

Hydrogen Diffusion in Si: A Tight-Binding Molecular Dynamics Study

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We present the tight-binding molecular dynamics simulation of hydrogen diffusion in Si for $600 < T < 1600\text{K}$. The diffusion path and diffusion mechanism are observed during very long simulations. Temperature dependence of the self-diffusion coefficient of H atom in the present study is in good quantitative agreement with an earlier study by Panazarini and Colombo[1]. Our calculations indicate that the hydrogen moves via hopping between the positions 1\AA distant from a Si atom along a Si-Si bond. The hydrogen self-diffusion thus occurs through sequences of single hops, which is in contrast to the previous studies that have shown long hops to be the responsible for the diffusion at $T > 1000\text{K}$.

Key words: tight-binding method, molecular dynamics, hydrogen diffusion

1. INTRODUCTION

Hydrogen in semiconductors has been a long-term issue in solid state physics. Its importance is related not only to that hydrogen plasma has been used in the fabrication processes of Si crystals or III-V compounds, but also to the strong effects on optical and electrical properties of semiconductor materials. Also it is proved that hydrogen in crystal makes the speed of crystal growth increase. Although many researches have been performed to determine the rate of diffusion of hydrogen in crystalline silicon, the precise value of the rate has not yet been known. The diffusion constant depends strongly on temperature, not necessarily in a perfect Arrhenius manner. That is because diffusion tends to be influenced by collective effects, low temperature quantum effects, impurities, defects, etc. Hence a precise determination of the diffusion parameters is extremely difficult in experiment. The purpose of this work is to clarify the diffusion path of a hydrogen atom in Si crystal and its mechanism using tight-binding molecular-dynamics simulations.

2. MODEL OF ANALYSIS

We have calculated the hydrogen self diffusion in Si crystal over a wide range of temperatures ($600 < T < 1600\text{K}$) using tight-binding molecular dynamics (TBMD) method. TBMD is a simulation scheme where the interatomic forces governing the atomic trajectories are derived from the underlying electronic structure of the simulated system through the Hellman-Feynman theorem.

In the present work we adopt the tight-binding parameter given by Bowler *et al* [2]. We use periodically repeated cubic supercell containing 64 Si atoms with a H atom. The equation of motion for each atom is integrated using the velocity-Verlet

algorithm with the time step of 0.483fs. The diffusion mechanism and paths at 600K, 800K, 1000K, 1400K, and 1600K are observed during 150ps for each temperature. Figure 1 depicts the initial positions of atoms in the MD cell.

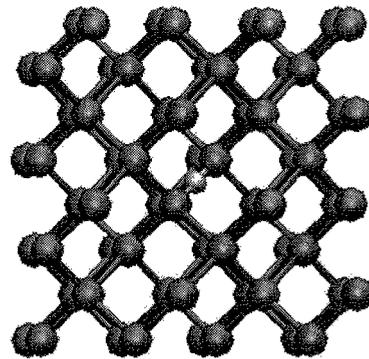


Fig. 1 Projected view of model system: Sixty-four Si atoms and one H atom.

3. DIFFUSION COEFFICIENT

In this section we discuss the temperature dependence of self-diffusion coefficient of hydrogen atom in Si crystal. First, we monitor the mean square displacement (MSD) of a hydrogen atom at each temperature to investigate microscopic mechanism of hydrogen diffusion. Figure 2 shows MSD of the hydrogen atom in various temperatures.

In Fig.2(a), we observe the hydrogen does not diffuse at 600K. At $T=800\text{K}$ it is found that the hydrogen begins to hop at certain moments. It is shown that the hydrogen resides at stable position for a while, and then it hops to another stable position. The same diffusion mechanism can also be observed in Fig.2(c) and (d),

but the frequency of hopping is higher as the temperature increases.

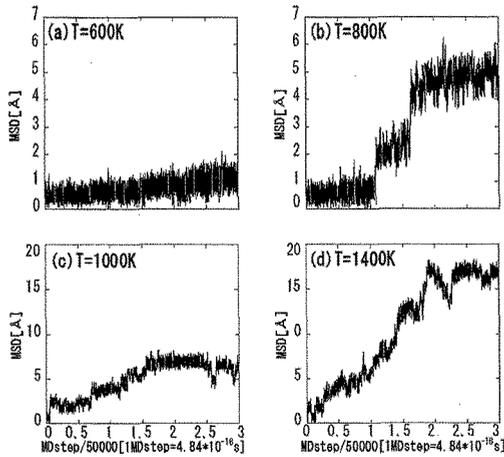


Fig. 2 Mean-square displacement of H in Si crystal at T=600,800,1000,1400K

Figure 3 shows the self-diffusion coefficients of hydrogen atom, as a function of inverse temperature, in the present study together with experimental data. In the present calculation, the diffusion coefficient is calculated from the relation,

$$D(T) \cong \frac{MSD}{6\Delta t},$$

where Δt is the relevant time period in the measurement of MSD.

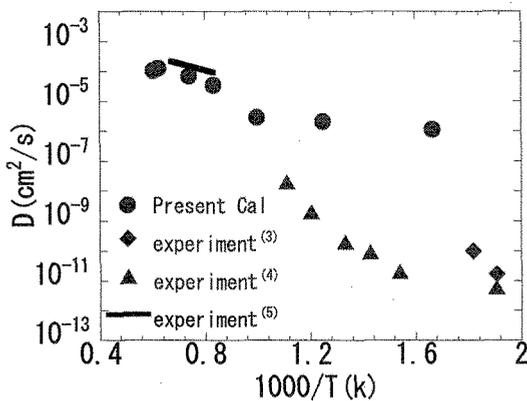


Fig. 3 Self-diffusion coefficient for hydrogen atom. Black circles: present calculation. Other symbols: experimental data from Refs.[3-5].

Table 1 Activation energy for H diffusion

	$D_0(\text{cm}^2\text{s}^{-1})$	$E_A(\text{eV})$
Present Cal	1.51×10^{-3}	0.42
Experiment[5]	9.41×10^{-3}	0.48

It is shown that our results are in good agreement with the experimental results for the higher temperature domain ($T > 1000\text{K}$). The activation energy for hydrogen diffusion is also estimated from the Arrhenius's formula. The present value of activation energy agrees reasonably well with the experimental result for high temperature. However, the differences between our results and experimental data are seen in the low-temperature domain. Experimental measurement of hydrogen diffusion at low temperatures is in general influenced strongly by the presence of defects, whereas we do not consider the influence of the defect in the present simulation. Another group claimed [6] that the mechanisms of diffusion below and beyond $T=1000\text{K}$ were different from each other. Our results indicate, on the other hand, that the diffusion coefficient of hydrogen obeys a single Arrhenius's plot, indicating that microscopic mechanisms of hydrogen diffusion are the same in all temperature domains studied here.

4. MICROSCOPIC ANALYSIS OF HYDROGEN DIFFUSION

In this section we discuss microscopic analyses of hydrogen diffusion. First, we observe correlation function of hydrogen displacement as a function of time [6].

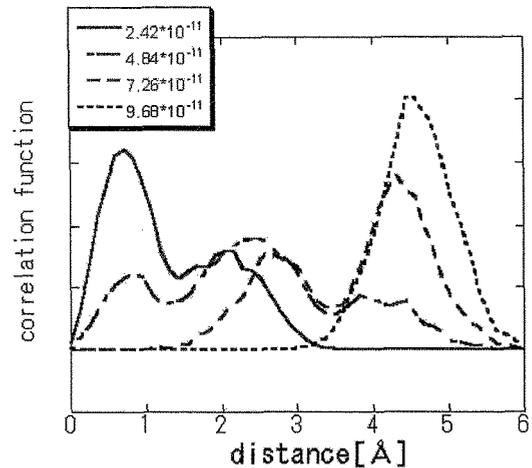


Fig. 4 Correlation function at 800K as a function of distance for four different correlation times: 24.2 ps, 48.4 ps, 72.6 ps, and 96.8 ps.

A physically appropriate characterization of single-atom motion can be provided by the correlation function that gives the probability of finding a particle at r at time t given that it was at the origin at $t=0$. At short time, single hops dominate the motion. As the time increases, the particle moves on further away. Moreover, figure 4 shows that some peaks exist in certain distances other than the nearest-neighbor site. It is thus evident that the diffusive motion proceeds via a sequence of single jumps (to a reasonable approximation). The results for higher temperatures domain show almost same as those for 800K.

Next, we observe time evolution of distance between H atom and the four nearest Si atoms. Figure 5 depicts distances between these Si (the 12th, 57th, 58th, and 59th) and the hydrogen at 800K. Figure 6 shows schematically the hopping path in the hydrogen diffusion.

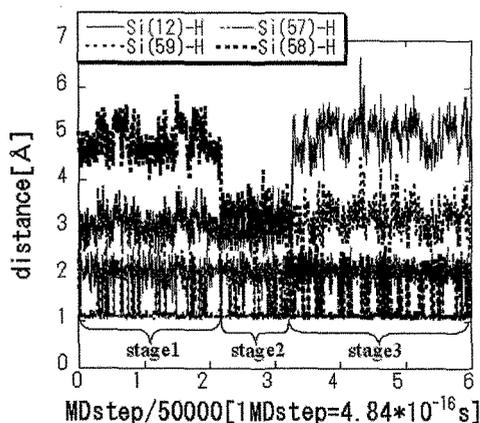


Fig.5 Distance between Si (the 12th, 57th, 58th, and 59th) and the hydrogen at 800K.

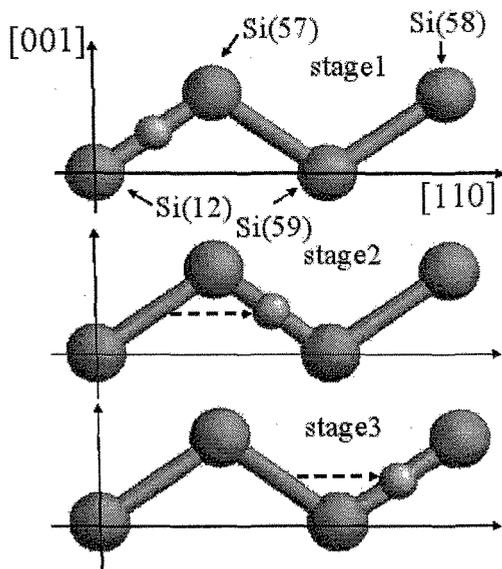


Fig.6 Schematic pictures of the hopping sequence in the hydrogen diffusion.

In the stage 1 of Fig. 5 and 6, it is shown that hydrogen is closest or secondarily closest to 12th or 57th Si atom. It keeps about 1 Å distance from itself to one of the Si atoms (the 12th and 57th), and moves around the stable points. In the stage 2, the hydrogen hops to the position that is 1 Å apart from the atom of 57th or 59th Si. Subsequently, in the stage 3, it jumps to another position close to the atom of 59th or 58th Si. It is thus shown that the H diffusion is performed by a

series of single hops. Such a diffusion mechanism is seen also in higher temperatures. As temperature increases, the “resident time” of hydrogen becomes short and it hops to the positions nearly continuously.

Next, we observe the hydrogen trajectory obtained at 800K for 150ps. Figure 7 shows the initial position of Si and the hydrogen trajectory. It is shown that hydrogen is moving in the [110] direction and is hardly moving in the [001] direction. This is equivalent to the result of Fig. 6. When the hydrogen immigrates into the stable position on Si-Si bond, the bond between Si atoms is stretched due to partial breakage by the hydrogen atom. When the hydrogen moves out from the position to another, the bond is recovered to the original length. Similar behavior can be observed at higher temperatures domain. We thus conclude that the hydrogen self-diffusion is performed via a sequence of single hops.

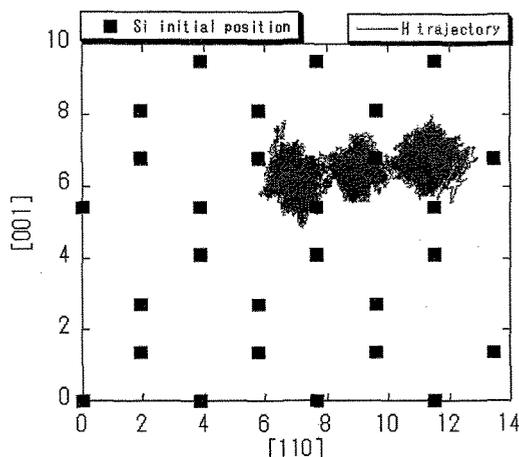


Fig.7 Hydrogen trajectory at T=800K during a 150ps long simulation. Si lattice is represented in its initial position.

5. CONCLUSION

The mechanism of self-diffusion of atomic hydrogen in Si crystal is analyzed using tight-binding molecular-dynamics simulation. The mean-square displacements, the diffusion coefficients, and the correlation functions of hydrogen displacement, etc. are calculated to characterize the microscopic mechanism of hydrogen diffusion. It is shown that our simulation reproduces experimental values of the diffusion coefficients in higher temperature domain.

The diffusion path is observed as a sequence of single hops between the nearest stable sites that are on Si-Si bonds and about 1 Å from one of the Si atoms. Our calculation is in contrast to the previous study claiming that the higher diffusion coefficients in the high temperature domain than those in the lower domain are attributed to different hopping mechanisms such as those due to long-range jump in a single hop.

The present study indicates that such a diffusion mechanism may be responsible for the lower temperatures, and may lead to the higher diffusion coefficients, than those reported experimentally. More accurate measurements in experiment at these temperatures are thus desired.

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The visual analyses for atomic configurations and trajectories in the present study have been performed on our immersive virtual-reality system, consisting of an SGI Onyx300 and a 60inch video projector by BARCO, equipped at the Graduate School of Natural Science and Technology of Okayama University, Japan.

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