Thermally activated reorientation of di-interstitial defects in silicon

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Abstract

We propose a di-interstitial model for the P6 center commonly observed in ion implanted silicon. The di-interstitial structure and transition paths between different defect orientations can explain the thermally activated transition of the P6 center from low-temperature \( C_{1h} \) to room-temperature \( D_{2d} \) symmetry. The activation energy for the defect reorientation determined by \( ab\ initio \) calculations is 0.5 eV in agreement with the experiment. Our di-interstitial model establishes a link between point defects and extended defects, di-interstitials providing the nuclei for the growth.
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Transient enhanced diffusion (TED) in boron-implanted silicon is the limiting factor in controlling dopant profiles for submicron Si-based devices. Interstitial defects in bulk Si generated during implantation have been identified as the sources for boron TED [1–3]. A class of macroscopical interstitial defects, namely \{311\} defects, was suggested to emit interstitials that can contribute to the enhancement of boron diffusion under typical implantation conditions [1,2]. Decreasing the ion implantation energy can suppress the formation of macroscopic \{311\} defects, thus reducing boron TED. However, boron TED exists even at very low implantation energy (below 10 keV) in samples with no visible \{311\} defects [3]. This implies that microscopic interstitial defects, e.g., interstitial clusters, contribute to boron TED.

The activation energy of boron TED, a measure of the energy required to dissociate interstitials from the interstitial complexes, is lower in samples without visible \{311\} defects. Interstitial clusters can become important sources for boron TED at low temperature at which the extended \{311\} defects are still stable against dissociation. Several defect states have been associated with interstitial clusters [1–3]. One of them is the P6 center commonly observed by electron paramagnetic resonance (EPR) measurements in low-energy ion-implanted, proton- or neutron-irradiated silicon [4,5]. The P6 center has \{100\} symmetry, distinct from the typical \{110\} symmetry of vacancy-related defects. At low temperature (200 K), the symmetry of the P6 center is either \(C_2\) or \(C_{1h}\) with a twofold axis parallel to the \(\langle 100 \rangle\) direction. A thermally-activated symmetry transition occurs at room temperature (300 K) and the symmetry of the P6 center becomes \(D_{2d}\) [7]. Motional averaging effects have been suggested to cause the transition [4,5]. Complementary measurements of the \(^{29}\)Si hyperfine structure and the stress alignment indicate that the P6 center arises from \textit{di-interstitial} defects. The stable di-interstitial is an important “precursor” of interstitial clusters and more extended defects such as \{311\} defects. Yet, the structure and dynamics of the di-interstitial have not been fully understood at an atomic scale and no first-principle calculations are available to our knowledge.

In this letter, we propose a microscopic structure of a \textit{di-interstitial} whose low-
The atomic and electronic structure of di-interstitial defects are determined by ab initio total energy calculations within the local density approximation (LDA) and generalized gradient approximation (GGA) \[8,9\]. The local minimum and metastable structures are obtained by structural minimizations using the conjugate gradient method. Starting geometries are stable configurations obtained by molecular dynamics simulations and structural relaxations using tight-binding Hamiltonians \[10–12\]. In the ab initio calculations, the structural minimizations employ two supercell sizes: (i) supercell A consisting of 120 atoms and (ii) supercell B consisting of 72 atoms. The total energy and structure are well converged with the plane-wave energy cutoff of 140 eV and \(4k\)-points in supercell A \[13\].

Figure 1(a) shows our di-interstitial model of \(C_{1h}\) symmetry, with the twofold axis parallel to the z axis \[7\]. The basic constituents of the model are a center atom \(I_0\) and dumbbell atoms \(I_1-I_2\). Lee recently proposed a di-interstitial model composed of the same building blocks \[5,14\]. Our model differs from Lee’s model in (i) the orientation of the dumbbell atoms and (ii) the location of the center atom. The dumbbell structure, aligned parallel to the \([110]\) direction, resembles the \(\langle 110 \rangle\) interstitialcy, the most stable point defect \[15\]. Our suggestion that the di-interstitial can be formed when an interstitial is captured by the \(\langle 110 \rangle\) interstitialcy is supported by the positive binding energy of the \(C_{1h}\) di-interstitial with respect to isolated interstitials (Table I).

Four equivalent \(C_{1h}\) di-interstitial configurations, distinguished by the location of the center atom, can be constructed with three interstitials sharing one regular lattice site denoted as \(o\) in Fig. 2(a). The low temperature symmetry containing a twofold symmetry axis
parallel to (100) is consistent with the $C_{1h}$ symmetry of our model \cite{4,5}. Figure 2(b) illustrates the four equivalent sites under $D_{2d}$ symmetry which the center atom can occupy \cite{4}. Thermal averaging motions among four $C_{1h}$ configurations with a small activation energy barrier can result in the room temperature $D_{2d}$ symmetry.

Indeed, we can identify transition paths that lead to the thermal averaging motion between four local minima. Three transitions – denoted as $T_i$, $i = x, y, z$, according to the twofold symmetry axis of its saddle point – have the same energy barrier of 0.5 eV.

\textbf{$T_z$ transition:} The transition from the center atomic site $I_0$ to its mirror image $\otimes$, \textit{cf}, Fig. 1(a), with respect to the $\{\bar{1}10\}$ plane can occur by a displacement of the atom $I_0$ along the [110] direction. The saddle point of the $T_z$ transition has $C_{2v}$ symmetry with a symmetry axis along $z$. The orientation of the dumbbell atoms remains the same after the $T_z$ transition.

\textbf{$T_x$ transition (Fig. 1(b))}: A displacement of $I_1$ along the [101] direction results in a $I_0$-$I_1$ dumbbell pair and the atom $I_2$ becomes the center atom denoted as $I_0^*$. The symmetry axis of the saddle point ($C_{2v}$ in Fig. 1(b)) is parallel to the [100] direction. The $T_y$ transition is similar to the $T_x$ transition, $I_2$ moving along the [011] direction. As the result of the $T_x$ and $T_y$ transitions, the orientation of the dumbbell atoms changes from the [110] direction to the $\bar{1}10$ direction.

The room temperature $D_{2d}$ symmetry can be explained by the thermal averaging motion of three interstitials $I_0, I_1$ and $I_2$ alternatively occupying the four center atomic sites (Fig. 2(b)). Note that the $T_i$ transitions leading to the thermal motional averaging of the $D_{2d}$ symmetry involve a displacement of only one of three interstitials along a $C_{2v}$ saddle point at each transition. The schematics of the potential surface along the high symmetry path is presented in Fig. 3. No other local minima are found along the path $C_{1h} - C_{2v} - C_{1h}$.

The experimental $D_{2d}$ symmetry is very plausible within our model, since the low transition energy barrier of 0.5 eV permits frequent $T_x, T_y$ and $T_z$ transitions to motionally average the four $C_{1h}$ configurations accessible to three interstitials.
Structure and energetics of di-interstitial. Table I shows the formation energies $E_f$ and binding energies $E_b$ of the $C_{1h}$ di-interstitial, the metastable $C_{2v}$ di-interstitial and the $\langle 110 \rangle$ interstitial. Our LDA formation energy of the $\langle 110 \rangle$ interstitial agrees with that obtained by a previous LDA calculation \[15\]. In general, the bond lengths involved with the defect core atoms $I_0, I_1$ and $I_2$ are slightly longer than the bulk bond length of 2.35 Å. Charge density analyses confirm that the defect bonds are indeed weaker than the ideal bulk bonds. The strongest bond for both $C_{1h}$ and $C_{2v}$ di-interstitials is formed between the dumbbell atoms $I_1$ and $I_2$.

Supercell B composed of 72 atoms is not large enough to quantitatively describe the energetics and structural properties of the $C_{1h}$ and $C_{2v}$ di-interstitials. We find a reduction in the transition energy barrier $\Delta$ from 0.6 (supercell B) to 0.5 eV (supercell A) due to the relaxation of the third- and fourth-neighbor-shell atoms from the defect core. The bond lengths associated with the defect core can differ by as much as 0.3 Å between supercells A and B. The structural properties of supercell B are qualitatively different from those obtained by supercell A \[16\]. However, supercell A is sufficiently large for the converged energetics and structural properties \[13,17\].

We find large discrepancies between LDA and GGA in the formation $E_f$ and binding energies $E_b$, obtained by supercell calculations with different number of atoms. This is attributed to the larger bulk cohesive energy of GGA compared to LDA. On the other hand, the relative stability of the $C_{1h}$ and $C_{2v}$ di-interstitials indicated by $\Delta$ and structural properties are insensitive to the choice of the exchange-correlation potential $V_{xc}$. The formation energy differences between supercells A and B are of the order of 0.1 eV within LDA. Similar differences are obtained with GGA. The dynamical process for the symmetry transition schematically shown in Fig. 3 is not influenced by $V_{xc}$. Typical differences between LDA and GGA results are less than 0.005 Å in bond lengths and less than 0.5° in bond angles for the same supercell size.

Electronic structure of di-interstitial. The experimental analysis of the EPR signal of the positively charged P6 center indicates that the donor level is strongly localized on the center
atom [3]. Figure 4 shows that the defect gap states of the $C_{1h}$ di-interstitial are strongly localized. The donor level has strong $p$-character mostly localized on the atom $I_0$, while the acceptor level is mainly localized on the dumbbell atoms $I_1-I_2$. The donor level of the $C_{1h}$ di-interstitial is located at $E_v + 0.1$ eV and the acceptor level at $E_c - 0.2$ eV.

For the metastable $C_{2v}$ di-interstitial, the donor and acceptor levels become almost degenerate and form a deep level at $E_v + 0.4$ eV. The metastable $C_{2v}$ di-interstitial becomes a stable defect when it is positively charged. The dashed line in Fig. 3 presents a schematic potential surface along the high symmetry path. Self-consistent calculations give a smaller energy difference of 0.14 eV between $C_{1h}^{++}$ and $C_{2v}^{++}$ configurations. Our calculations on neutral and doubly-charged di-interstitials further support the effective $D_{2d}$ symmetry of the P6 center even at room temperature.

**Link to extended defects.** The stable di-interstitial is the link between point defects and extended defects. The dumbbell atoms of the di-interstitial are reminiscent of the $\langle 110 \rangle$ interstitialcy, suggesting the di-interstitial is formed by an existing $\langle 110 \rangle$ interstitialcy capturing an interstitial. Previously, we found a stability hierarchy of interstitial defects from molecular dynamics simulations with a tight-binding Hamiltonian [10]: the formation energy decreases in the order of interstitial clusters $\rightarrow$ interstitial chains $\rightarrow$ $\{311\}$ defects. A strong tendency of clustering of interstitials has been also predicted from classical molecular dynamics simulations [18]. When the interstitials are saturated such as in ion-implanted samples, the di-interstitials can play the role of nuclei for the extended interstitial defects, initially by providing interstitial sinks to form elongated interstitial clusters and eventually interstitial chains. We note that di-interstitials, larger interstitial clusters, and interstitial chains are composed of a common building block, the $\langle 110 \rangle$ interstitialcy [10]. The aggregation of interstitial chains, in turn, can lead to the formation of extended $\{311\}$ defects.

In conclusion, we present first-principle calculations for structural and electronic properties of di-interstitial defects and relate our stable di-interstitial structure to the P6 center. The $C_{1h}$ di-interstitial model and the transition paths involving the metastable $C_{2v}$ di-interstitial can account for different symmetries of the P6 center both at low and room
temperature. The activation energy of the defect reorientation is 0.5 eV in excellent agreement with experiments. The localization of the donor level also agrees with the experimental characterization.

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[13] We checked the convergence by increasing the number of k-points to 32 and the plane wave energy cutoff to 200 eV for the 72-atom supercell. The formation energy of the ⟨110⟩ interstitialcy changes by 60 meV and the relaxed structure is indistinguishable from calculations using 4 k-points and 140 eV. The energy difference between the $C_{1h}$ and $C_{2v}$ di-interstitials is converged within few meV. The structural properties and relative energetics are well converged for supercell A calculations, confirmed by the less than 10 meV difference in the formation energies between 300- and 120-atom supercell calculations using a TB Hamiltonian of Ref. [12].

[14] We find the di-interstitial model proposed by Lee [5] is unstable. The local minimum structure obtained by the conjugate gradient minimization under $C_2$ symmetry constraints has a binding energy of 0.1 eV, much smaller than 1.8 eV of the $C_{1h}$ di-interstitial.

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[16] The dumbbell atoms in supercell B are pushed toward the atoms $b$ and $b^*$ making long bonds ($\sim 2.6\AA$) with the next-nearest-neighbor shell atoms.

[17] We find that the tight-binding Hamiltonian by Lenosky et al. [12] describes the structures and relative energetics of the di-interstitials and the ⟨110⟩ interstitialcy quantitatively well compared to ab initio calculations.

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TABLE I. Di-interstitial (DI) formation energies $E_f$ and binding energies $E_b$. The binding energy is defined as $E_b = -(E_f - 2E_f(I))$, where $E_f(I)$ is the formation energy of an isolated $\langle 110 \rangle$Interstitialcy. Supercell A consists of 120 bulk atoms, while supercell B consists of 72 bulk atoms. The orientation of the super cells is $[110] \times [\bar{1}10] \times [001]$. The energy barrier $\Delta$ is the total energy difference between $C_{1h}$ and $C_{2v}$ di-interstitials for the same supercell.

|          | Supercell A |            | Supercell B |            |
|----------|-------------|------------|-------------|------------|
|          | LDA         | GGA        | LDA         | GGA        |
| $C_{1h}$ DI | $E_f$      | 4.93 6.01 | 4.92 6.03   |
|          | $E_b$       | 1.78 1.86 | 2.02 2.10   |
| $C_{2v}$ DI | $E_f$      | 5.40 6.51 | 5.48 6.60   |
|          | $E_b$       | 1.30 1.36 | 1.46 1.53   |
|          | $\Delta$   | 0.47 0.50 | 0.55 0.57   |
| $\langle 110 \rangle$ I | $E_f(I)$ | 3.35 3.93 | 3.47 4.07   |
FIGURES

FIG. 1. (a) Atomic structure of a $C_{1h}$ di-interstitial projected on the $\{\bar{1}10\}$ and $\{110\}$ planes and (b) atomic structures of the di-interstitial core during a transition between two $C_{1h}$ configurations. A regular lattice site located at the origin of the axes is shared by three atoms – (i) the center atom $I_0$ and (ii) the $(110)$ dumbbell atoms $I_1$-$I_2$. The site $\times$ is related to the site $I_0$ via a mirror reflection across the $\{\bar{1}10\}$ plane. Three transition paths $T_x$, $T_y$ and $T_z$ with the same energy barrier of 0.5 eV are identified. The $C_{2v}$ symmetry of the saddle point has a twofold axis parallel to the subscript of the transition $T_i$, $i = x, y, z$. For example, the transition $T_x$ in (b) displaces the center atom $I_0$ to $I_0^*$ site and the twofold axis of the saddle point in the middle is parallel to the $[100]$ direction.

FIG. 2. (a) Atomic structure of a $C_{1h}$ interstitial and (b) schematics representing the four equivalent sites of the center atom $I_0$ under $D_{2d}$ symmetry operations. The regular site indicated by $\circ$ is shared by three interstitials $I_0$, $I_1$ and $I_2$. The atomic indices are assigned based on the distance from the origin and the symmetry to aid visualization. The experimental $D_{2d}$ symmetry of the di-interstitial at room temperature can be explained by the thermal averaging motion of $I_0$, $I_1$ and $I_2$ alternatively occupying four equivalent sites. As the result of a $T_i$ transition, the center atom $I_0$ “effectively” moves to the corresponding site as indicated by the arrows. Note that black atoms lie below the grey atoms along $z$ axis.

FIG. 3. Schematic potential surfaces along the highly symmetric path of $C_{1h} - C_{2v} - C_{1h}$ transitions for the neutral state (solid line) and for the positively charged state (dashed lines) at a given chemical potential $\mu$. The neutral $C_{2v}$ di-interstitial is metastable and the energy barrier $\Delta$ is 0.5 eV. In contrast, the positively charged $C_{2v}$ di-interstitial is stable and the energy difference $\delta$ between $C_{1h}$ and $C_{2v}$ di-interstitials is only 0.14 eV.
FIG. 4. (a) Isosurfaces of gap state amplitudes of the $C_{1h}$ di-interstitial, (b) local density of states (LDOS) on the center atom $I_0$ (solid line) and the dumbbell atoms $I_1$-$I_2$ (dashed line) of the $C_{1h}$ di-interstitial and (c) those of the $C_{2v}$ di-interstitial. The reference energy of (b) and (c) is $E_v$, the valence band maximum of bulk silicon in the 120-atom supercell A. The calculated bulk conduction band minimum, $E_c$, is indicated by an arrow and is about 0.8 eV from $E_v$. The energy gap of the $C_{1h}$ di-interstitial is about 0.5 eV, while the donor and acceptor levels of the $C_{2v}$ di-interstitial are almost degenerate. LDOS of the gap states is highlighted by the black (gray) areas for the donor (acceptor) level.
Kim et al., Fig. 1
Kim et al., Fig. 2
Kim et al., Fig. 3
(a) Donor

(b) $C_{1h}$

(c) $C_{2v}$

Energy (eV)

Donor Acceptor

$D$, $A$

$E_v$, $E_c$

$I_0$, $I_1-I_2$

Kim et al., Fig. 4