Self-Interstitial Clustering in Crystalline Silicon

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We have proposed a novel model of a self-interstitial defect in crystalline Si. It contains four Si interstitials and has the structural features as follows: All silicon atoms are four coordinated, in contrast to previously proposed models; the defect is characterized by five-, six-, and seven-membered atomic rings. The total energy, the relaxed atomic configuration, and the electronic structure of the defect have been determined using the transferable semiempirical tight binding method. [S0031-9007(97)03265-1]

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It is well established that self-interstitial atoms play an important role in various dynamic phenomena in Si crystal such as self-diffusion [1] and impurity diffusion [2]. The existence of self-interstitial atoms, however, has experimentally been confirmed only when they form very extended clusters. This implies that self-interstitial atoms and their complexes give rise to neither active energy levels inside the band gap nor optical centers. Furthermore, in contrast to lattice vacancies and their complexes [3], electron paramagnetic resonance has yielded no convincing structural information about defects of self-interstitial atoms even at low temperature. Therefore the structures of the primary point defects have always been under debate despite their practical and fundamental importance.

A number of atomic configuration models have been proposed about a self-interstitial in Si [4,5]: split ⟨100⟩, tetrahedral, octahedral, bond-centered, hexagonal configurations, and extended configurations [6,7]. Some models of self-interstitial clusters have also been proposed [5]. In all the models, self-interstitials leave unsaturated bonds of apparently higher energy except the model by Jackson [7]. The bonds in this model are, however, distorted unrealistically. On the other hand, the structures of extended clusters, containing more than hundreds of self-interstitials, have been analyzed in detail [8,9]. From these studies about stable extended clusters, a consensus has already emerged that lattice reconstruction occurs in the interior of Si crystal involving interstitials so as to remove dangling bonds. These extended agglomerates, which may not exist at the thermodynamical equilibrium, are definitely involved in various dynamic phenomena related to interstitials, as recently illustrated in Ref. [2]. However, the lack of information about the structure of self-interstitials and the interstitial clusters of intermediate size prevents us from understanding the phenomena at the atomic level. In this Letter, we propose a fully reconstructed cluster model of four self-interstitials and show that it possesses reasonably low energy.

We show that four self-interstitials can be inserted in Si crystal with the four-bond requirement maintained. The atomic configuration shown in Fig. 1 constitutes the cluster and its interface with perfect crystal. The cluster is characterized by successive five- and seven-membered atom rings. The seven-membered rings appear when the structure is embedded in crystal. As shown later, the electronic calculation shows that neither three-coordinated atoms with dangling bonds nor five-coordinated atoms with floating bonds exist.

For computing the electronic structure, a super cell which consists of 720 Si atoms is assumed. Four additional Si atoms are then inserted in the center of the supercell, giving rise to the structure shown in Fig. 1. Since the cluster model is fully bonded, we should estimate not only the energy increase at the core of the cluster but also

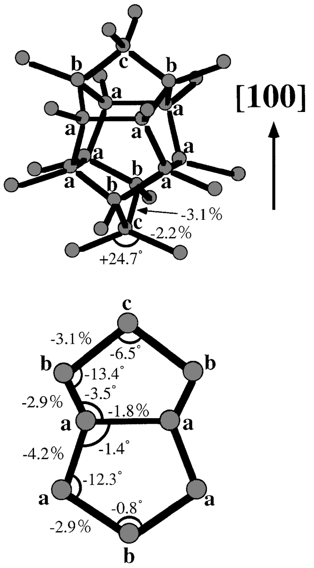

FIG. 1. Top: Relaxed configuration of the four interstitial cluster I_4 in Si. The cluster is clearly seen since the perfect crystal around it is removed. Bottom: A part of the cluster. Equivalent atoms are designated by the same characters.

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elastic energy. We expect that the large supercell, containing a total of 724 Si atoms, is large enough to obtain full lattice relaxation in the perfect crystal near the cluster, thereby evaluating the elastic energy. The lattice constant of the supercell is determined, prior to electronic calculation, by energy-minimization calculations using the Stillinger-Weber (SW) potential [10]: Edge lengths of the cell are 2.30 nm along the $[011]$ and $[0\bar{1}1]$ directions, and 2.73 nm along the $[100]$ direction. The cell expands slightly in the $[100]$ direction by 0.03 nm.

The relaxed structure is obtained by minimizing the total energy of the cell using the transferable semiempirical tight binding (SETB) method [11,12] with the valence atomic-orbital basis. The method is adopted to the situation better than the more accurate first principle methods, by which it is difficult to handle the large supercell. Furthermore it is noted that the SETB method and the related method yield the quantitatively similar results of total energies as those obtained by first principle computations in a grain boundary in Si, which has a similar structural character as the cluster, and isolated interstitial in Si as discussed in Refs. [13] and [14]. The total energy is a sum of the band-structure energy E_{bs} and the repulsive energy E_{rep}. E_{rep} is expressed as a sum of the short-range interatomic repulsive potentials. We take the energy at the Γ point in the Brillouin zone as E_{bs}, since the supercell is sufficiently large. It is known [11] that the transferable SETB method reproduces energies of variously coordinated structures of Si better than the usual SETB method, since the short-range interatomic repulsive potentials are properly corrected in terms of the effective coordination numbers of atoms. For self-consistency, an on-site electron repulsion term is included through the form of a Hubbard-like Hamiltonian with the value of U [15].

Table I summarizes the computed energies and bond distortions of the interstitial cluster. The energy increase per self-interstitial of the cluster is estimated to be 2.46 eV. This value is much less than that estimated for an isolated self-interstitial, that is, in the range from about 3 to 7 eV, depending on the assumed interstitial sites such as the split $\langle 100 \rangle$, or tetrahedral sites and the method of computation such as SW potential [16], the tight binding [17] and *ab initio* [18] calculation. The distortions of bond length and angle against those of perfect crystal, Δr and $\Delta\theta$ are relatively small: $-4.2\% < \Delta r < +1.3\%$ and $-22.3° < \Delta\theta < +24.7°$ as summarized in Fig. 1 and Table I. Bond-length distortions in the cluster are about two times as large as those of more extended $\{113\}$ [9] and $\{100\}$ planar interstitial defects (Table I). Accordingly, more extended defects are energetically favorable, provided a mechanism exists for accumulating self-interstitials in crystal. In the relaxed configuration, the cluster belongs to the point group C_{2v}, the rotational axis of which is parallel to the $\langle 100 \rangle$ direction.

Electronic structure of the cluster in crystalline Si is depicted in Fig. 2(a). The energy states at the Γ point in the Brillouin zone are represented by the horizontal lines. Figure 2(b) shows the electronic structure of perfect crystal computed by the same procedure, allowing us to examine the size of the bulk band gap in this computational technique. Here, we assume a supercell of perfect crystal which contains a total of 720 Si atoms and possesses the ideal lattice parameter. The gap size is poorly estimated to be 2.21 eV, even though it is known that the computation technique well reproduces the valence band and the lower part of the conduction band as well as total energies and atomic coordinates [11]. The states depicted by the longer horizontal lines in Fig. 2(a) are *defect-localized states* of the interstitial cluster. In contrast to active impurity levels, we shall define them as states whose electron probability is significantly localized near the cluster; more than 75% of the probability of the state is localized inside the spherical region, located at the center of the supercell, whose volume is about 20% of that of the supercell. A defect-localized state (0.37 eV) appears inside the minimum band gap, and it is occupied by two electrons in the ground state. Another defect-localized state is found below the valence-band edges (-12.57 eV). Valence electrons fill up the states up to 0.37 eV in the ground state.

Local densities of states (LDOS's) of atoms a, b, and c in Fig. 1 are shown in Fig. 3. The dashed line in the profile

TABLE I. Energy value and bond distortions of the relaxed configuration of the interstitial cluster I_4. E_{is} is the total energy per self-interstitial compared with the perfect crystal. Computations of the planar interstitial clusters are also summarized for the sake of comparison. Values in parentheses are obtained using the SW potentials.

Models	E_{is} (eV)	Δr (%)	$\Delta\theta$ (degree)
I_4	2.46 (2.10)	-4.2 to $+1.3$ (-5.0 to $+1.5$)	-22.3 to $+24.7$ (-22.2 to $+22.7$)
$\{100\}$	··· (0.74)	··· (-1.4 to $+2.5$)	··· (-14.0 to $+17.4$)
$\{113\}$ |IIO| (Refs. [13,19])	0.68 (0.88)	-2.2 to $+1.9$ (-2.1 to $+1.7$)	-20.1 to $+23.3$ (-20.6 to $+22.4$)
A single interstitial	5.0–6.5 (Ref. [16]) 4.4–5.9 (Ref. [17]) 3.2–4.7 (Ref. [18])	···	···

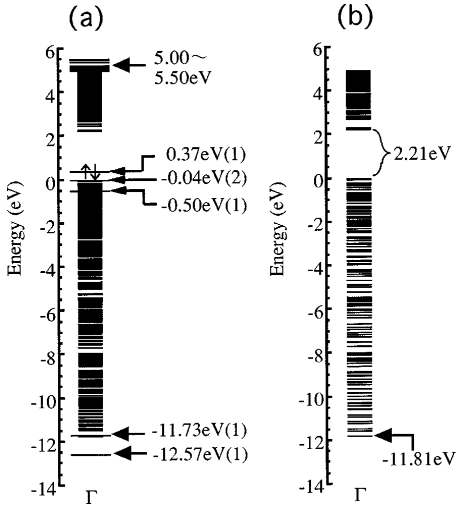

FIG. 2. Electronic structure at the Γ point in the Brillouin zone. (a) The interstitial cluster; (b) the perfect crystal. Values in parentheses express the degenerate degrees.

of LDOS is due to an atom in perfect crystal. The atoms a, b, and c suffer from larger bond distortions as follows: a: $-4.2\% < \Delta r < -1.8\%$, $-12.3° < \Delta\theta < +11.5°$; b: $-3.1\% < \Delta r < -2.9\%$, $-13.4° < \Delta\theta < +12.1°$; c: $-3.1\% < \Delta r < -2.2\%$, $-6.5° < \Delta\theta < +24.7°$. In addition, these atoms constitute odd membered rings. We are aware that the apparent peak (at about -6 eV) appears due to the s-p^3 hybridization in Figs. 3(a), 3(b), and 3(c), and that two additional peaks in LDOS's, designated by vertical arrows, correspond to the two states (0.37 and -12.57 eV) described above. The appearance of peaks both below and above the valence band has never been found in reconstructed grain boundaries and extended defects in Si [13,14]. In the LDOS's of other atoms in the supercell, such peculiar two peaks do not appear apparently as we expected.

The origin of the defect-localized states inside the band gap can be accounted for in a simple way. After examining the wave functions of the defect-localized states (0.37 and -12.57 eV), we noticed that they tend to possess a higher amplitude than that of the value of homogenized states, i.e., $1/724$, at the atoms only in the center of the supercell that form the bonds shortened by over 0.5%. As is well known, the smaller lattice constant (or the shorter bond length) gives rise to the wider valence and conduction bands [20]. Therefore, the wider energy bands nearby the cluster stick out of the bulk bands, resulting in the defect localized states inside the bulk band gap. Similarly, the gap states due to greatly stretched bonds (so called weak bonds) appear in grain boundaries in Si [14]. Therefore, it can be said in general that the gap states can be induced by great distortions of bond length in Si in the absence of dangling bonds.

Figure 4(a) shows the ⟨100⟩ split interstitial configuration [4], which many researchers believe as the most stable interstitial configuration in Si and is responsible for the extremely fast migration of interstitials. For interpreting the complicated bond topology of the cluster, it is assumed that four split interstitials arrange on a {100} plane as shown in Fig. 4(b). The neighboring interstitial sites are the second nearest neighbor (snn) distance away. The three coordinated atoms, represented by the brighter hatched circles, then form additional bonds, represented by dashed lines [Fig. 4(b)]. This procedure simply leads to the cluster. A bond topology including successive five-membered rings as in the cluster is also seen in the core model of the 30° partial dislocation [21]. The electronic states for the reconstructed dislocation [22] are similar to those for the cluster. So the cluster exhibits the common features of defects in

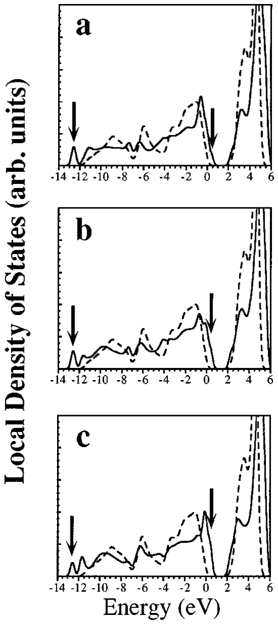

FIG. 3. LDOS's of the atoms labeled a, b, and c in Fig. 1.

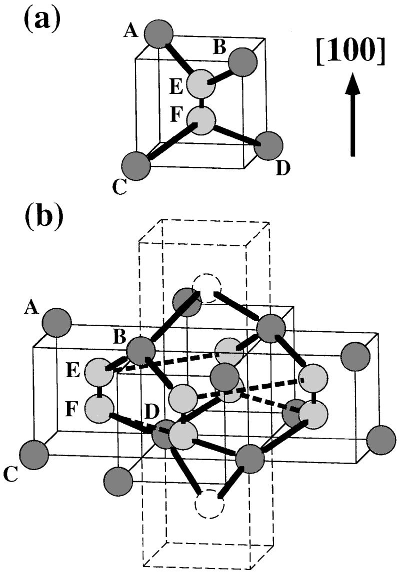

FIG. 4. Relation between the interstitial cluster and the ⟨100⟩ split interstitial. See text.

the diamond-type crystal. The structure model of a self-interstitial [6] has the similar successive five-membered rings, but is not fully reconstructed.

The migration paths of an isolated interstitial to form the cluster cannot be clarified yet in a quantitative manner, since, at this moment, sufficiently accurate dynamic computations based on an electronic theory have not yet been available for handling several hundreds of atoms. Here let us discuss briefly the agglomeration process of the cluster based on an energy calculation [23]. Considering two split $\langle 100\rangle$ interstitials in the supercell, we find that the energy per interstitial is reduced by over 1.0 eV when an interstitial site locates within the snn distance of the other. Among the four possible snn pair configurations, two kinds of configurations, one of which is seen as a part in Fig. 4(b), gain over 1.3 eV in energy per self-interstitial. A $[100]$ split interstitial gives rise to inhomogeneous distortion in the nearby crystal lattice: The compression side appears above and below it along $[100]$ and the dilatation side extends on (100). Each interstitial in the favorable pairs locates at the dilatation side of the other, decreasing the elastic energy. The agglomeration of three interstitials on $\{100\}$ further reduces the energy per interstitial by over 0.9 eV. Hence, we think that the agglomeration progresses in succession, causing rebonding [not necessarily the same way as illustrated in Fig. 4(b)], consequently reducing energy further, and then the stable reconstructed cluster of four interstitials is formed. When further agglomeration occurs in this way, then one may expect series of clusters which contain multiples of four interstitials and an extended planar defect on $\{100\}$ as a two dimensional extension, according to the mechanism of reducing bond distortions, mentioned earlier. The extended $\{100\}$ planar structure, originally proposed in diamond [24] and Ge [25], has actually been observed in Ge by high-resolution transmission electron microscopy [26]. Hence we think that the clusters and extended agglomerates are generated stable regardless of their thermodynamical stability when sufficient accumulation of the primary defect is achieved, e.g., by electron irradiation and ion implantation.

In summary, we have proposed the four self-interstitials cluster fully reconstructed in Si. The electronic energy calculation has shown that the cluster can be more stable than isolated interstitial configurations and that its existence can be examined only by exploring the band edges as well as the inside of the valence band. This work brings useful information for the understanding of self-interstitials not only in Si but other covalent materials involving interstitial impurities.

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