First-principle Study for Neutral Indium Migration in Silicon

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ABSTRACT

In this paper, we report our *ab-initio* calculation on total energy, minimum energy path, and migration energy for kinetic Monte Carlo (KMC) modeling of the indium diffusion in silicon substrate. Stable configurations during indium diffusion were obtained from the calculation of the total energy and the estimation of minimum energy path (MEP) with nudged elastic band (NEB) method. After finding the MEP, the energy barrier for the diffusion of Indium particle was found to be approximately 0.8 eV from the calculation of the total energies at the minimum and transition state.

Keywords: Indium, *Ab-initio*, Migration energy, Minimum energy path

1 INTRODUCTION

As CMOS devices are scaled down to nanometer regime, it is even more stringent to control the impurity profiles at the front-end process. Especially, the necessity for ultra shallow junction in nano-CMOS technology pushes the emergence of a novel alternative material technology with low diffusivity coefficient and less activation energy for the impurity doping process. Recently, indium has been attracting a great deal of interest as a candidate for a p-type dopant, especially for the fabrication of a retrograde p-tub as well as a halo region for n-channel FETs. In other words, indium has been considered to be an alternative to a boron atom due to its relatively heavier mass. Nevertheless, we do not understand the exact diffusion mechanism including diffusion parameters when we compared to the case of boron.

Indium is considered to diffuse mainly through the interstitial-mediated mechanism during the thermal annealing process. Recently, kinetic Monte Carlo (KMC) method has been widely employed for the modeling of thermal annealing process in nano-CMOS devices. It is needed to employ the KMC method to simulate the diffusion of indium atoms at an atomistic scale. However, we do not have enough parametric values in the art to perform the KMC calculation. Therefore, we performed *ab-initio* calculations in an effort to obtain the parameters such as the input parameters of a migration event, one of the main events in thermal annealing.

In this work, we investigated the atomic-scale diffusion mechanism and tried to find a minimum energy path (MEP) of indium diffusion for the acquisition of the migration energy in silicon via *ab-initio* calculations and transition state theory tools. Our theoretical study allowed us to have a good insight on the understanding of the indium diffusion and contributed to the KMC modeling of indium atoms, which are quite new in semiconductor industry.

2 DIFFUSION PATH

First of all, we performed a defect structure calculation in a cubic super-cell, comprising 216 silicon atoms with a single neutral indium atom. The *ab-initio* calculations were implemented within density functional theory (DFT) with VASP (Vienna *Ab-initio* Simulation Package) [1-3] which combines ultrasoft pseudopotentials [4] and generalized gradient approximation (GGA) in the Perdew and Wang formulation. In this work, we employed a cutoff energy of E_c = 150.62 eV, and a 2 × 2 × 2 grid for the *k*-points mesh of Monkhorst-Pack [5], and a 3 × 3 × 3 simple cubic super-cell (216 atoms).

In this work, we initiated our *ab-initio* study with an assumption that the energy landscape of indium in silicon is quite similar to that of boron because both species have the same number of valence electrons. Therefore, we calculated the energy for a specific defect configuration of indium in silicon from the recognition that indium will have a similar defect configuration to the boron configuration, correspondingly [6, 7].

Table 1: Energies of the Si:In defect configurations from VASP calculations: Relative energy values are referred to the respective ground-state configuration, $In_s + Si_i^{Td}$.

Configuration	Relative energy [eV]
InSi-X	46.11
InSi-S	58.09
In_i^{Td}	0.43
$In_i + Si_i^{Td}$	0.00
In_i^{Hx}	1.63

In Table 1 is shown a list of a defect configuration of indium, which we can guess from the knowledge of the boron atoms. The calculated energy values for each defect configuration are also shown in Table 1. The energy values are adjusted with reference to the ground state of indium.

Firstly, our *ab-initio* calculation revealed that the lowest-energy configuration of indium is (In_s + Si_i^{Td}), which means that indium atom sits on a substitutional site and stabilizes a silicon self-interstitial in a nearby tetrahedral position while the second lowest-energy structure is found to be In_i^{Td}. It should be noted that the second lowest energy configuration (In_i^{Td}) of indium is different from the case of boron [8].

Our *ab-initio* calculation produced a energy gap between the ground-state In_s + Si_i^{Td} and the next higher energy level In_i^{Td}, which is 0.43 eV. In addition, we can think of a couple of dumbbell configurations, InSi-X and InSi-S. The InSi-X consists of a silicon self-interstitial and a indium atom sharing the same lattice site, with the Si-indium dimer lying in the <110> direction. Furthermore, we use the notation of InSi-S if the Si-indium dimer lying in the <100>.

Since the energies of the above-mentioned dumbbell configurations, consisting of silicon self-interstitial and an indium atom sharing the same lattice site, are found to be 46. 11 and 58.09 eV, respectively, we can conclude that indium does not constitute such kind of dumbbell configurations during the diffusion process. It is well known in the literature [8] that the diffusion path of boron is:

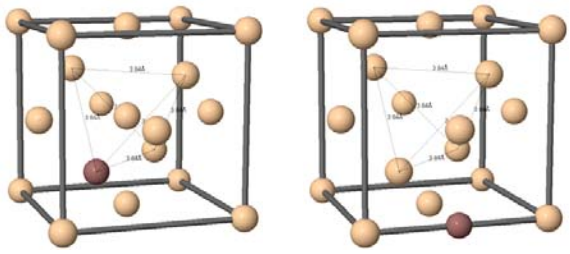
$$B_s + Si_i^{Td} \rightarrow B_i^{Hx} \rightarrow B_s + Si_i^{Td}.$$

However, we can conclude that the diffusion path of indium is different from that of boron due to the afore-mentioned reasons. In other words, our *ab-initio* calculation revealed that the diffusion path of neutral indium is thought to be as the following.

$$In_s + Si_i^{Td} \rightarrow In_i^{Td} \rightarrow In_s + Si_i^{Td}.$$

In addition, the contribution of In_i^{Hx} does not seem to be considerable to the diffusion of indium when we compare with the diffusion path of boron. We can recognize that the energy level for the In_i^{Hx} state is 1.63 eV, which is relatively higher than the second energy level In_i^{Td}, 0.43 eV.

Fig. 1(a) is a schematic diagram illustrating the atomic configuration in the three-dimensional lattice site for the ground state In_s + Si_i^{Td} wherein the indium is placed at the silicon site in a substitutional manner. The substituted indium is represented by a dark-colored sphere while the silicon atoms are denoted by light-colored spheres. Now, the indium atom at the ground state experiences a transition to a second level state, In_i^{Td}, as illustrated in Fig. 1(b). We can notice that indium atom is now positioned at the tetrahedral site in accordance with the diffusion route.



(a) (b)

Fig. 1. Defect configurations: In atoms (dark radius), Si self-interstitial (light radius) are shown over the underlying diamond lattice. The In_s + Si_i^{Td} (a) and the interstitial In at the tetrahedral position, In_i^{Td} (b) are shown.

During the theoretical calculation on the energy level for a specific transition state, we found that the calculated energy level when the indium atom is located at the middle point along an edge of a cubic cell is different from the one calculated when the indium atom lies at the center of a cubic cell by an amount of 0.02 eV. We would like to make a comment on this numerical issue at this point since there may exist a technical limit of size of the super cell in the ab-initio calculation. As we mentioned earlier, the size of our super cell comprised 216 atoms including the indium ion. Due to the limit of the number of atoms employed in the ab-initio calculation, a lattice point in a certain unit cell can be erroneously regarded as a different lattice point even if the lattice point in question is exactly the same lattice point from the standpoint of the adjacent unit cell.

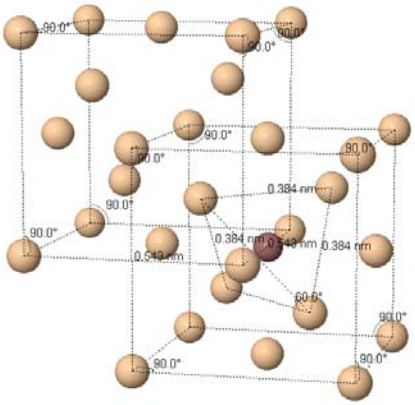


Fig. 2. Another position of tetrahedral site in the cubic unit cell. In atom (dark radius) in the middle of edge is located in body center of other unit cell.

Fig. 2 is a schematic diagram illustrating the above explanation in detail. The dark-colored sphere can be considered to be positioned at the center of a unit cell while it can also be regarded as being located at the middle of the edge of a nearby unit cell. If the indium atom experiences a transition to the body center in the same unit cell, the indium atom should be switched to the silicon self-interstitial in the tetrahedral site (Si_i^{Td} of In_s + Si_i^{Td}) because

the silicon atom is located at the body center. We believe that the indium atom diffuses to the tetrahedral site at the middle of edge because the energy barrier of diffusion path for the switching mechanism is relatively high.

3 MINIMUM ENERGY PATH

Now, we estimated minimum energy path and migration energy with reference to on our diffusion path described in the previous section through VASP and transition state theory (TST) tools. In order to find the migration energy for indium diffusion, we had to calculate a minimum energy path (MEP). In this work, we employed the nudged elastic band (NEB) method [9] for the calculation of MEP, which is the optimization procedure for a number of intermediate images along the reaction path. Each initial image is forced to converge to a possible lowest energy with keeping the spacing to the neighboring images constant. We believe that the NEB is an efficient method to find a saddle point and minimum energy path between the given initial and final states during the diffusion.

In the previous section, we found that the initial state is $In_s + Si_i^{Td}$ while the final state is In_i^{Td}. Repeating the transitions between those two states, the neutral indium diffuses in silicon. Consequently, we can now obtain the energy barrier for indium migration if we investigate the MEP from the initial state to the final state.

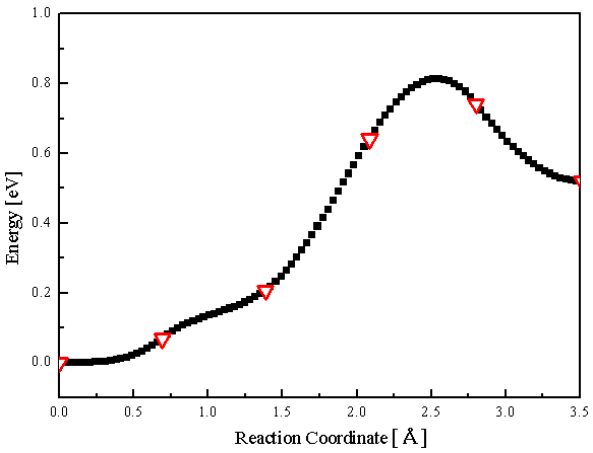


Fig. 3. The relative energy along the MEP of Si:In from $In_s + Si_i^{Td}$ to In_i^{Td} by nudged elastic band method. The triangle indicate the simulation images and the square line is interpolation by using the force parallel to the band.

Figure 3 is a diagram illustrating the calculated minimum energy path for indium via the NEB method with four intermediate images. The initial intermediate images, denoted with triangles, are linearly interpolated between the initial and final images. Along the y-axis is shown the relative energy along the MEP of Si: In from the initial state ($In_s + Si_i^{Td}$) to the final state (In_i^{Td}). The interval between the initial intermediate images is interpolated with reference to the force being calculated during the simulation. In order to obtain an estimate of the saddle point and to sketch the MEP, it is important to interpolate between the images of the converged elastic band [9]. The energy and force of converged elastic band is shown in Fig. 4.

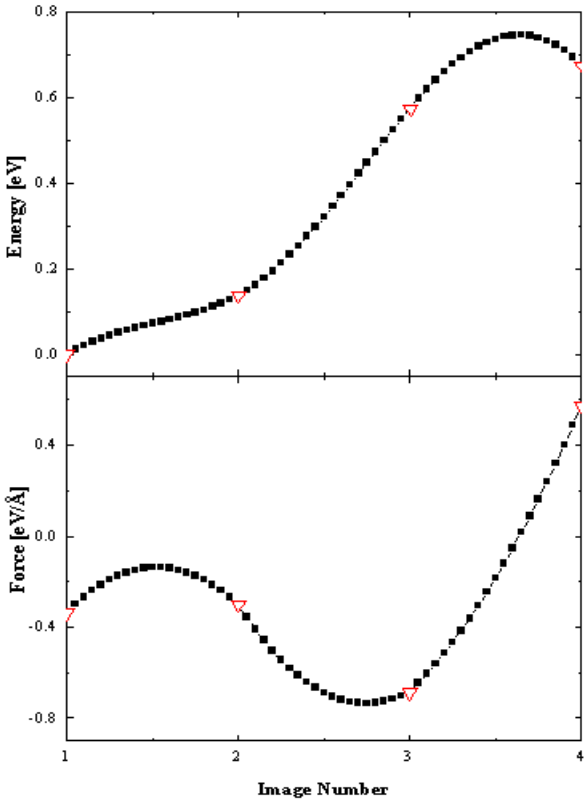


Fig. 4. The energy and force of interpolation between the intermediate images (square line): The force parallel to the band is used information for the interpolation.

Referring to Fig. 4, the relative energy tends to exhibit a positive slope when the force is negative, while the relative energy decreases when the force is positive. The migration energy is now estimated as an energy difference to experience a transition from a local energy minimum state to another local minimum along the diffusion path. Our simulation revealed that the migration energy of In-interstitial defects is approximately 0.8 eV, which is in good agreement with prior report [7]. It is believed that the migration energy of indium can be spun in the range between 0.5 – 1.2 eV.

4 CONCLUSION

In conclusion, we report our theoretical study on the activation energy for the diffusion of indium as well as minimum energy path. We were successful in finding out the migration path of the interstitial-mediated mechanism. *Ab-initio* study in this work comprises steps of performing

the electronic structure relaxation and obtaining its total energy at the local minimum. We could come up with the atomistic configurations and migration energy during indium diffusion in silicon, wherein we tried to find out saddle points from a minimum and reaction pathway between those two stable states by using TST. After we found the transition state, we tried to get the energy barrier for diffusing the particle through the calculation of the exact total energy at the transition state. We could also realize that the parameter extraction for In-related defects can be essential for exact modeling of the experimental diffusion profiles in the manufacture of the next-generation CMOS devices.

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