Planar Self-Interstitial in Silicon

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(Received 22 March 1999)

The aim of this paper is to demonstrate, for the first time, the possible existence of planar point defect silicon self-interstitials in the {311} plane. The results offer a plausible explanation as to why self-interstitials aggregate to form {311} defect clusters during ion implantation. These interstitials do not leave any dangling bonds and can be considered to be "extended," due to spread out perturbations.

PACS numbers: 61.72.Ji, 61.72.Tt

Low energy implantation is one of the most promising options available today to realize shallow junctions less than 0.1 μm. However, it is well known that damage generated during ion implantation causes anomalous transient enhanced diffusion of dopant atoms (mainly boron) during annealing. It has become increasingly clear that future progress in very large scale integration scaling is critically dependent upon an atomic level understanding of the defects controlling this phenomenon. The primary influence of ion implantation on the boron diffusion is thought to occur via the interaction with silicon interstitials [1]. These interstitials are released from {311} defects, which are essentially large condensates of silicon interstitials with a {311} habit plane [2].

Historically, the nature of the single self-interstitial has aroused considerable interest and controversy due to its elusive nature [3]. More recently, theoretical calculations have revealed that the ground state of the silicon self-interstitial is the neutral $\langle 110\rangle$ split interstitial [4–7]. This configuration, which is strongly centered on the (110) plane was originally proposed by Bar-Yam and Joannopoulos [8]. The possibility of the split configuration as a ground state interstitial was first proposed by Schober [4] using the semiempirical Stillinger-Weber potential [9]. With a formation energy of approximately 3.3 eV, the defect has been found to "extend" over a large site with strong rebonding effects. The hexagonal site interstitial has also been found to have an almost identical energy of ~3.4 eV [6,7].

To date, atomic level models of {311} clusters, which are fitted to high-resolution transmission electron microscopy images of the defect [10–12], are based on the insertion of a pair of silicon interstitials in the center of the six-membered ring in silicon [13]. It is worth pointing out at this stage that the split $\langle 110\rangle$ interstitial shares its site with a substitutional atom and does not feature in the current atomic level {311} cluster models/images when viewed in any of the three relevant projections. Mechanisms are yet to be proposed to explain the transition from the split $\langle 110\rangle$ site to the center-of-the-ring configuration present in the clusters.

In this paper, for the first time, we propose a model of the silicon point defect interstitial with a relationship to the {311}/{332} crystallographic planes of silicon. This model finally explains the long-standing puzzle as to why these odd crystallographic planes feature in the defect studies of silicon, in comparison to other conventional planes. The proposed defects lie in the center of the six-membered ring and form the basic building block, which by capture of other interstitials can lead to the atomic level models of the {311} clusters. The results of [14], which indicate that *planar* atomic level models of {311} clusters have the lowest energy, further validates our observations, albeit at a point defect level. Furthermore, the planar point defect leaves no dangling bonds agreeing with the elusive nature of the silicon self-interstitial in the past [3,5]. In addition, the large number of configurations found, and their extended nature, also fits with the large self-entropy of self-diffusion in silicon [5].

In this paper, we present an empirical potential study of the self-interstitial point defect in silicon, which we refer to as the planar {311} interstitial. While it is well accepted that an "empirical" description of a point defect has limited quantitative accuracy in comparison to *ab initio* techniques, the empirical approach provides a useful insight into the nature of point defects. The Ackland potential [15] has been used in the present study, because of its unique bond-based nature and asymmetric bonding structures, which are otherwise not easily examined using conventional *ab initio* methods. Previous work using *ab initio* methods has focused only on point defects with site and configurational symmetry. A direct comparison with the structures proposed herein, to our knowledge, is yet to be demonstrated using current techniques. The total energy in the Ackland potential can be expressed as

$$E = \frac{1}{2}\sum_{i=1}^{N}\sum_{j=1}^{N} A e^{-\alpha r_{ij}} - \frac{1}{2}\sum_{i=1}^{N}\sum_{k=1}^{4} B r_{ik} e^{-\beta r_{ik}} + \sum_{i}\sum_{n=1}^{3}\sum_{m=n+1}^{4} C\left[\cos(\omega R_{k_m k_n}) + \frac{1}{3}\right]^2 .$$

The first term represents the repulsive pairwise interaction which each ion has with every other ion. The second term represents the sum over all valence electrons of the bond energy, with each ion bonded to four neighbors. The last term is essential to stabilize reconstructed defect formation energies. The form of this term is set such that the minimum of the energy should occur for the tetrahedral bond angle for the diamond structure in silicon. The C value can be changed to yield different quantitative values of formation energies. In the current study, the value of C was 1.2.

Our Monte Carlo simulations were performed at 300 K using a $4 \times 4 \times 4$ computational cell with a total of 512 atoms. Periodic boundary conditions were employed in a constant NVT (number of particles, volume, and temperature) ensemble. Energy minimizations were performed using the Metropolis Monte Carlo algorithm with multiple moves. Accumulated averages for every 5000 moves were taken, after an initial period of 35 000 moves for equilibration. A total of 125 000 events were considered for each of the simulations. The bonding configurations were fixed at the beginning, with regular tetrahedral or hexagonal site positions for the interstitial. In the following, $T1$ represents the center of the cell tetrahedral site, whereas $T2$ represents a covalent tetrahedral site. H represents a starting hexagonal position.

In total, about 50 bonding configurations with no dangling bonds were examined in detail. Based on their formation energies after relaxation, these could be divided into the following categories: (a) Formation energies of 3.1–3.3 eV (10 out of 50). (b) Formation energies of 3.6–3.9 eV (20 out of 50). (c) Formation energies >4 eV (20 out of 50).

The defects in (a) were found to be near planar, with the interstitial along with the neighbors relaxing in the {311} family of planes. In our simulations one of the atoms was found slightly away from the plane by about 0.5 a.u. The average distance of all five atoms from the plane was 0.27 a.u. In addition, three of the configurations, with starting positions $T2$, were also found with the interstitial and its neighbors in the (332) plane. The average nearest neighbor distance between the interstitial and all its neighbors was reduced to a single bond length. The interstitials, which form seven-membered rings, were spread out and caused distortions beyond third neighbor distance. In Fig. 1, the relaxed structure of an interstitial in the $(\bar{3}\,\bar{1}1)$ plane is shown. The bonding configuration of this defect has been described earlier by us as a minimum energy tetrahedral site configuration in Ref. [16]. However, the relationship of this configuration with the $(\bar{3}\,\bar{1}1)$ plane is reported here for the first time. One of the {311} configurations investigated was such that the interstitial motion was always along the ⟨111⟩ direction. Interestingly, no configuration was found to lie in the {110} or the {111} planes.

The relaxation plane for interstitials in category (b) appears to be overwhelmingly (233) for the cases studied, but definitely not the {311} or the (332). It was found that if the starting site was changed from T1 it was possible for the relaxation plane to change to {311} *even though the bonding configuration was the same.* In such a case, we repeatedly found that if the relaxation plane was {311} the formation energy was 3.3 eV, whereas for the (233) plane it was 3.7 eV. This difference in energy was also found to be the same even for simulation cells of size $3 \times 3 \times 3$ and $5 \times 5 \times 5$ where the defect could be introduced at the center. We believe the experimental evidence of predominant {311} habit planes in clusters further confirms that {311} and the (233) planes have dissimilar energies [1,2,10,12,14]. This result also provides a possibility of migration from a {311} to a (233) plane without any change of bonds.

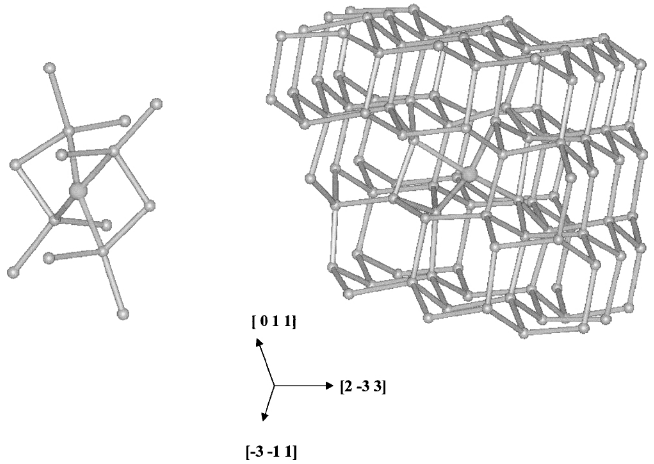

FIG. 1. Planar interstitial relaxed in the $(-3\ -1\,1)$ plane. The inset shows a closeup view of the interstitial, rotated to indicate its planar nature.

The third category of interstitials was found to be nonplanar, with a strong tendency towards tetrahedral bond angles and nonsymmetric rings as shown in Fig. 2. The formation energies of these interstitials was 4–5 eV.

Besides the nonplanar structures, a number of split ⟨110⟩ configurations were also examined. The formation energies were all found to be higher than 4 eV. One such split interstitial configuration with no dangling bonds is shown in Fig. 3. This structure is aligned in the $[1\bar{1}0]$ direction. Both atoms lie slightly displaced in the

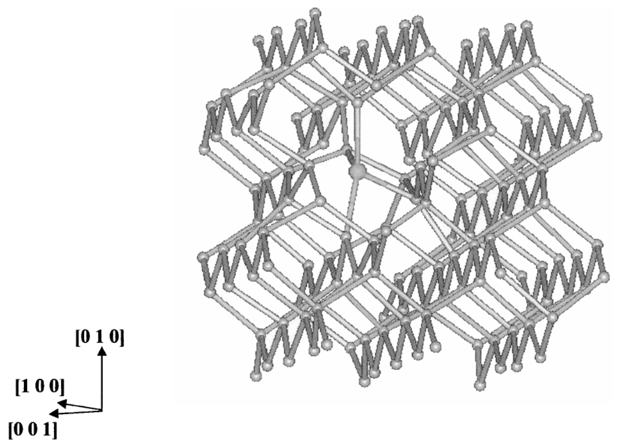

FIG. 2. A nonplanar interstitial with formation energy 4.6 eV.

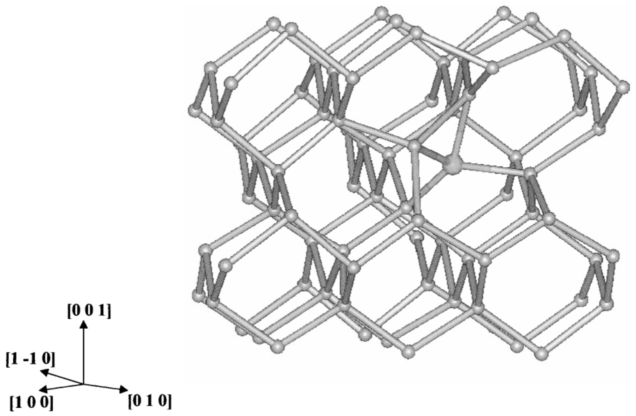

FIG. 3. A split interstitial aligned in the $[1\ -1\,0]$ direction.

z direction, with one atom above and one below the xy plane. The formation energy of this interstitial was found to be 4.4 eV. Another similar configuration in the [110] direction with both atoms lying slightly below the xy plane as in Ref. [6] was found to have a formation energy of 4.6 eV. It is possible to minimize the formation energy for the split interstitials to about 3.3 eV by changing the value of C. However, in such a case, the formation energy of our interstitials is far lower. A split interstitial in the $\langle 001 \rangle$ direction with two dangling bonds [16], one on each atom, has a formation energy of 4.4 eV.

In the current exercise, not every possible bonding configuration has been attempted because symmetry considerations can lead to several configurations with similar low energy. This study points to the possibility that the self-interstitial may exist in a large number of configurations, and have migration paths from one $\{311\}$ plane to another via intermediate $\{332\}$ planes or even tetrahedrally bonded/split $\langle 110 \rangle$ configurations at high temperatures. It is interesting to observe that the planar structures yield lowest energy even though the form of the potential is such that the minimum of the energy occurs for the tetrahedral bond angle. From theoretical considerations it can be shown that only planar defects, in comparison to tetrahedrally bonded defects, have molecular orbitals that match most closely with those of disturbed tetrahedral sites (which are neighbors of the interstitial atoms).

Conventionally, the procedure to minimize dangling bonds in interstitial chains along $\langle 110 \rangle$ is to insert two interstitials in the center of the six-membered ring [13]. However, the current study also presents a number of interesting possibilities to build chains in the $\langle 110 \rangle$ direction. The propagation of such interstitial chains using the current interstitials need not involve "cooperative atomic" processes [11,14,17], which require the simultaneous motion of more than one atom at a time. Further, the (332) interstitials could possibly explain features such as steps and diffuse streaks observed in $\{311\}$ clusters [11].

The possibility of a large number of configurations for the self-interstitial combined with the perturbations extending over several sites can explain the puzzle regarding the high entropy of self-diffusion in silicon of approximately $9k_B$. Previous calculations of the split $\langle 110 \rangle$ interstitial, with its extended perturbations, also yielded a similar entropy value [5].

To conclude, a planar self-interstitial defect in silicon has been presented in this Letter. For minimum energy configurations, the defect and the four neighbors to which it is bonded are found to lie predominantly in the $\{311\}$ planes. A configuration which tries to attain tetrahedral bonding, on the other hand, yields a far higher formation energy for the same value of C. Using the Ackland potential, an interstitial which is split in the [110] direction is found to have a higher formation energy by 1 eV. The interstitials proposed herein can give a plausible reason for the formation of $\{311\}$ clusters which are widely observed during ion implantation in silicon.

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