongated interstitial clusters, we obtain a constant binding energy $E_b = -(E_f^c - E_f^{\langle 110\rangle}) = 2.45$ eV which corresponds to the energy required to release an interstitial from existing clusters.

Figure 1 presents the atomic structure of the defect cores of three planar {311} defects projected on the {011} plane. Within first-principles LDA, the formations energy per interstitial are (a) $E_f^{/II/} = 0.71$ eV, (b) $E_f^{/IO/} = 0.76$ eV, and (c) $E_f^{/IIIO/} = 0.55$ eV. These values are lower than that of an isolated interstitial chain, confirming the condensation of interstitial chains to form more stable {311} defects. Note that periodic boundary conditions were used in both [011] and $[2\bar{3}\bar{3}]$ directions. We characterize planar {311} defects by $\gamma = M/n_c$, the ratio of the number of sites M the chains can occupy to the number of interstitial chains. Typical {311} defects observed by high-resolution transmission electron microscopy contain random combinations of I's and O's with an average packing ratio $\bar{\gamma} = (M/n_c)_{\text{avg}} \sim 3/2$ [5]. Representing a planar {311} defect as a random collection of I's and O's at the average packing ratio $\gamma = \bar{\gamma}$ [17], we obtain $E_f^{\{311\}}(\infty) = 0.69$ eV, which is in good agreement with 0.8 eV formation energy of large interstitial clusters ($n > 100$) by Cowern *et al.* [9].

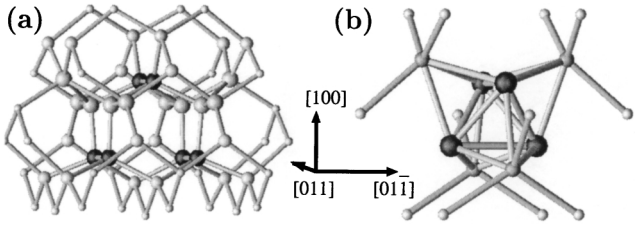

FIG. 2. Atomic structures of tri-interstitial clusters: (a) elongated configuration of C_{1h} symmetry and (b) compact configuration of D_{2d} symmetry. Both clusters contain dumbbell interstitials shown as solid black atoms as the building blocks. The elongated tri-interstitial cluster (a) contains three [011]-oriented dumbbells side by side in the $[01\bar{1}]$ direction. On the other hand, the compact tri-interstitial cluster (b) has two dumbbells having different orientations parallel to the [011] and $[01\bar{1}]$ directions.

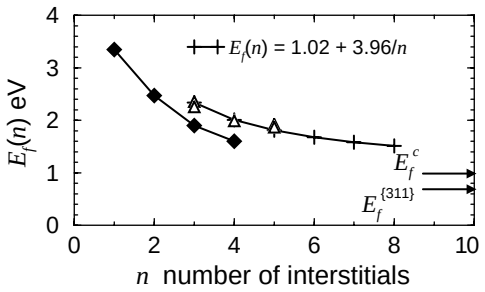

FIG. 3. Dependence of the interstitial-cluster formation energy (per interstitial) on the number of interstitials, n. The formation energy of an isolated interstitial $n = 1$ is 3.35 eV. The compact cluster (◆) is only initially more stable than the elongated (Δ) cluster; the odd-n elongated clusters have two nearly degenerate configurations. The trend equations (1) and (2) for $n_c = 1$ (+) show the growing stability of the elongated cluster for increasing number of interstitials. In particular, for "infinite" interstitial defects, the formation energies for the {311} and chain defects are 0.7 and 1.02 eV, respectively.

Finally, we construct the average formation energy per interstitial of a finite rodlike {311} defect with n_c interstitial chains as

$$E_f^{\{311\}}(n_c) = E_f^{\{311\}}(\infty) + [E_f^c - E_f^{\{311\}}(\infty)]/n_c\,. \quad (2)$$

This connects two limits, $n_c = 1$ for an isolated interstitial chain and $n_c = \infty$ for infinite planar {311} defects. Our previous TB calculations also found that the formation energy per interstitial decreases as more interstitial chains are added to an existing rodlike defect when the average packing ratio is close to $\bar{\gamma} \sim 3/2$ [11].

Figure 4 presents a stability diagram of planar {311} defects as a function of the total number of interstitials n and the number of interstitial chains n_c based on Eqs. (1) and (2). The energetics of interstitial defects favors the

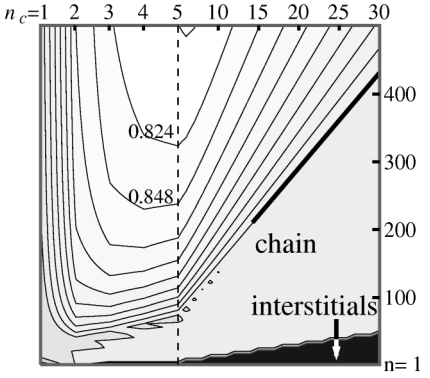

FIG. 4. Contour plot of formation energies $E_f(n)$ of rodlike {311} defects composed of n interstitials and n_c-interstitial chains. The formation energy per interstitial decreases as n increases, and n_c decreases for the same n. If $n_c > 0.07n$ for large n, rodlike defects are less stable than an isolated n-interstitial chain. The dark area denotes the rodlike {311} configurations whose binding energy is negative with respect to isolated interstitials, i.e., $E_f(n) > E_f^{\langle 110\rangle} = 3.35$ eV.

growth of larger and elongated {311} defects: Rodlike {311} defects become more stable (a) as n increases and (b) as n_c decreases. These trends are consistent with the elongated shapes of rodlike defects [4,5] which minimize the higher-energy cost of forming a (233) boundary. The thick line in Fig. 4 denotes the critical ratio $n_c/n \sim 0.07$ beyond which a finite-interstitial chain becomes more stable than quasi-two-dimensional {311} defects. The dark area denotes that rodlike or chain defects become unstable against *isolated* interstitials. We estimate that the *smallest* stable planar {311} defect contains about 40 interstitials and the width and length are $w \sim 3w_0 = 19$ Å and $l \sim 14l_0 = 27$ Å, respectively.

The general trend for large interstitial clusters does not apply to small interstitial clusters. Our formation energy of Eqs. (1) and (2) takes into account only a class of interstitial defects showing stability hierarchy from elongated clusters to chains and eventually to rodlike {311} defects. Indeed, we find that the ground stable configuration of small clusters of $n = 2$–4 is not the truncated interstitial chains. Figure 3 compares the formation energies of compact configurations shown as diamonds with those of elongated interstitial clusters. The compact tri-interstitial shown in Fig. 2(b) has 0.4 eV lower formation energy than the elongated tri-interstitial cluster in Fig. 2(a). As suggested by Arai *et al.* [10] and Cowern *et al.* [9], we cannot rule out the possibility that interstitial defects can contain such compact interstitial clusters. Our calculations, however, do not find larger interstitial defects derived from compact 4-interstitial clusters as a lower-energy configuration than elongated interstitial clusters. We have investigated an 8-interstitial cluster, composed of two compact 4-interstitial clusters, and found it to be less stable than the elongated interstitial cluster. Line and planar defects consisting of compact 4-interstitial clusters are less stable than {311} defects based on combinations of I's and O's as shown in Fig. 1. A combination of compact 4-interstitial clusters has the advantage of having all atoms fourfold coordinated. However, the density of interstitials is higher than that of interstitial defects composed of interstitial chains and ⟨110⟩ dumbbells. The most energetically favorable way of incorporating compact 4-interstitial clusters into rodlike {311} defects is at the defect boundaries in the [233] direction, since this configuration reduces the number of five-coordinated atoms.

Recently, Leung *et al.* compared the formation energies of isolated interstitials using different exchange-correlation potential [18]. We also find that the formation energy within generalized gradient approximation (GGA) [19] is higher than that within LDA for a given interstitial defect configuration [14,20]. However, the general trends in formation energies found in LDA persist in GGA [20].

In modeling the growth of interstitial defects, *capture radii* of interstitials for n-interstitial defects enter as important parameters [9]. The common assumption that the capture radius is proportional to the defect size n does not

reflect the anisotropy of the energy cost to add/subtract an interstitial. For rodlike {311} defects, capturing interstitials at the n_c chain ends, thus growing in the [011] direction, is energetically favorable over adding interstitials to form a new chain by an order of $\exp[(E_{\text{end}}/2 - E_f^{\{311\}})/k_BT]$. Therefore, the capture radius of interstitials for rodlike defects should reflect the defect shape, proportional to the number of interstitial chains n_c or to the width in the [233] direction.

The growth model of rodlike {311} defects has been related to the Ostwald ripening process [7–9]: during the thermal annealing, the average size increases, while the density decreases [2]. The energetics predicted by our calculations and models indicate that a rodlike {311} defect can grow when free interstitials are available, since incorporating supersaturated interstitials into the existing rodlike {311} defects, preferably in the [011] direction, always make the defects more stable. The kinetic aspects of the Ostwald ripening of interstitial clusters, such as the time evolution of the average size $\bar{n}$, however, call for macroscopic modeling based on the kinetic Monte Carlo method [8], using the trend in formation energies prescribed by Eqs. (1) and (2).

In conclusion, trends in formation energies of n-interstitial defects are proposed based on those of underlying structures—interstitial chains. Growth of larger and elongated rodlike {311} defects in the interstitial supersaturation condition is predicted based on the energetics. The stable configuration is found to be compact for small clusters, elongated for medium clusters, and planar for large clusters. The effective interstitial capture radius by interstitial defects should reflect the shape as well as the size for more accurate modeling of the interstitial defect growth and the roles interstitial defects play in transient enhanced diffusion.

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