Role of the bond defect for structural transformations between crystalline and amorphous silicon: A molecular-dynamics study

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The relation between the bond defect, which is a topological defect, and structural transformations between crystalline and amorphous silicon, is studied by molecular-dynamics simulations. The investigation of 1-keV boron implantation into crystalline silicon proves that the bond defect can also be generated directly by collisional-induced bond switching in addition to its formation by incomplete recombination of primary defects. This supports the assumption that the bond defect may play an important role in the amorphization process of silicon by light ions. The analysis of the interface between (001) silicon and amorphous silicon shows that there are two typical defect configurations at the interface which result from two different orientations of the bond defect with respect to the interface. Thus the bond defect appears to be a characteristic structural feature of the interface. Moreover, annealing results indicate that the bond defect acts as a growth site for interface-mediated crystallization.

I. INTRODUCTION

A knowledge of the microscopic processes of defect generation and annihilation is essential for understanding and controlling changes of material properties induced by ion irradiation or thermal treatment. Molecular-dynamics (MD) simulations provide the opportunity to study these processes at an atomic level, and significant results were obtained in the last years. In connection with computer simulations of phase transitions and interaction of point defects in silicon as well as with structural models of the interface between amorphous silicon (*a*-Si) and crystalline silicon (*c*-Si), topological defects have been discussed in the literature. Such topological defects are defects characterized by broken and rearranged bonds without leaving dangling bonds and without any number defect. It is expected that the topological defects may play an important role in structural transformations between *c*-Si and *a*-Si induced by collisional or thermal processes.

Wooten and co-workers[1,2] elaborated a procedure to generate a continuous random network model of *a*-Si by repeatedly breaking and rearranging of two bonds of a randomly selected pair of neighboring atoms in *c*-Si due to rotation of this atom pair in a (110) plane (bond switching) without leaving dangling bonds. It is interesting to note that the relaxed atomic configuration after one bond switch corresponds to the topological defect found by Stillinger and Weber[3] in their MD simulation of the melting process of *c*-Si. A defect-related procedure to transform *c*-Si into *a*-Si was given by the model of Motooka and co-workers.[4,5] In this model the elementary step of bond switching is replaced by introducing a divacancy–di-intersitial pair (DD pair). The relaxed configuration of the DD pair is mentioned to be the same as that after one bond switch. Recently, Tang *et al.*[6] studied the recombination of interstitial-vacancy (IV) pairs in silicon using tight-binding MD simulations. They showed that when a single vacancy and a ⟨110⟩ split interstitial approach each other along the ⟨110⟩ direction from a distance larger than two bond lengths, a metastable defect structure, named an IV complex, is formed with a barrier for its thermally activated annihilation of about 1.1 eV. The existence of such a barrier, which has been confirmed by *ab initio* studies of the IV complex performed in Ref. 7, is in accordance with experimentally based suggestions.[8] The high binding energy of 4.3 eV (Ref. 6) indicates that the IV complex cannot dissociate at typical annealing temperatures. As reported,[7] the analysis of the bonding properties of this metastable defect structure and the description of its annihilation path have led to the characterization of this defect structure as a bond defect, since it is independent of the details of the formation process. It is expected[6] that the bond defect plays an important role in the kinetics of Si amorphization by light ions.

Saito and Ohdomari[9,10] developed a hand-built model for the construction of the *a*-Si/(001)Si interface. In order to obtain the transition from the crystalline Si to the random network, Si atoms are added on top of the original (001)Si surface so as to disturb the periodicity of the lattice but keep the fourfold coordination [according to rules similar to those given by Spaepen[11] for the construction of an *a*-Si(111)Si interface], which means the formation of topological defects at the interface.

In this work classical MD simulations are used to investigate the generation of bond defects due to light ion impact on silicon and to analyze the microstructure of an *a*-Si/(001)Si interface with respect to the bond defect configuration. Furthermore, the significance of the bond defect for interface-mediated crystallization is studied.

II. MD SIMULATIONS

The simulations were done with a standard MD code[12] using the Stillinger-Weber interatomic potential,[3] which provides a reasonable description of point defects, small defect clusters, and low-energy defect production in Si as well.[13–15] The repulsive part of the two-body term of the potential is splined to the Ziegler-Biersack-Littmark (ZBI) potential[16] as

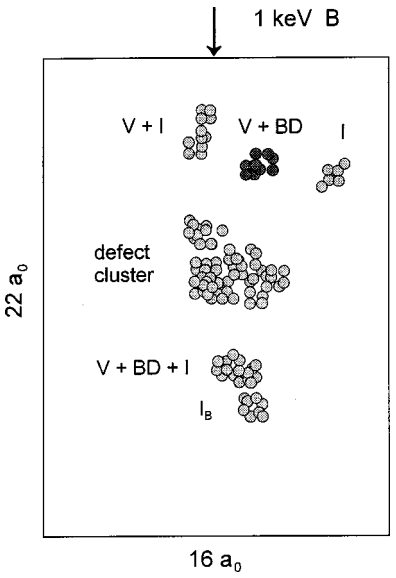

FIG. 1. Distribution of the primary damage (atoms with potential energy larger than 0.2 eV above the crystalline ground state) caused by implantation of a 1-keV B ion at an angle of 9° off the surface normal into (001)Si at a temperature of 80 K. The MD cell is given by the box (where a_0 is the lattice parameter) and the type of defects are indicated by V (vacancy), I (self-interstitial), I_B (boron interstitial), and BD (bond defect). The defect region marked by dark gray circles is shown in more detail in Fig. 2.

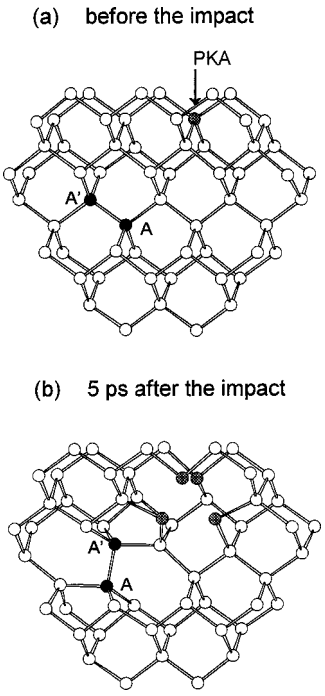

FIG. 2. Configuration of the atoms marked by dark gray circles in Fig. 1 (some surrounding atoms are added) before (a) and 5 ps after (b) the B impact. The primary knock-on Si atom (PKA) which initiates the formation of the bond defect is marked by a gray circle in the initial configuration (a). The final configuration (b) consists of a vacancy marked by its surrounding atoms (gray circles), and a bond defect the rotated atom pair of which is given by the black circles.

described in Ref. 17. The integration of the equations of motion is performed using the velocity form of the Verlet algorithm and a time step of 0.3892 fs. In order to check the reliability of the treatment for the following investigations, the structure as well as the binding energy and the formation energy of an isolated bond defect have been calculated and compared with the results of tight-binding MD simulations and *ab initio* calculations.[6,7] The good agreement justifies the use of classical MD simulation with the Stillinger-Weber potential. This is important because these investigations require sufficiently large MD cells which can be treated by classical MD simulations but not quantum-mechanical MD simulations.

For the simulation of the boron implantation the MD cell consists of $16\times16\times22$ unit cells (45 056 atoms). Periodic boundary conditions in the x and y directions, a free surface, and a fixed bottom plane in the z direction are applied. The two planes next to the bottom plane are kept at a constant temperature of 80 K. For B-Si interaction the ZBL potential is used, and a variable time step is chosen determined by the velocity of the fastest atom.

The a-Si/c-Si interface system has a size of $8\times8\times10$ unit cells (5120 atoms) using periodic boundary conditions in x and y directions, and a free surface and two fixed bottom planes in the z direction. It is prepared by melting and cooling of the upper half of the MD cell. The preparation procedure was described in detail in Refs. 18 and 19.

III. RESULTS AND DISCUSSION

By comparison it becomes clear that all the differently prepared topological defects mentioned in the literature provide the same atomic configuration. Therefore, we will refer to this throughout the paper as a ''bond defect,'' in agreement with the notation in Ref. 7. According to the literature, a bond defect can be created by an artificial bond switch[1,2] and by an incomplete recombination of primary defects[4–7] caused by ion irradiation. The possibility of a direct generation of a bond defect in a collision cascade caused by light ion irradiation has not been proved up to now, to our knowledge and is therefore studied in the following. For this purpose the implantation of 1-keV boron ions into crystalline silicon is simulated. In order to concentrate on primary defects a low target temperature of 80 K is chosen. The B ion starts above the free (001) surface with an angle of 9° off the surface normal. After the ion impact the system is allowed to evolve for 5 ps to obtain the relaxed state of primary damage produced by the collision cascade. As it is typical and well known for light ion irradiation, the resulting damage consists of isolated point defects and small defect clusters caused by small subcascades.[20] A more detailed analysis of the defect structures proved that, besides vacancies, interstitials, and clusters of them, bond defects are also generated directly in the collision cascade as characteristic primary defects. A typical situation is shown in Fig. 1, where the damage distribution 5 ps after the impact caused by one B ion is visualized by displaying only atoms with a potential energy larger than 0.2 eV above the crystalline ground state. The different types of defects are indicated. For one of the defect regions, marked by dark gray circles, the atomic configuration is shown in detail in Fig. 2. The evolution from the initial state [Fig. 2(a)] to the final state [Fig. 2(b)] takes place as follows. The B ion knocks the Si atom represented by the gray circle in Fig. 2(a). This primary knock-on atom (PKA)

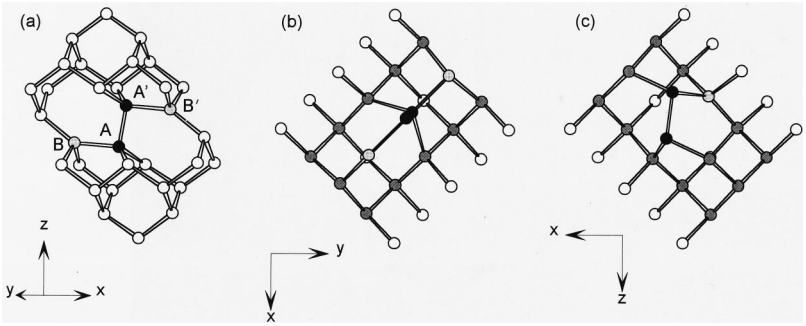

FIG. 3. Relaxed local atomic configuration of the isolated bond defect at 0 K (a) and the (001) projection (b) and (010) projection (c) of a part of this configuration (see text). The two black circles represent the rotated atom pair AA' and the dimers AB and $A'B'$ are marked by a pair of a black circle and a light gray circle.

starts moving with about 100 eV in the ⟨010⟩ direction, as indicated by the arrow, leaves behind a vacancy, and initiates a short replacement collision sequence along the ⟨010⟩ direction. The vacancy migrates to a neighboring site. Its final place is marked by the surrounding atoms represented by the gray circles in Fig. 2(b). The final position of the PKA (the end of the replacement collision sequence) is outside the given section of the MD cell. Due to the excitation connected with the replacement collision sequence, two bonds of the neighboring atoms A and A' have been broken and rearranged, which generates a bond defect. This process is a collective ballistic one because all of the neighbors of atoms A and A' forming the bond defect have been more or less shifted but not displaced. This result proves that in the case of ion irradiation bond defects are not only the result of the interaction of primarily generated vacancies and interstitials, but can also be generated directly due to a collisional-induced bond-switching process which transforms chair-type six-membered rings that are characteristic of the diamond cubic lattice into five- and seven-membered rings [see Fig. 2(b)]. In the case considered the replacement collision sequence plays an important role.

The results of Wooten and co-workers[1,2] and Motooka and co-workers[4,5] showed that the bond defect is obviously a basic element for the transformation of crystalline silicon into amorphous silicon. Therefore, this defect should play a role for the transition from the crystalline structure to the amorphous structure at the *a*-Si/*c*-Si interface. This is studied for the (001) interface. Figure 3 shows possible (001) interface structures caused by an isolated bond defect. The structure of an isolated bond defect is given in Fig. 3(a). If the atoms above the four central atoms of the bond defect (the rotated atom pair A and A' marked by black circles and the two dimer atoms B and B' marked by light gray circles) are removed, the remaining structure can be considered as a small portion of an unrelaxed (001)Si surface with the bond defect on top of it. Its top view (several atoms are added) is shown in Fig. 3(b) where two five-membered rings (including one dimer) and two seven-membered rings (including the other dimer) are marked by dark gray circles. Figure 3(b) shows only one of the three possible orientations of the bond defect with respect to the (001) surface, where the bond between the rotated atom pair is oriented approximately perpendicularly to the surface. The other two orientations of the bond defect with respect to the (001) surface which are equivalent to each other are characterized by the bond between the rotated atom pair being directed approximately parallel to the surface. The top view of the corresponding configuration is shown in Fig. 3(c). Again, several atoms are added while others are removed. For illustration one five-membered ring, one seven-membered ring including one dimer, and two deformed six-membered rings are marked by dark gray circles. In the following the two configurations given in Figs. 3(b) and 3(c) are called perpendicular and parallel interface configurations of the bond defect. Considering the hand-built interface model of Saito and Ohdomari,[9,10] it can be stated that their basic element for the construction of the *a*-Si/(001)Si interface is equal to the parallel interface configuration of the bond defect [compare Fig. 3(c) with Fig. 1(b) of Ref. 10]. This indicates that the bond defect should be important for the microstructure of the *a*-Si/(001)Si interface which is investigated in the following.

The *a*-Si/(001)Si interface has been prepared by MD simulation of melting and cooling one half of the MD cell as described in Refs. 18 and 19. The analysis of the interfacial

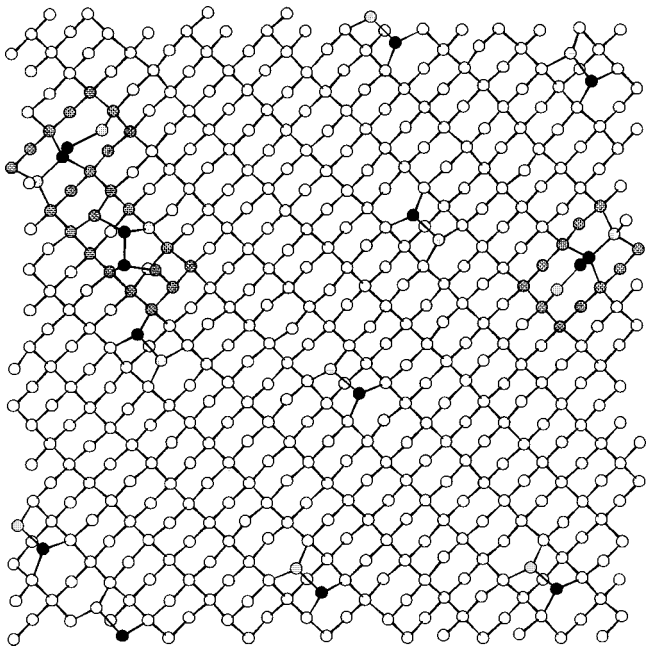

FIG. 4. Two crystalline and the first and second noncrystalline atomic (001) layers of the *a*-Si/(001)Si interface system. The black circles represent atoms of the rotated atom pairs of the bond defects. A pair of a black circle and a light gray atom represents a dimer.

microstructure showed that both interface configurations of the bond defect described above are present, and that they are characteristic configurations at the (001) interface. An example of a typical interface structure relaxed at room temperature for 350 ps is depicted in Fig. 4. It shows the top view of four (001) atomic layers at the interface. The two lower layers are completely crystalline, and the two layers on top of them show some defect regions the atoms of which are marked by gray and black circles (the black and light gray circles mark atoms of the rotated atom pairs of the bond defects and the dimer atoms belonging to them, respectively, as used in Fig. 3). The defect regions which represent the transition to *a*-Si at the interface can be characterized by the two interface configurations of the bond defect given in Figs. 3(b) and 3(c). One parallel configuration [compare with Fig. 3(c)] and two perpendicular configurations [compare with Fig. 3(b)] are completely seen in Fig. 4 (of course, they are a bit deformed because of the noncrystalline continuation above). The nine dimers in the top layer of Fig. 4 are only the lower parts of perpendicular interface configurations of the bond defect. This is due to the fact that the *a*-Si/(001)Si interface is not confined to a single atomic layer. The configurations would be fully visible if a further (001) atomic layer is added. The results show that the transition from (001)Si to *a*-Si starts with the parallel and perpendicular configurations of the bond defect. While the parallel configuration corresponds to the structural feature observed in the interface model of Saito and Ohdomari,[9,10] the perpendicular configuration gives rise to dimers similar to those on the (2×1)-reconstructed free (001) Si surface. Such dimers were also observed in recent tight-binding MD simulations of an *a*-Si/(001)Si interface in Ref. 21. Because the two interface configurations of the bond defect are characteristic links between (001) Si and *a*-Si, crystallization processes at the interface take place by their annihilation. In the case of thermal annealing at 1000 K all defect configurations visible in Fig. 4 (except one) are annihilated after 155 ps, which means the interface has moved toward the amorphous side. It is interesting to note that the interface again shows such bond defect configurations, which means that these defects are self-sustaining. In most cases the annihilation path was found to be the same as that described by Tang *et al.*[6] and Cargnoni, Gatti, and Colombo[7] for the isolated bond defect in *c*-Si. However, there are also deviations from this path due to the configuration of the overlaying *a*-Si. In a previous paper[19] we showed that the annihilation of the interface configuration of the bond defect, i.e., crystallization, can be initiated by low-energy (a few eV) recoils. The minimum of the kinetic energy necessary for the annihilation is obtained if one of the defect atoms is made a low-energy recoil with the motion directed along the annihilation path of the bond defect.

IV. CONCLUSION

It can be concluded that the bond defect as a topological defect results in an atomic configuration which introduces five-and seven-membered rings in a definite manner into the Si crystal lattice independent of the details of the defect formation process according to the different considered approaches. That implies a unified picture for the introduction of topological disorder into the diamond cubic lattice, leading to the formation of amorphous silicon structures. In the case of light ion irradiation the bond defect cannot only be created by the incomplete recombination of primary defects during annealing as previously reported,[4–7] but can also be obtained directly by ballistic processes in the collision cascade. Together with the fact that the bond defect is considered a basic element for generating random network models of *a*-Si, these results support the assumption of Tang *et al.*[6] that the bond defect should play an important role in the amorphization of silicon by light ions.

The two characteristic structures found at the *a*-Si/(001)Si interface have been shown to be two interface configurations of the bond defect corresponding to two different orientations of the bond defect with respect to the interface. This indicates that the bond defect appears to be a characteristic structural feature of an *a*-Si/(001)Si interface. Moreover, as shown by the results of the annealing at 1000 K, the bond defect is important for a microscopically based understanding of solid-phase epitaxial growth.

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