Di-interstitial Diffusivity and Migration Path Calculations Based on Tight-Binding Hamiltonian Molecular Dynamics

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Abstract – Molecular dynamics calculations were performed for the di-interstitial-silicon based on the tight-binding model for silicon Calculation results indicate that the di-interstitial can diffuse into a crystalline silicon as fast as the mono-interstitial silicon. Three kinds of the stable configurations were found named T, Z, and W-configuration. The T-configuration is the lowest while the W is higher energy level configuration. A critial-path method (a saddle-point search algorism) revealed that the di-interstitial migration pathway. The T to W transition needs about 0.96eV of the barrier energy. And the W to W transition can be occurred less than 0.1eV barrier energy. Therefore, di-interstitial can show a long-range hop via the W-W transition which should be thermally initiated by the T-W transition (reorientation).

I. INTRODUCTION

Dopant diffusion profiles in silicon are strongly influenced by non-equilibrium point defect concentration in silicon. For instance, diffusion enhancement occurs even after laser annealing[1]. Supersaturation of the point defects occurs via the dissolution of the small clusters and extended defects, such as {311} defects.

Recently, the growth mechanism of {311} defects has been discussed[2], and a di-interstitial has received attention as a "building-block or "precursor" of them [3]. A few calculations have been reported for the di-interstitial. Kim et al.[4] suggested that the thermal reorientation of the di-interstitial corresponds to the $P6$ center observed in irradiated silicon[3].

In this study, molecular dynamics (MD) simulations were performed to investigate the di-interstitial, based on the tight-binding Hamiltonian. A large value for the di-interstitial diffusivity was obtained, and a typical di-interstitial migration pathway was investigated.

II. CALCULATION METHOD

The classical Stillinger-Weber potential MD calculation has already been performed for the di-interstitial, and its large diffusivity reported in [5]. However, further evidence or results of more accurate calculations, such as quantum-mechanics-based band structure calculations, have not been available yet.

For this purpose, *ab initio* calculations such as the density functional methods based on the local-density approximation (LDA) or a generalized gradient approximation (GGA) would be the most definitive. Unfortunately, the system sizes for such *ab inito* calculations are very limited due to their huge computational demands.

Therefore, we performed MD simulations based on a tight-binding Hamiltonian developed by Kwon *et al.*[6][7], which approximately reproduces the LDA results of the formation energies of point defects, and enables us to compute a larger system size and longer diffusion time than the LDA calculations.

Single(mono)-interstitial, di-interstitial, and tri-interstitial diffusions were simulated by means of NVT ensemble MD using periodic supercells with 64, 216, and 512 (+1, +2 or +3) atoms involved. Single vacancy diffusions were also simulated by using similar supercells. Diffusion constants were extracted from the 64-atom MD result after a 1000-ps diffusion time period divided into 1-fs steps. A typical computation time for one diffusion constant was about 110 hours on an ALPHA 21264 500MHz workstation.

As many as possible of the most stable configurations and their formation energies for the di-interstitial were obtained using a conjugate gradient (CG) full-relaxation (cooling) scheme applied for all the snap-shots of the high temperature MD, but extended up to 512-atom cells. Some of the specific configuration energy levels were checked by our LDA program[8].

The migration pathways between two distant stable configurations were identified using a restricted geometry optimization scheme[9]. This scheme is similar to the critical path method[10]. A saddle point configuration can be obtained approximately based on the geometry optimization according to the calculated *force* $\boldsymbol{F}$ onto the each atom, with the restraint within the hyperplane in $3N$ dimensional space, normal to the direction toward the destination of the stable geometry (Eq. 1).

$$\tilde{\boldsymbol{F}} = \boldsymbol{F} - \frac{(\boldsymbol{F}, \triangle \boldsymbol{R})\triangle \boldsymbol{R}}{|\triangle \boldsymbol{R}|^2} \qquad (1)$$

where, $\tilde{\boldsymbol{F}}$ represents the modified *force* vector for the restricted geometry optimization in $3N$ dimensional space, $\triangle \boldsymbol{R}$ is the step movement vector heading toward the final stable configuration, and N is the number of atoms.

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III. RESULTS AND DISCUSSION

Our tight-binding MD calculation result shows that the di-interstitial is highly mobile as shown in Fig. 1.

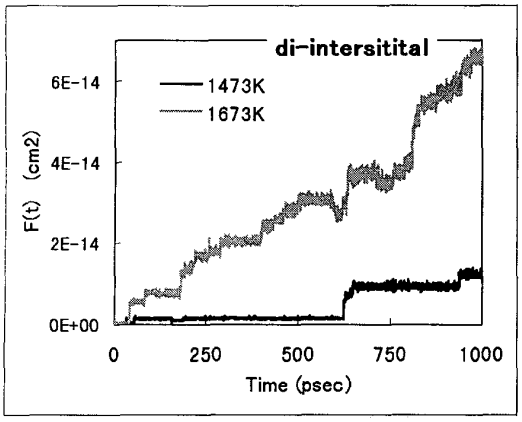

Figure 1: Calculation results of tight-binding molecular dynamics simulation for the di-interstitial silicon. F(t) represents the total square displacement of the atoms. 64+2 atom cell was used.

A diffusion constant (D) can be calculated from the displacements of all atoms in the simulation cell by using Eq. 2. Note that our calculation results for the diffusion constants for the single(mono)-interstitial are almost identical to the previous ones[11]. No diffusion was observed for tri-interstitials in our calculation.

$$D = \lim_{t\to\infty} \frac{F(t)}{6t} = \lim_{t\to\infty} \frac{\sum_i \left[\boldsymbol{r}_i(t) - \boldsymbol{r}_i(0)\right]^2}{6t} \qquad (2)$$

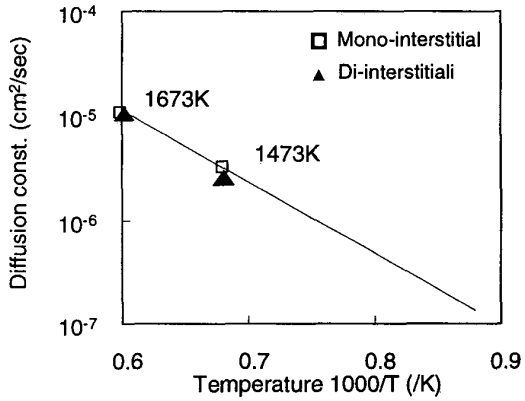

Figure 2: Calculation results of tight-binding molecular dynamics simulation for di-interstitial silicon. Diffusion constants were extracted from the data in Fig. 1 using Einstein relationship. The di-interstitial diffusivity is comparable to that of the mono-interstitial.

Di-interstitial diffusion constants were found to be comparable to the mono-interstitial silicon as shown in Fig. 2.

Moreover, the di-interstitial migration behavior is observed to be not only somewhat discrete, but it also has along range hopping motions. To clarify this behavior, the di-interstitial migration pathway was studied considering stable and saddle point configurations.

Performing the CG full-relaxation attempts for every possible snap-shot of the MD results, we found three kinds of the stable configurations, which we denote here as the T-, W-, and Z-structure (Fig. 3). T-structure and W-structure are found to be corresponding to C_{1h} and C_{2v} in [4], respectively.

The T-structure is the most stable configuration, and its

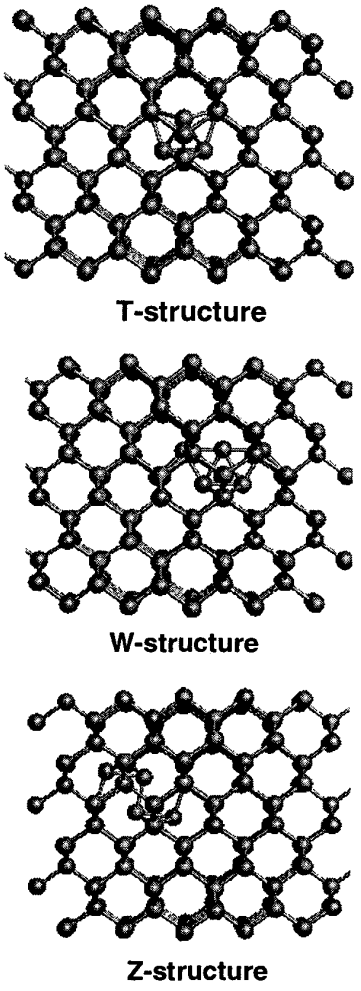

Figure 3: Stable configurations for the di-interstitials obtained by using conjugate-gradient geometry optimization scheme for tight-binding Hamiltonian model potential. Named here, T-structure (upper), W-structure (middle), and Z-structure (lower).

Table 1: Di-interstitial silicon binding energy values calculated by several atomic potentials.

Model	Cell-size	E_{bin} (eV)
TB	64	2.75
TB	216	2.20
LDA	72[4]	2.02
LDA	120[4]	1.78
Stillinger-Weber[5]		1.60

formation energy is 5.64 eV calculated by using 216(+2) atom supercell. W-structure gives the formation energy of 6.07 eV. Z-structure which gives mid-range formation energy, and is appeared as the most stable configuration for the Stillinger-Weber potential model. Relative energy levels for T, W, and Z configurations were confirmed by *ab inito* LDA calculation. Among these stable configurations, the W-structure was found to be a key for figuring out the di-interstitial diffusion behavior.

Using a restricted geometry optimization scheme (saddle point search scheme[9]), it was found that the T-to-W transition needs about 0.96 eV to overcome the barrier energy, while the W-to-W transition has a barrier energy of less than 0.1eV (Fig. 4), so it acts as it was an occasional superhighway on the migration path. Therefore, the di-interstitial can exhibit a long range hop via the W-W transition which is initiated thermally by the T-W transition.

Calculated di-interstitial binding energies (E_{bin}^{I2}) are summarized in Table 1.

The value of about 2 eV indicates that a fair number of di-interstitials would appear for high supersaturations of excess interstitials, such as during the transient enhanced diffusion (TED) case. Preliminary simulations have been performed incorporating mobile di-interstitials assuming the reaction model shown in Table 2.

One possibility is that di-interstitials, assumed to be highly mobile, may reconcile the inconsistency in surface recombination rates (K_I^{surf}) between the OED ($D_I/K_I \approx 20\mu m$[13]) and TED ($D_I/K_I \approx 0.1 \sim 0.01\mu m$[14]) cases, assuming that the di-interstitial undergoes fast annihilation on the silicon {100} surface where the regrowth step prefers the dimers[12]. In this case, however, the mobility of BI_2 may also be of interest for exploring further the impact on conventional diffusion models.

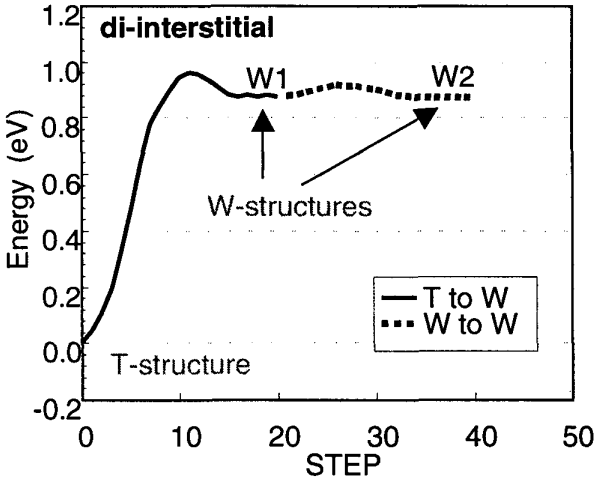

Figure 4: Calculated energy barrier along the typical di-interstitial migration pathway based on the tight-binding Hamiltonian model.

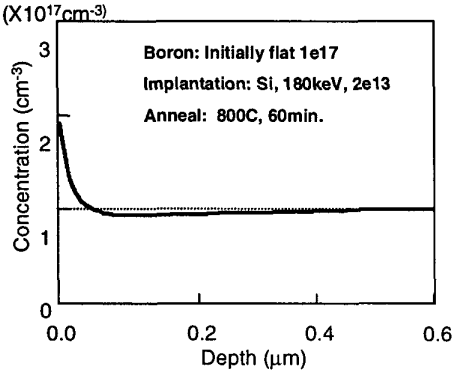

Figure 5: A tentative simulation result for boron redistribution incorporating mobile di-interstitials. This calculation model assumes $D_I/K_I = 20\mu m$ and $D_{I2}/K_{I2} = 0.01\mu m$. In order to obtain sufficient boron pile-up for reproducing the reverse short channel effect, the model requires $D_{BI} \approx D_{BI2}$.

Table 2: A set of the hypothetical reactions in the model for calculating the data in Fig. 5.

$$I + I \Leftrightarrow I_2$$
$$I \Leftrightarrow I_{Cluster}$$
$$I_2 \Leftrightarrow 2I_{Cluster}$$
$$B + I \Leftrightarrow BI$$
$$B + I_2 \Leftrightarrow BI_2$$

IV. SUMMARY

Molecular dynamics simulations were performed for the crystalline silicon containing a di-interstitial silicon, based on the semi-empirical tight-binding Hamiltonian which was reasonably parameterized with *ab initio* LDA calculation. The simulation results show that di-interstitials diffuse into crystalline silicon as fast as single(mono)-interstitials. A possible mechanism for di-interstitial migration was discussed by evaluating barrier energies among several stable configurations. Some aspects for the dopant diffusion model were presented regarding mobile di-interstitials.

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