Model for amorphization processes in ion-implanted Si

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A model for amorphization processes in ion-implanted Si has been proposed, in which a divacancy and di-interstitial (D-D) pair introduced in the crystalline Si lattice give rise to a local atomic arrangement including five- and seven-member rings. Stable atomic configurations were determined in supercells of 216 Si atoms, including randomly distributed D-D pairs, by employing the Tersoff potential for the interatomic force calculations. Based on the proposed model, radial distribution functions, bond-angle distribution, and phonon densities of states were calculated as functions of the number of the D-D pairs and it was found that complete amorphization starts to occur when the number of D-D pairs per atom exceeds ~ 0.2 or approximately 2 D-D pairs are formed in the fcc cubic lattice.

Ion-beam-induced epitaxial crystallization of Si (Ref. 1) is potentially important for microelectronics applications such as low-temperature solid-phase epitaxy of amorphous Si (a-Si) on crystalline Si (c-Si). Linnros, Holmen, and Svensson proposed that single vacancy at the amorphous and crystalline (a/c) interface induced crystallization,[1] while Jackson recently suggests that ion-induced crystallization cannot be ascribed to vacancies but rather is due to dangling bonds in the amorphous phase.[2] Recent experiments also suggest that divacancies at the a/c interface lead to amorphization.[3] Besides this layer-by-layer amorphization process, ion-induced amorphization processes of c-Si have been also studied in which amorphization initially occurs at the end-of-range region where vacancies can be combined with interstitials probably provided from the EOR region.[4] Although various phenomenological models have been proposed for these amorphization[5] and crystallization[6] processes mediated by ion-beam-induced defects, it is not well understood how ion-beam-induced defects lead to amorphization and crystallization.

In this paper, as a first step to the detailed analysis on the roles of various defects for amorphization and crystallization processes of Si, I propose a model in which amorphization occurs as a consequence of the accumulation of divacancies and di-interstitials in bulk c-Si. In the proposed model, a divacancy is combined with a di-interstitial in the c-Si lattice which results in a local atomic configuration including five- and seven-member rings similar to that obtained by the bond-switching model for the generation of a-Si developed by Wooten, Winer, and Weaire.[7] Based on the proposed model combined with the Tersoff potential[8] for the interatomic force calculations, radial distribution functions, bond-angle distribution, and phonon density of states were calculated as a function of the number of the divacancy–di-interstitial pairs randomly introduced in c-Si model clusters.

Typical computational methods to generate atomic configurations of a-Si are simulations of (1) rapid freezing processes of liquid Si (Ref. 9) and of (2) growth processes by serial addition of atoms to a starting seed or substrate surface.[10] Both methods (1) and (2) correspond to realis-

tic physical processes, and molecular dynamics and Monte Carlo methods are employed for the computer simulations. However, these methods cannot be applied to describe ion-beam-induced amorphization.

The present model is a physical modification of the bond-switching model of Wooten, Winer, and Weaire[7] in which the five- and seven-member rings, whose existence is a prominent feature of a-Si, are introduced in the c-Si lattice by using somewhat unphysical rules.[11] A more physical way leading to a local atomic configuration, which is almost equivalent to that obtained from the bond-switching model, was found to be made by introducing a divacancy and di-interstitial in the c-Si lattice as schematically shown in Fig. 1. Atomic sites one to six form the six-member ring that is the basic structural unit
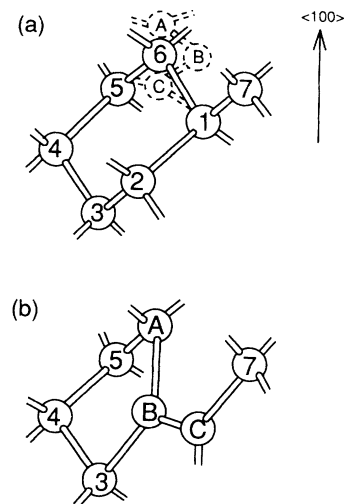

FIG. 1. (a) Basic structural unit for c-Si showing the six-member ring. A $\langle 100 \rangle$-split di-interstitial is shown by the dashed line and the atomic sites A, B, and C. (b) Local atomic rearrangement after introducing a divacancy–di-interstitial pair and being relaxed by the procedure described in the text. Atomic sites 3, 4, 5, A, and B form a five-member ring and 3, B, and C give a part of a seven-member ring.
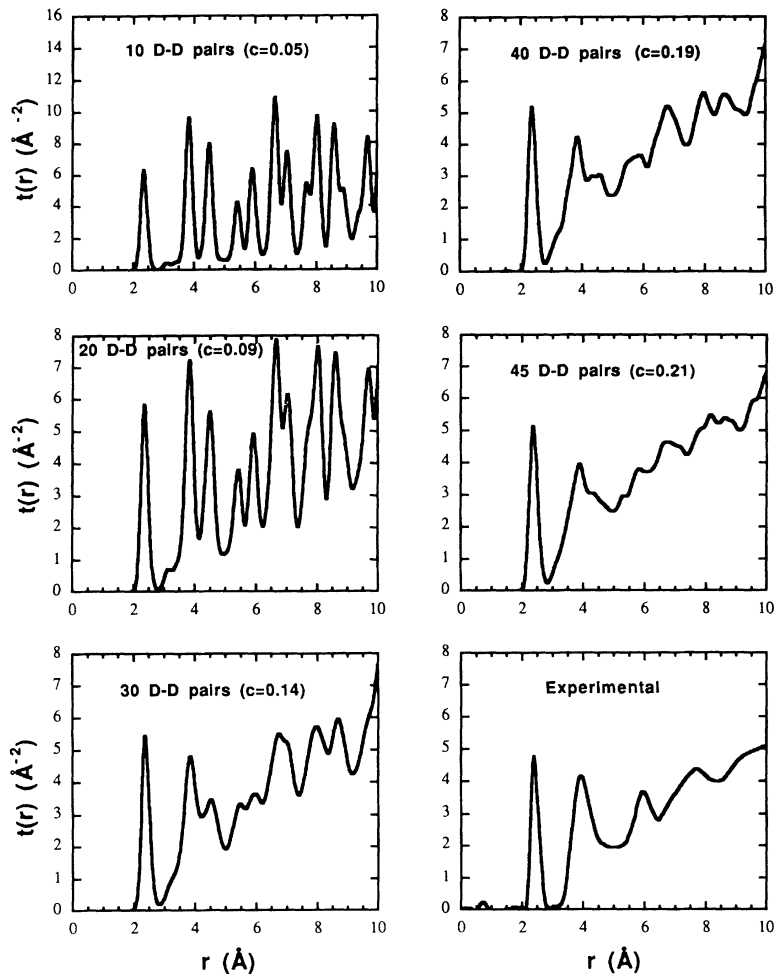
FIG. 2. Calculated results of RDF for the model clusters with various numbers of the D-D pairs. All the RDF's are in the form of the correlation function and the calculated RDF's are Gaussian broadened with a full width of 0.23 Å at half maximum in order to facilitate comparison with experiment (Ref. 6). The experimental RDF is taken from Ref. 16.

of c-Si [Fig. 1(a)]. A divacancy was introduced at the sites one and two, and the site six was replaced by a ⟨100⟩-split di-interstitial[12] illustrated by the broken line and the atomic sites A, B, and C. Then the Steinhardt relaxation procedure[13] was employed to determine the stable configuration. The atomic forces on the Si atoms were calculated using the Tersoff potential[8] based on a diamond cubic cluster composed of 216 Si atoms with periodic boundary conditions. Figure 1(b) shows the local atomic rearrangement after the relaxation. It can be seen that five- and seven-member rings are generated. [The latter is partly shown in Fig. 1(b).] There also exist threefold coordinated atoms B and C. It should be noted that all Si atoms are fourfold coordinated and no dangling bond can be generated in the bond-switching model.

In addition to the Steinhardt relaxation, simulated annealing was also carried out based on smart Monte Carlo simulation[14] in which each atomic displacement in the direction of the force was perturbed by a random displacement due to thermal agitation. Although the total energies were slightly lowered, no essential difference was seen in the atomic configurations. Thus, all of the following results were those obtained by simply repeating the Steinhardt relaxation processes until the maximum force becomes smaller than a critical value, 0.5 eV/Å.[15]
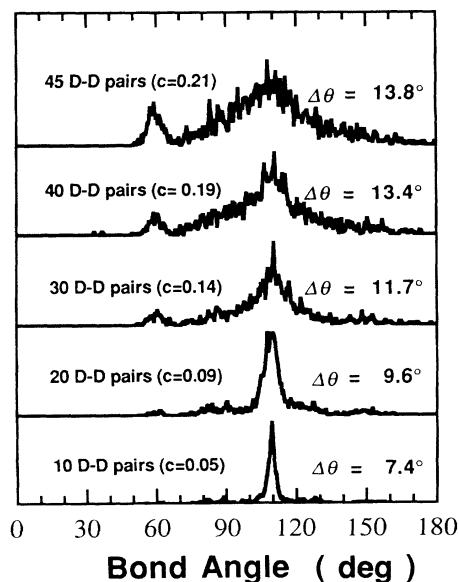
Figures 2 and 3 show the radial distribution function

FIG. 3. Calculated bond-angle distributions for the model clusters with various numbers of the D-D pairs. $\Delta\theta$ indicates the calculated deviation of the bond angles from the tetrahedral angle, 109.47°.

(RDF) and bond-angle distribution, respectively, as a function of the number of the divacancy–di-interstitial $(D\text{-}D)$ pairs randomly introduced in the model cluster. In Figs. 2 and 3, c indicates the number of the $D\text{-}D$ pairs per Si atom. The nearest-neighbor peak at $r=2.35$ Å is almost unchanged for the c values from 0.05 to 0.21, while the third-nearest-neighbor peak at $r=4.50$ Å decreases as c is increased and it almost disappears due to being merged into the second-nearest peak $(r=3.84$ Å$)$ at $c=0.21$ (see Fig. 2). These results for RDF vs c are similar to those calculated by the bond-switching technique.[11] The calculated RDF at $c=0.21$ is in fairly good agreement with that observed experimentally[16] for a-Ge scaled to a-Si as shown in Fig. 2. This indicates that complete amorphization starts to occur at $c \sim 0.2$, i.e., when approximately two $D\text{-}D$ pairs per fcc unit cube are introduced.

It has been known that there is a linear relationship between bond-angle deviation $\Delta\theta$ from the tetrahedral angle $(109.47°)$ and the peak width of a-Si transverse-optical (TO) vibrational modes,[17] and that $\Delta\theta$ is typically ranging from ~ 7 and $13°$.[18] The calculated change in $\Delta\theta$ from the bond-angle distribution for $c=0.05-0.21$ (see Fig. 3) is in good agreement with that obtained from the Raman spectra of ion-implanted Si with various ion species and doses.[19] This suggests that amorphization processes in ion-implanted Si can be described as an accumulation of the $D\text{-}D$ pairs in the present model. The calculated atomic configurations corresponding to $c=0.05$ and 0.21 are illustrated in Figs. 4(a) and 4(b), respectively.

Various statistical parameters were calculated for the atomic configuration of $c=0.21$ [Fig. 4(b)]. The numbers of five-, six-, and seven-member rings were 0.45, 0.88, and 1.48 per atom, respectively. The corresponding values in the bond-switching model are ~ 0.4, 0.9, and 1.0 per atom, respectively,[11] suggesting that there is some structural difference between the present model and the bond-switching model. In fact, it was noticed that there were 0.2 per atom three-member rings in the present atomic structure. This is the origin of the peak centered at $60°$ in the bond-angle distribution (see Fig. 3). The appearance and electronic structure of the three-member ring (triangular configuration) have been reported in the atomic structure of a-Si obtained by relaxing an initial random atomic arrangement based on the first-principle total-energy minimization.[15]

An essential difference of the present model from the bond-switching model is the presence of dangling bonds or electron-spin resonance (ESR) active sites. The dangling bond site can be identified as the threefold coordinated atom. The fivefold coordinated atoms have been also suggested as ESR-active sites.[20] Although the average coordination number was 4.2, threefold and fivefold coordinated atoms were also included in the present structure. The densities of these threefold and fivefold coordinated atoms were 8.8 and 17.6%, respectively. Biswas, Grest, and Soukoulis[21] obtained 6.5(8.3)% three(five)fold coordinated atoms in their a-Si structure generated by quenching liquid Si using a molecular-dynamics simulation. These values are much larger than typical spin densities of a-Si, $\sim 10^{20}$ cm^{-3} determined by
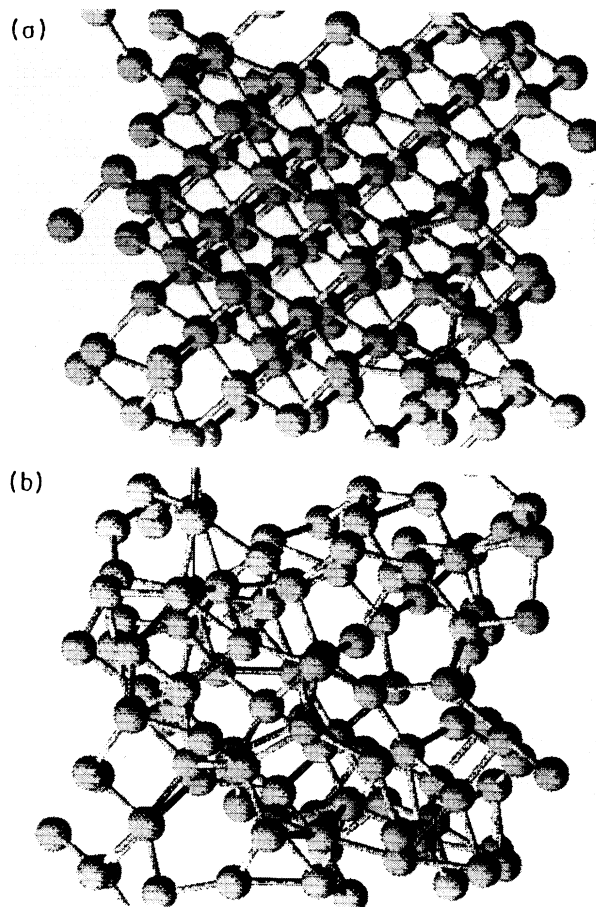
(a)

(b)

FIG. 4. Calculated atomic configurations for (a) $c=0.05$ and (b) $c=0.21$.

ESR.[22] The reason is not known at present.

The phonon local density of states (LDOS) was also calculated by applying the recursion method[23] to Si clusters constructed by the supercells of 216 atoms. The dynamical matrix was determined by taking analytic derivatives of the Tersoff potential for the relaxed Si clusters including various numbers of the $D\text{-}D$ pairs. The starting atomic displacements were cited on various Si atoms in the central region of the model cluster composed of approximately 6500 atoms and recursion coefficients $\{a_n, b_{n+1}; n=0,1,2,\ldots\}$ were determined up to $n=15$. The quadrature method[24] was then used in calculating the phonon LDOS and the total DOS was obtained by averaging the LDOS from ten starting Si atoms in the central region. The calculated results for the typical phonon DOS corresponding to the c values from 0.05 to 0.21 are shown in Fig. 5. The calculated phonon DOS for c-Si is also shown for reference. The TO peak centered at ~ 480 cm^{-1} is broadened as c is increased, consistent with the Raman results described above. The calculated phonon DOS for $c=0.21$ resembles that of rf sputtered a-Si obtained by neutron diffraction measurements.[25] This indicates, in accordance with the calculated results for RDF and $\Delta\theta$ described in Figs. 2 and 3, respectively, that complete amorphization starts to occur at $c \sim 0.2$.
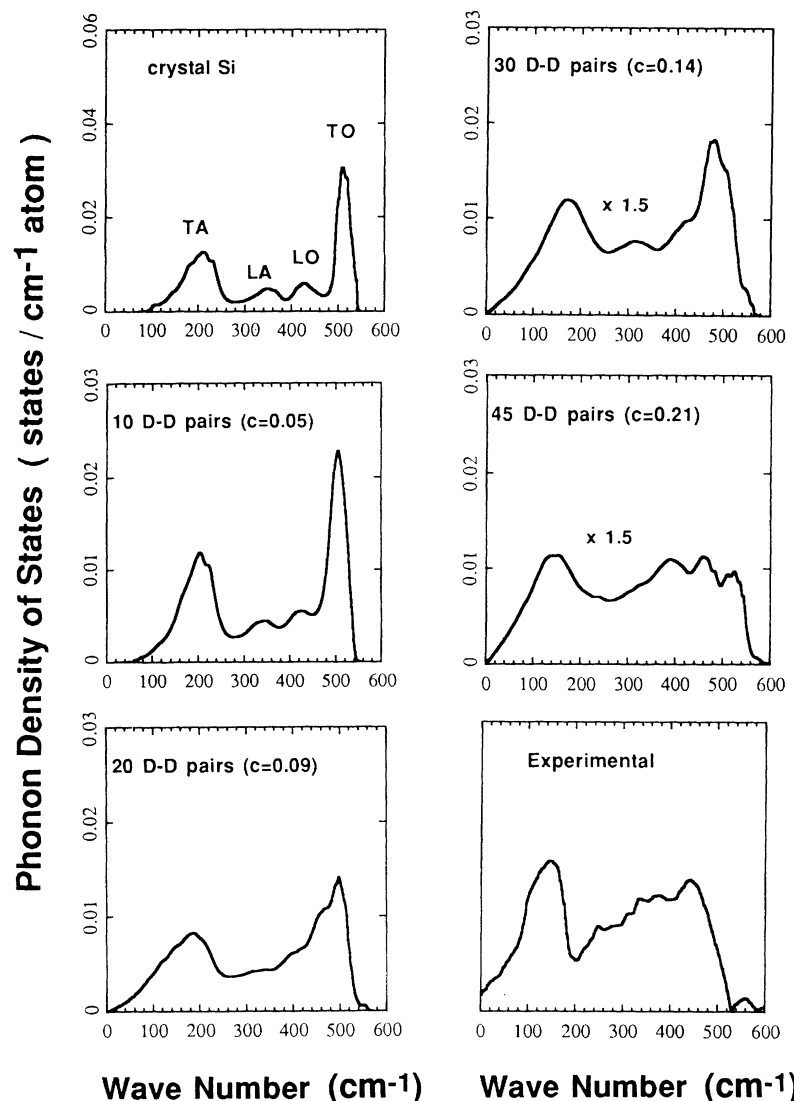
FIG. 5. Calculated total phonon DOS for the model clusters with various numbers of the D-D pairs. The experimental phonon DOS is adapted from Fig. 1 in Ref. 25 and the unit is arbitral.

The proposed model suggests that amorphization is essentially controlled by a combination of vacancies and interstitials. Vacancy-vacancy and interstitial-interstitial combinations may primarily result in the formation of voids, dislocations, and stacking faults. Thus, amorphization processes can be considered to be competitive with the formation of these stable extended defects and to be effective for suppression of their formation.

Although more complicated amorphization processes including higher-order defects such as tetravacancies[26] can be expected to occur especially in collision cascades, the present model describes a possible amorphization process controlled by rather simple defects such as divacancies and di-interstitials, and gives a useful picture to analyze the crystalline and amorphous (c/a) interface in Si. Linnros, Elliman, and Brown,[3] based on the observa-

tion of the ion-bombardment-induced reversible movement of the c/a interface, proposed that the accumulation of divacancies at the c/a interface leads to amorphization, while single vacancies at the c/a interface mediate crystallization. It is suggested, based on the present model, that layer-by-layer amorphization occurs due to the creation of the D-D pairs at the c/a interface. These simulations, including crystallization processes mediated by ion-induced defects such as single vacancies[1] and dangling bonds[2] at the c/a interface in Si, are currently under way.

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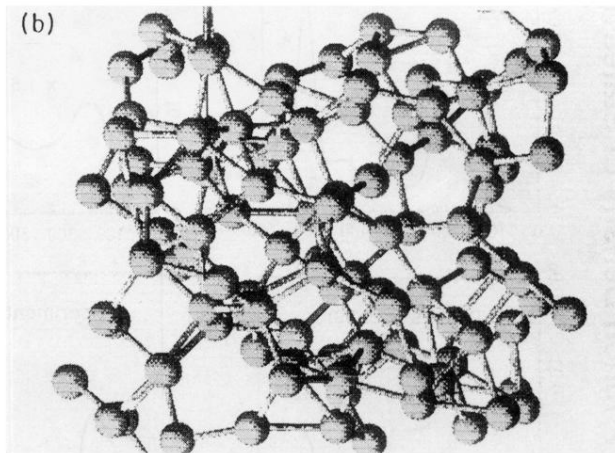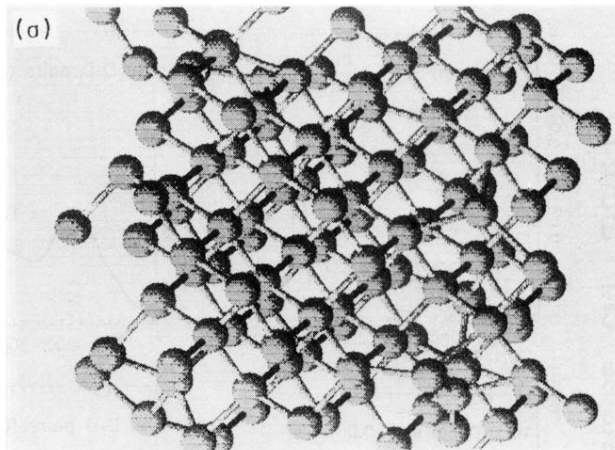
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