Growth of Precursors in Silicon Using Pseudopotential Calculations

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(Received 25 April 2001; published 5 February 2002)

Based on the results of pseudopotential calculations, the progression of a single interstitial into small compact clusters and ultimately into chainlike defects is examined. For clusters that consist of more than eight interstitials, the capture of bond-centered interstitials reveals a change in the growth mechanism leading to enhanced stability of clusters. The five-interstitial model is proposed to be a plausible candidate for optically active *W* centers, observed in ion irradiated silicon.

DOI: 10.1103/PhysRevLett.88.085501 PACS numbers: 61.72.Bb

The necessity to study self-interstitials in silicon is dictated by both fundamental and technological importance. Self-interstitials released from extended defects cause an unacceptable increase in junction depth and the series resistance of the device through transient enhanced diffusion (TED). With constant miniaturization, it becomes essential to understand and model this phenomenon at an atomistic scale. The extended defects have been proposed to be {311} clusters, which consist of interstitials precipitating on {311} planes as a single monolayer of hexagonal silicon [1]. The growth of {311} clusters is preceded by a phase comprising submicroscopic defects (precursors), which are less stable but cause ultrafast *anomalous* diffusion [2]. At low doses and energies, small interstitial clusters are the only driving force of TED [2]. The accurate prediction of dopant profiles depends upon precise estimation of the binding energy of these clusters, as this determines the rate at which they are captured or released. However, the identification of these small interstitial defects using experimental techniques such as deep level transient spectroscopy (DLTS), electron paramagnetic resonance (EPR), and photoluminescence remains difficult. Such investigations primarily report the electronic and optical properties of the defects, although the geometry of actual configurations cannot be derived in detail. Hence the determination of structural composition of small precursor clusters often relies on theory.

In spite of significant effort, there is scarce information regarding the nature of precursor clusters in silicon. Kim *et al.* investigated trends in growth from elongated interstitial clusters to rodlike defects [3,4]. The elongated clusters were found to have a monotonic dependence of formation energy with size. Kim and coworkers also reported compact clusters up to size 3, with the di-interstitial model assigned to the EPR-active P6 center [3,4]. Colombo investigated compact self-interstitial clusters that comprise up to 11 interstitials using the tight-binding molecular dynamics (TBMD) method and found oscillating dependence of the formation energy with cluster size [5–7]. Of the structures proposed to date, the lowest formation energy of 1.5 eV/atom has been attributed to the I_4, a four-interstitial cluster proposed by Arai *et al.* [8,9]. The I_4, characterized by its fourfold coordination, bears no clear structural link with smaller sized tri- and di-interstitial models. Furthermore, the I_4 model is a "complete" structure, and cannot easily be extended further to permit capture of more interstitials without a significantly high cost in energy. In this work, we propose new models of compact self-interstitial clusters, which consist of up to 10 interstitials, using *ab initio* technique. Structural information is provided together with the extracted values of binding energy. A possible mechanism of transition from precursors to chainlike extended {311} defects is also described.

The calculations use the plane wave pseudopotential method based upon density functional theory [10], implemented in CASTEP code [11]. For exchange and correlation effects, the local density approximation is used [12]. The interaction between ions and valence electrons is described by the Kleinmann-Bylander nonlocal pseudopotentials generated by the Kerker method [13,14]. The supercells used are rhombohedral with cell dimensions 15.36 Å × 15.36 Å × 15.36 Å and cell angles 60°. Γ-point for Brillouin zone sampling with 140 eV cutoff energy is used for relaxation of the structures and thereafter four special k points with 280 eV cutoff energy for evaluation of formation energy [15,16]. An increase in cutoff energy during relaxation with Γ-point calculation to 280 eV is found to change the formation energy by 0.02 eV. However, for evaluation of formation energy using four special k points, if the cutoff is increased to 350 eV, the formation energy is found to monotonically reduce with increasing cluster size [17]. This yields an estimated error in the calculated binding energy of ± 0.1 eV. The atoms are relaxed under the influence of Hellmann-Feynman forces until their values fall below 0.04 eV/Å [18]. If these forces are calculated below 0.02 eV/Å, the energy changes by 0.02 eV.

For the sake of clarity, the clusters are designated as $J_n^{(m)}$ where n is the number of interstitials and m is the index of the cluster consisting of n interstitials. For brevity the cluster that consists of n interstitials is referred to as the cluster of size n, with a total formation energy given by

$$E_n^{\text{form}} = \left(E_{N+n} - \frac{N+n}{N} E_N \right) \quad (1)$$

where N is the number of atoms in the calculational

supercell, n is the number of interstitials, E_N and E_{N+n} are the total energies of perfect supercell and supercell with n interstitials, respectively. The formation energy per interstitial can be calculated simply as $E_n^{\text{int}} = E_{\text{int}}^{\text{form}}/n$. To gain sufficient insight into the energetics of cluster growth the binding energy is defined as

$$E_{\text{int}}^{\text{bind}} = (E_1^{\text{form}} + E_{n+1}^{\text{form}}) - E_n^{\text{form}}. \quad (2)$$

This definition corresponds to the energy gain when an extra interstitial is added to an existing cluster; an approach identical to that employed by Cowern *et al.* in [19,20].

Earlier reported configurations are analyzed to benchmark current calculations. The calculated formation energy of the ground state $\langle 110 \rangle$ interstitial is 3.38 eV in good agreement with reported values of 3.2 ± 0.1 eV [21] using *ab initio* technique. The total formation energy of the $J_2^{(1)}$ di-interstitial is 4.96 eV in comparison with the 4.92 eV calculated in [3], whereas that of the tri-interstitial is 6.01 eV also in agreement with the value of 5.92 eV reported in [4].

Larger models beyond size 3 are obtained by adding a $\langle 110 \rangle$ interstitial to a preexisting configuration. In our case, the larger clusters are obtained by "splitting" sites, adjacent to an existing cluster, until the number of atoms sharing the site reaches four. Such larger clusters can also be considered as the aggregation of single-, di-, and triatomic models with a maximum number of mutual bonds. In addition to the models obtained by adding one interstitial, configurations can be built from the smaller models by adding a di-interstitial $J_2^{(1)}$ as a whole. These structures are analyzed because they have equal or lower total formation energies than those obtained by adding one interstitial at a time.

The four-interstitial models can be formed either by aggregation of a $J_3^{(1)}$ and an interstitial [Fig. 1(a)] or by a combination of two di-interstitials $J_2^{(1)}$ [Fig. 1(b)]. The latter consists of six atoms that form the prism with two triangular bases [Fig. 1(b)] and possesses lower total formation energy of 8.24 eV than the model $J_4^{(1)}$ (8.83 eV). Five- and six-interstitial clusters, $J_5^{(1)}$ ($E_{\text{total}}^{\text{form}} = 10.04$ eV) and $J_6^{(1)}$ ($E_{\text{total}}^{\text{form}} = 12.00$ eV), are obtained by adding interstitials to four atomic models $J_4^{(1)}$ or $J_4^{(2)}$, forming single- and bicapped prisms (Figs. 1c and 1d). Models with three or less interstitials share one empty site of crystalline structure, whereas those between 4–6 interstitials share two adjacent sites. The model $J_5^{(1)}$ has two groups of atoms [indicated by arrows in Fig. 1(c)] in the {111} plane that form triangles close to equilateral.

The self-interstitial aggregate that consists of seven atoms in Fig. 1(e), $J_7^{(1)}$ ($E_{\text{total}}^{\text{form}} = 14.30$ eV), is constructed from model $J_6^{(1)}$ by capturing an interstitial. It is formed by a combination of two tri-interstitials and one split interstitial. Alternatively, an aggregation of one tri-interstitial and two di-interstitial clusters yields $J_7^{(2)}$, degenerate in energy with $J_7^{(1)}$ ($E_{\text{total}}^{\text{form}} = 14.33$ eV).

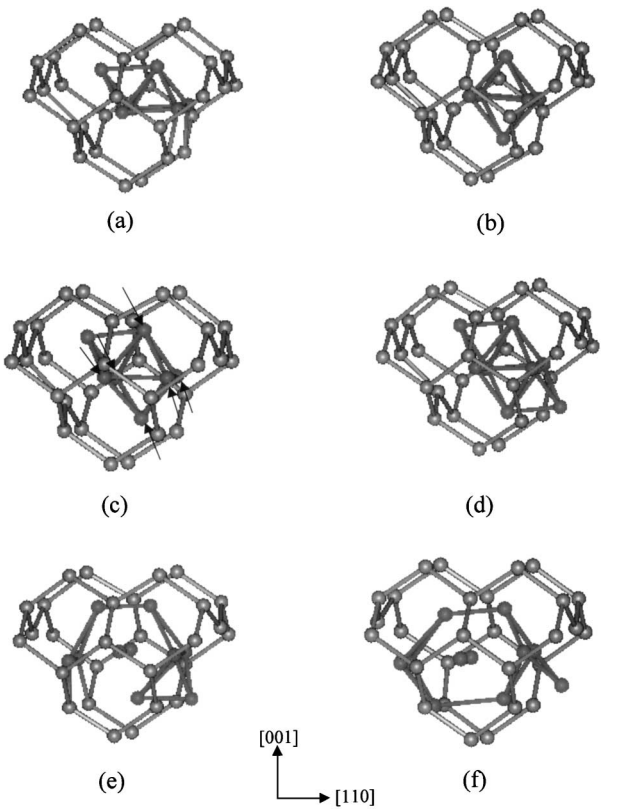

FIG. 1. The proposed models of clusters of sizes 4–8: (a) $J_4^{(1)}$, (b) $J_4^{(2)}$, (c) $J_5^{(1)}$, (d) $J_6^{(1)}$, (e) $J_7^{(1)}$, and (f) $J_8^{(1)}$. Not all the surrounding atoms of crystalline bulk are indicated in the figures. Atoms indicated by arrows in $J_5^{(1)}$ (c) form equilateral triangles in the {111} plane.

Model $J_8^{(1)}$ is obtained from either $J_7^{(1)}$ or $J_7^{(2)}$ by adding an interstitial [Fig. 1(f)] ($E_{\text{total}}^{\text{form}} = 15.92$ eV). The eight-atomic model has a lower formation energy per interstitial in comparison to seven- and nine-interstitial clusters because it is a combination of two tri-interstitials, which possess low formation energy and one di-interstitial. The di-interstitial within this group cannot be extended further into a tri-interstitial because the position of the atoms is such that the space occupied by these atoms does not occur at the substitutional site, as in the perfect structure. Thus, the $J_8^{(1)}$ cluster represents the structure with the highest density of atoms obtained by combining split interstitial sites. The nine-interstitial model $J_9^{(1)}$ ($E_{\text{total}}^{\text{form}} = 18.25$ eV) formed by adding a single interstitial to $J_8^{(1)}$ has a lower binding than $J_8^{(1)}$ because of the presence of this split interstitial. Deduction of cluster binding energies from interstitial supersaturation during TED has established the strong binding of the size 8 cluster in silicon [19,20]. This binding is found essential to match TED boron implant anneal between 600–800 °C [19,20]. This evidence has also been corroborated independently by Schiettekatte *et al.* in [22]. Obviously, the clusters can be grown beyond size 9 using the same methodology.

However, in this work constraints are imposed by the size of the supercell.

The electronic structure of the investigated configurations beyond size 2 reveals that groups of three atoms form triangles with a tricentered total charge density distribution. Specifically, in model $J_5^{(1)}$ the groups of atoms indicated by the arrows [Fig. 1(c)] form triangles close to equilateral in the {111} plane. The charge density contours in the plane of atoms occupying the base of cluster $J_5^{(1)}$ is depicted in Fig. 2(a). These triatomic rings and corresponding three-centered orbitals have been reported in amorphous carbon and have also been analyzed in boron clusters in crystalline silicon [23,24]. The model $J_5^{(1)}$ is featured by the defect localized state in the gap at $E_v + 0.25$ eV (where E_v is at the top level of the valence band calculated for perfect supercell). This gap state is particularly localized in the plane of atoms indicated by arrows [Fig. 1(c)], with a corresponding electronic distribution depicted in Fig. 2(b). These properties of $J_5^{(1)}$ make this model a possible candidate for optically active W centers, which possess the symmetry of the point group C_{3v} with symmetry axis along ⟨111⟩ direction [25]. An alternative tri-interstitial model, which comprises three bond-centered interstitials with fully saturated bonds, was recently proposed as the candidate for W center in silicon [26]. However, the formation energy of this model is higher by 1.5 eV than $J_3^{(1)}$ using the current method.

The calculated binding energies as a function of cluster size are presented in Fig. 3. The binding energy is found to oscillate with distinctive and reducing maximas at sizes 3, 5, and 8. The reduction in binding energy with size can possible be attributed to the predominance of cell size effects for the large clusters in these calculations. The extracted energy dependence from the cluster size differs from the tight binding studies reported by Colombo *et al.* [5–7]. Using Eq. (2) the binding energies of Colombo are found to alternate from maximum to minimum for odd and even numbered clusters beyond size 3. A comparison of our $J_5^{(1)}$ model and the five-interstitial structure discussed by Colombo [5–7] was carried out particularly because this structure was reported to be a transition point between compact and elongated clusters which form rodlike defects. However, Colombo's model was found to be 0.4 eV higher in energy than the $J_5^{(1)}$ structure.

The transformation from compact to chainlike defects is possible beyond size 8, when the capture of bond-centered interstitial becomes energetically favorable. In Fig. 4 model $J_9^{(2)}$ ($E_{\text{total}}^{\text{form}} = 18.10$ eV) incorporating a bond-centered interstitial with the eight-interstitial cluster is depicted. The atoms indicated by highlighted circles [Fig. 4(a)] form a rod, which after reorientation is similar to that in a {110} chain, which is the basic unit in large {311} defects. The total formation energy of this model is lower by 0.15 eV than the split-interstitial cluster $J_9^{(1)}$. Calculations also reveal that the addition of the second bond-centered interstitial, model $J_{10}^{(1)}$ ($E_{\text{total}}^{\text{form}} = 19.50$ eV) [Fig. 4(b)], is associated with an even higher binding energy of 1.97 eV, further reinforcing the possibility of chainlike defect nucleation. Cluster $J_{10}^{(1)}$ is a combination of the split interstitial cluster with the rhombus defect, earlier reported in [27]. This work indicates how high formation energies for initiating chainlike defects can be avoided.

To conclude, the growth mechanism of split-interstitial clusters evaluated using pseudopotential technique shows oscillatory behavior with progressive maximas at sizes 3, 5, and 8. Apart from the model I_4, the models possess lower formation energy than several other clusters known to date. The proposed model $J_5^{(1)}$ possesses symmetry properties of optically active W centers. Beyond size 8, the capture of bond-centered interstitials indicates how the initiation of chainlike defects present in {311} clusters becomes energetically favorable. The binding energies presented herein

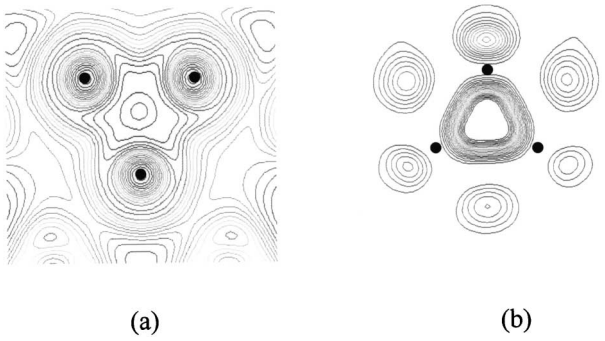

FIG. 2. (a) Valence charge density in {111} plane of atoms of five-interstitial model. The dark dots represent the atoms in the base of the single-capped prism [Fig. 1(c)]. (b) The charge density distribution of the defect localized gap state in the same {111} plane. Atoms are represented by dark dots.

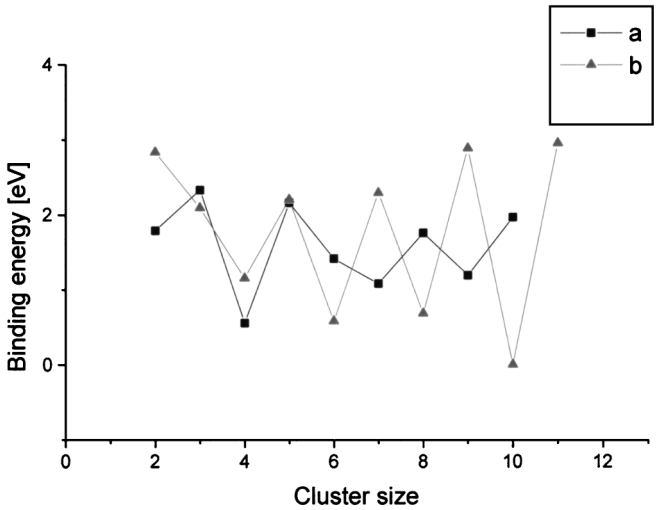

FIG. 3. (a) Binding energy of the clusters in the investigated sequence of self-interstitial models. (b) Binding energies from cluster size calculated using Eq. (2) based on the values reported by Colombo [5–7].

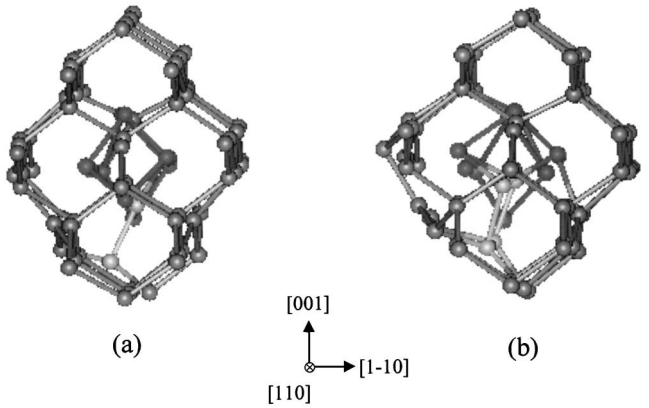

FIG. 4. Chain nucleation in the process of cluster growth. (a) Model $J_9^{(1)}$. Atoms indicated by light atoms form the rod in $\langle 110 \rangle$ channel of crystalline structure. (b) Model $J_{10}^{(1)}$ is formed from $J_8^{(1)}$ by adding two bond-centered interstitials.

can be incorporated into kinetic Monte Carlo/continuum modeling of annealing of ion-implanted boron in silicon.

The authors thank the U.K. Car-Parrinello consortium, Molecular Simulations Inc. and CLRC Daresbury Laboratory for their permission to use CASTEP code under the license agreement (CASTEP for academic institutions). We also thank Professor D. Oxley for his helpful criticisms of the manuscript.

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