

Mechanism of Impurity Diffusion in Silicon with a Point Defect: Tight-Binding Molecular Dynamics Simulation

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Tight-binding molecular dynamics simulations, based on the KBWS model, are performed to study correlation between a point defect (i.e., vacancy) and a rare-gas like impurity atom in Si crystal. The local Si structure near the vacancy transforms to an octahedral structure (i.e., split-vacancy structure) by inserting the impurity atom at an intermediate position between the vacancy site and one of its nearest-neighbor interstitial sites. In the case that the impurity atom is inserted at the interstitial site with an initial velocity, the Si structure near the vacancy deforms spontaneously to the octahedral structure. Possible effects of such a local deformation on the impurity diffusion at high temperatures are investigated through relatively long simulation runs.

Key words: tight binding model, defect, vacancy, diffusion, impurity.

1. INTRODUCTION

Impurity diffusion is one of open problems in solid-state physics. Understanding its mechanism will help us for fabricating new electronic/functional devices [1,2]. For example, ionic impurity-atom diffusion plays a major role in fuel cells, which are made basically of ceramics and are attracting much attention due to its utility in energy resource problems. Atomistic analyses of the impurity diffusion in ceramics and/or semiconductors, with or without defects, have thus been required [3,4].

In this paper, we focus on the correlation between a vacancy, created in the Si crystal with diamond structure, and a rare-gas like impurity atom. All the simulations are performed using the tight-binding molecular dynamics method based on the KBWS model [5]. It is successful in reproducing structural and electronic properties of the Si crystal in various conditions.

Section 2 outlines the computational method adopted in this study. Simulation results are explained in Sec. 3. Concluding remarks are given in Sec. 4.

2. COMPUTATIONAL PROCEDURE

For the interaction between the Si atoms, we adopt the KBWS tight-binding model. Atomic motions are simulated by numerical integration of the equations of motion with the Hamiltonian defined as:

$$H = \sum_i \frac{p_i^2}{2m} + \sum_n \langle \Psi_n | H_{TB} | \Psi_n \rangle + E_{rep} \quad (1)$$

The first term on the right hand side represents the kinetic energy of the nuclei. The second term is summation of filled eigenvalues of the tight-binding Hamiltonian H_{TB} with eigenstates Ψ_n . E_{rep} is the semi-empirical repulsive potential. We expand Ψ_n in terms of the atomic bases χ 's as

$$\Psi_n = \sum_{i,\alpha} c_{i\alpha}^n \chi_{i\alpha} \quad (2)$$

where i stands for the atomic index, α for the orbital index, n for the band index.

Secondary, we assume a rare gas-like impurity atom having a spherical shape with its characteristic radius similar to the He atom. The Si-impurity interaction potential is modeled as a 'modified' Lennard-Jones (a soft-core type) form:

$$\phi(r) = \alpha \left(\frac{\sigma}{r} \right)^{12} \quad (3)$$

with $\alpha=0.01\text{eV}$ and $\sigma=1.5\text{\AA}$ ('He' impurity). The impurity mass is set to 28.09 a.m.u. (same as that of Si atom).

3. RESULTS

Before calculating rates of the impurity diffusion, we firstly create a Si system in diamond structure with a vacancy. The number of Si atoms is 215 and a periodic boundary condition is applied. Figure 1 depicts principal positions (P0 and P1) in Si crystal in the present study. The P0 is the vacancy position and the P1 is one of the nearest neighbor interstitial sites of the vacancy. In Sec. 3.1 we initially insert the impurity atom at various positions located between P0 and P1, and the total system is relaxed to obtain the lowest potential-energy configuration. We then find that the structure with an octahedrally coordinated Si atom is formed. Correspondingly, in Sec. 3.2, we initially insert the impurity atom at P1 with a velocity toward P0, to see dynamic deformation of the atomic configuration initiated by the impurity motion. In Sec. 3.3, possible effects of the impurity-initiated local deformation of Si on the impurity diffusion are studied.

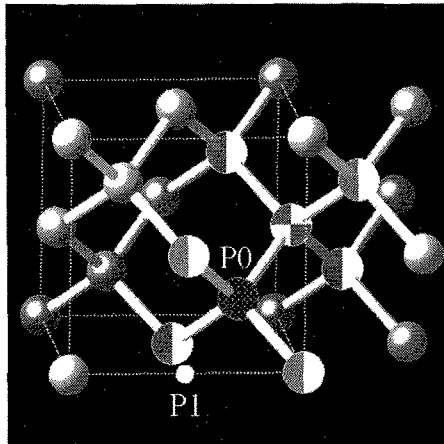


Fig.1. Characteristic positions in crystalline Si. The P0 represents the vacancy position, P1 the interstitial site that is one of the nearest neighbor ones to the vacancy position. Two-tone spheres are the Si atoms that are displaced substantially when the impurity atom is inserted at the middle of P0 and P1.

3.1 Static analyses

The impurity atom is inserted at P0, P0-P1, and P1; here P0-P1 represents the position at the middle of P0 and P1. In all three cases, we relax the total system by the steepest descent method. We then analyze several properties of the system: Atomic structure around the vacancy, the total potential energy, and bond-order potential[6]. The bond-order potential is defined as

$$E_{bond} = \sum_{i\alpha, j\beta} 2 \sum_n c_{i\alpha}^n c_{j\beta}^n H_{j\beta, i\alpha} f_{FD}, \quad (4)$$

where f_{FD} represents the Fermi distribution function at zero temperature and c the probability amplitude for each basis in Eq.(2).

When the impurity atom is inserted at P0 and P1, four atoms with two colors around the vacancy keep its original tetrahedral structure. On the other hand, when the impurity atom is inserted at P0-P1, the four-colored atom moves toward P0 and an octahedral structure (called the split-vacancy structure in Refs. [7,8]) is formed. The four-colored atom is then coordinated by the six two-colored atoms.

Figure 2 compares the final potential energies of the system in the three cases explained above. It is clear that the split-vacancy structure is the lowest-energy state. Figure 3 represents the bond-order potentials between the four-colored atom and the other two-colored atoms (hence six pairs) in three cases. In the split-vacancy structure, the values of six bond-order potentials are degenerate. It is because all the six bonds have the same length and are perpendicular to each other. Since the bond length between the four-colored atom and the two-colored atom in the split-vacancy structure is longer than that of the tetrahedral structure in Si crystal, the bond-order potential, which measures the bond strength, for the tetrahedral one is smaller than that of tetrahedral structure.

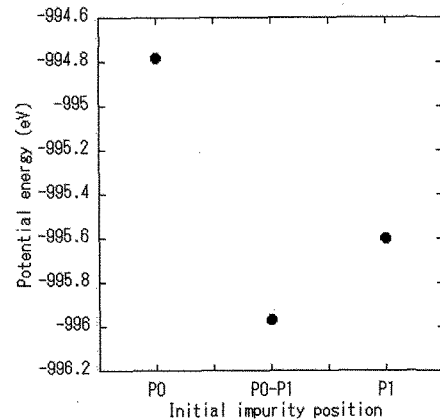


Fig.2 Total potential energy for three cases of the initial impurity position. (See text.)

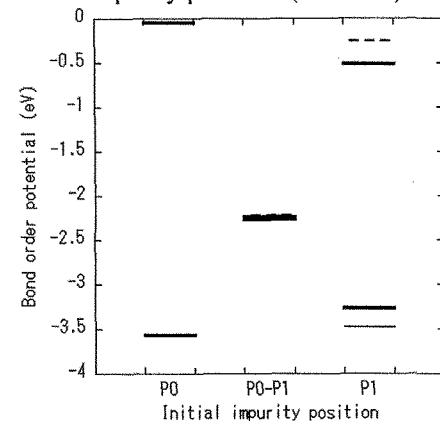


Fig.3 Bond-order potential for three cases of the initial impurity position. In the P0-P1 case, six values corresponding to six different bonds are the same.

3.2 Dynamics analyses

For the dynamical calculations, we insert the impurity atom at P1 and give a velocity v_i directing toward P1: v_i is set to be 20 Å/ps (1.0eV in kinetic energy) or 0.2 Å/ps (0.0001eV). The trajectories of all the Si atoms and the impurity atom are obtained by the molecular dynamics method with the velocity-Verlet algorithm. The time step used for the simulations is 1fs for both cases.

Figures 4 and 5 depict the time evolution of local atomic structures for the case of $v_i=2.0\text{Å/ps}$ and for 0.2Å/ps , respectively. In the case of $v_i=20\text{Å/ps}$, the initial tetrahedral structure around the vacancy transforms to the split-vacancy structure (see, Fig.4(c)). As a result, the impurity diffusion is decelerated. In the case of $v_i=0.2\text{Å/ps}$, the tetrahedral structure is kept as shown in Fig.5. As the impurity approach to P0 in the $v_i=0.2\text{Å/ps}$ case, three two-colored atoms in Fig. 1 collaborate as a "barrier" for the impurity motion directing toward P0. Distances between those three Si atoms decreases as the impurity approaches to them, and hence a path of the impurity atom is hindered. Since the transformation to the split-vacancy structure is observed only in the case with the kinetic energy of 1.0eV, we may conclude that there exists an energy barrier for transformation from the tetrahedral structure to the split-vacancy structure and the activation energy is less than 1.0eV.

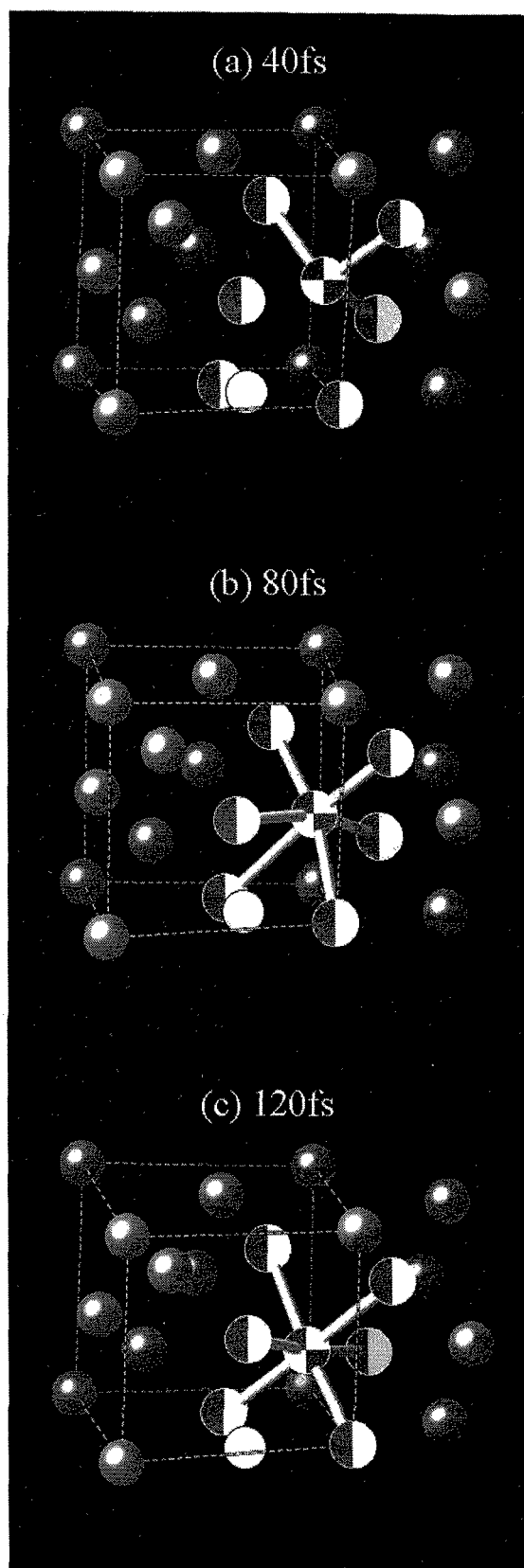


Fig. 4. Snapshots of the local atomic structure when the impurity is given a velocity $v_i=20\text{\AA}/\text{ps}$: (a) at 40ps, (b) at 80ps, (c) at 120ps. White sphere represents the impurity. Initial position of the impurity atom is P1. Only bonds, whose lengths are less than 2.8\AA , are drawn.

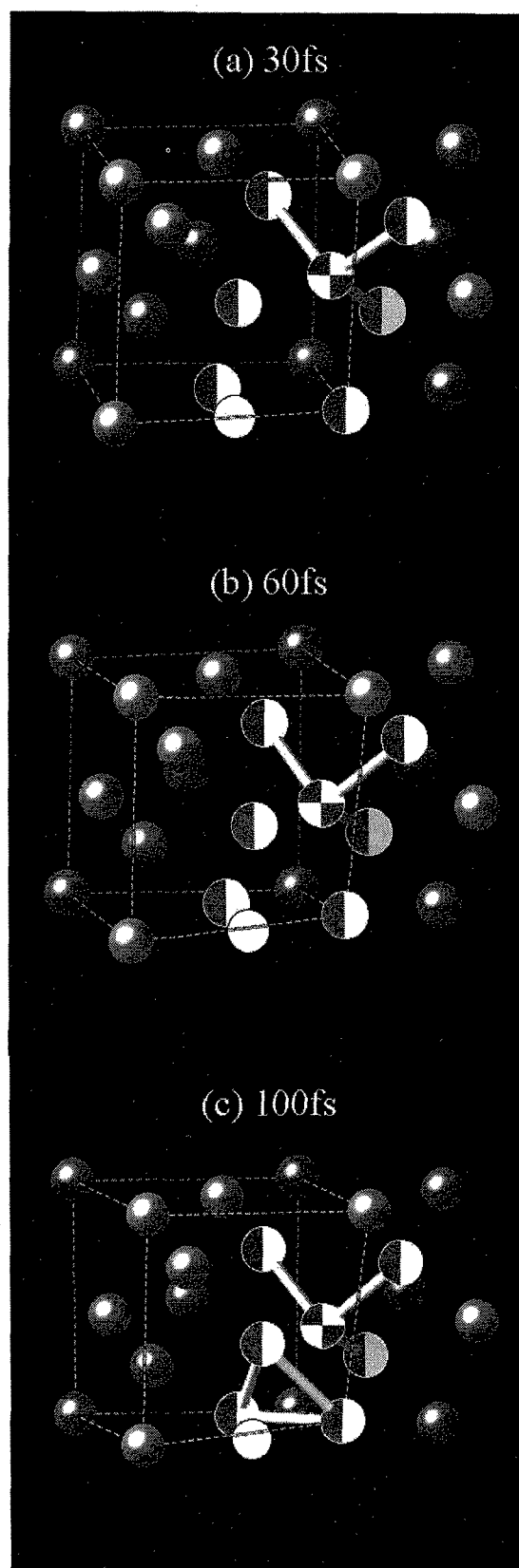


Fig.5. Same as Fig. 4, but for $v_i=0.2\text{\AA}/\text{ps}$: (a) at 30fs, (b) at 60fs, (c) at 100fs.

3.3 Impurity diffusion

We analyze correlation between the split-vacancy structure and the impurity diffusion by calculating the mean square displacement of the impurity atom. Here, we consider two different systems: (i) perfect Si crystal, (ii) crystalline Si with a vacancy. In both systems, temperature is kept constant at 1,000K and 1,500K. Total simulation time is 100ps. The number of Si atoms is 64 for the former system and 63 for the latter. Here smaller numbers of Si atoms than in the previous Section are used in order to save the cost of computation. Fig. 6 shows no substantial difference between the two systems as regards time evolution of the mean square displacement of the impurity atom.

To understand why the impurity diffusion is insensitive to local Si structure, we pay our attention to the histogram of coordination number of the Si. We find that the probability of 6-coordinated Si, that is, split-vacancy structure, is only about 0.1%. Such a low existence probability of the defect explains the observed insensitivity.

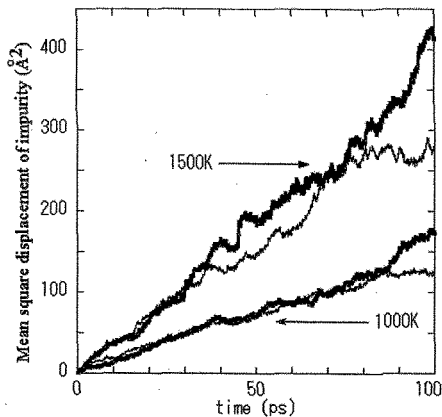


Fig.6. Time evolution of the mean square displacement of the impurity atom in Si systems. The thick lines correspond to the Si crystal, while thin lines to the Si with a vacancy.

4. CONCLUDING REMARKS

In this paper we have performed a tight-binding molecular dynamics study of Si systems to understand transformation of atomic configuration initiated by insertion an impurity atom in the presence of a vacancy. We thereby confirmed that the so-called split-vacancy structure is more stable than the initial single vacancy structure. We have found that the motion of the impurity atom near the vacancy acts to assist evolution of the original tetrahedral structure to the split-vacancy one. The energy barrier toward the split-vacancy structure was found not to exceed 1eV.

Possible effects of the split-vacancy structure on the impurity diffusion were also investigated. We have compared time evolutions of the mean square displacement of the impurity atom in both systems of crystal Si with and without a vacancy. No substantial difference between the two systems was found.

The system size in this study may not be large enough to draw a concrete conclusion. Moreover, we have adopted the rare-gas like impurity assuming a simple short-range repulsive potential with Si atoms. Other

types of impurity-Si interaction, such as those with a relatively long-ranged attractive potential, may influence the diffusion characteristics of the impurity atom.

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