Diffusion and Clustering in Heavily Arsenic-Doped Silicon: Discrepancies and Explanation

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Very different concentration dependences of As diffusivity in heavily doped silicon have been observed, but a consistent explanation of the underlying atomic-scale process is lacking. We present an extensive first-principles study on the As-vacancy interactions in heavily doped silicon in terms of which we have explained quantitatively the driving mechanism of the observed enhanced diffusion and revealed the *time dependence* of the redistribution of dopant atoms. By checking the details of As-vacancy interaction potential and the *time dependence* of diffusion and clustering, we find that the discrepancies between different experiments and between different atomistic simulations eventually disappear.

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The redistribution of dopant atoms, e.g., diffusion and clustering, in heavily doped Si has been of great interest for many years. Early experiment carried out by Fair and Weber (FW) [1] showed that the diffusivity of As increased with the dopant concentration, and then decreased for As concentrations greater than 3×10^{20} cm^{-3} at the temperature of 1000 °C (Fig. 3 in Ref. [1]). Different from the above results, the later work of Larsen *et al.* [2] clearly showed a steep increase of the diffusivity of As for dopant densities exceeding 2×10^{20} cm^{-3} using rapid thermal annealing at the temperature of 1050 °C (Fig. 3 in Ref. [2]). More recently, Solmi and Nobili (SN) [3] investigated the concentration dependence of the diffusivity of As and P upon furnace annealing at temperatures between 900 and 1050 °C. The concentration of doped As was up to 3×10^{21} cm^{-3}. Their results (Fig. 3 in Ref. [3]) demonstrated that the diffusivity of As at 1050 °C increased with dopant content up to 3.5×10^{20} cm^{-3}, and then was kept nearly constant for higher concentrations. This is different from both of the above two measurements. On the other hand, the diffusivity of As at 900 °C decreased for concentrations exceeding 2×10^{20} cm^{-3}, which was contrary to the results of Larsen *et al.* but in agreement with the early measurement of FW. No attempt has been made thus far to clarify such discrepancies.

In order to understand the dopant diffusion in heavily doped Si, Mathiot and Pfister (MP) [4] proposed a "percolation" model, in which an "infinite" cluster of As atoms in the fifth neighbor positions from each other exists in Si lattice, when the As concentration exceeds 2.5×10^{20} cm^{-3}. In this cluster, a third neighbor position from a given As atom is also a second neighbor position from another As atom, and as a consequence the vacancy (V) can freely diffuse from one impurity atom to another due to the lowering of the migration barrier. The percolation model was employed to explain the observed enhanced diffusions of As and P in heavily doped Si [2]. However, the diffusion was explicitly assumed via the simple vacancy-exchange mechanism without considering any details of the interaction potential between As and vacancy. Later, Ramamoorthy and Pantelides (RP) [5] pointed out that this model was not consistent with the fact that enhanced diffusion causes As clustering with vacancies. Such clustering would break up the percolation network into high concentration patches and halt enhanced diffusion. They suggested a *mobile* As_2V complex to explain the enhanced diffusion.

Atomistic simulations have also given divergent results. Dunham and Wu [6] obtained a good agreement with the experimental results of Larsen *et al.* [2], i.e., the diffusion of As is enhanced at high concentrations, using the lattice Monte Carlo method. They assumed a simple attractive dopant-vacancy potential which decreased linearly with the dopant-vacancy separations. Very recent work carried out by List and Ryssel [7] using the same method showed that the observed enhanced diffusion of As cannot be reproduced by employing attractive dopant-vacancy potentials. They attributed the discrepancies between their results with that of Dunham and Wu to the much shorter simulated diffusion times used in the work of later authors. Good agreement with experimental results could be obtained, however, with a model using a nonbinding As-vacancy interaction. This is clearly in contradiction with the results of all previous *ab initio* calculations [8–10] which showed that As indeed attracted vacancy with a binding energy of about 1.2 eV.

In this Letter, we present an extensive first-principles study of the As-vacancy interaction in terms of which we obtain a consistent explanation of the diffusion and clustering in heavily As-doped Si. We find that the interaction between As and vacancy is affected by other As atoms located as far as the ninth neighbor sites. The redistribution of As is greatly accelerated when two As atoms sit at the fifth or sixth neighbor sites with each other, which confirms and extends the percolation theory. This enhanced diffusion lasts only a short period of time accompanied with the formation of As_2V complexes. Contrary to the previous work of RP, we find that the As_2V complex is less *mobile* due to its high migration barrier. By checking the details of the As-vacancy interaction potential and the specific experimental conditions, we find that all of the discrepancies between different experiments and different atomistic simulations mentioned above actually disappear.

The calculations were performed using the *ab initio* pseudopotential plane wave method [11]. The ground state total energy was obtained within density functional theory in the local-density approximation to the exchange-correlation energy functional [12,13]. Nonlocal and norm-conserving pseudopotentials constructed by the scheme of Hamann [14] were used to describe the valence electron interactions with the atomic core. A periodic supercell with 64 atomic sites was employed to model the considered system. The integration of **k** points over Brillouin zone (BZ) was performed by summing a $2 \times 2 \times 2$ mesh in the first BZ. The kinetic energy cutoff of the plane wave basis is taken as 12 Ry. Atomic relaxations were considered to the point where the magnitude of the calculated Hellmann-Feynman forces on each atom was smaller than 1 mRy/bohr. Tests for bulk Si gave a lattice constant of 5.40 Å which is 0.5% smaller than the experimental value. Tests for defects gave a 3.57 eV of formation energy for a single vacancy in Si and a 1.21 eV of binding energy of the AsV pair, which are both in good agreement with the experimental measurements [15–17]. The convergence of the **k** point summation and the kinetic energy cutoff were checked by using a $4 \times 4 \times 4$ mesh in the first BZ and a 16 Ry energy cutoff. The results of the binding energy and the formation energy of the AsV pair differed by less than 0.1 eV, which gives an estimate of the accuracy of the calculation. Details of the calculation of formation energy for the AsV complex can be found in Ref. [10]. As in other *ab initio* calculations [5,8], we neglect the spin polarization and the correction to long range dipole interactions between neighboring cells which have a very small effect on the results of our calculations.

Figure 1 shows the distribution of atomic sites in the sixfold rings in Si crystal. As pointed out by MP, when two As atoms are fifth neighbors, the third neighbor of one As atom would be a second neighbor of the other. However, it can be seen in Fig. 1 that the second neighbor of As is also the first neighbor of another As at site 5. The vacancy does not need to pass over the third neighbor site of arsenic as considered by MP [4]. The easiest way for a vacancy diffusion from the first neighbor of As to another As located at sites 5 is along the path 1-2-5. At the same time, the third neighbor of As can be the first neighbor of another As at 6. The range of interaction between the AsV pair and another As can be extended at least up to the ninth neighbor sites of As, since the third neighbor site of one As is the second neighbor site of another As at site 9. The percolation network is therefore greatly extended.

The potential diagram for a vacancy migration from site 1 to 5 with and without another As at site 5 is shown in Fig. 2. It can be seen that, for a single AsV pair (another As is far away from AsV pair), the vacancy first overcomes an energy barrier of 0.92 eV (0.84 plus 0.08) arriving at a second neighbor site of As. It then passes over another barrier with a height of 0.46 eV going to site 5. Once a second As atom sits at site 5, the diffusion of vacancy from site 1 to 2 is from one first neighbor site of As to another first neighbor site of As at site 5. The total energy is lowered by 0.31 eV compared with the single AsV pair (another As is far away from the AsV pair). The migration barrier for this process is just 0.10 eV, significantly smaller than that of 0.92 eV for vacancy moving from site 1 to site 2 without another As at site 5. The energy barrier for As-V exchange is 0.45 eV in the case of vacancy moving from site 2 to site 5. The total energy increases by 0.20 eV after As-V exchange. The highest migration barrier for the whole process is 0.45 eV. The calculated formation energy E_f and the migration energy E_m for a single AsV pair are 2.37 and 1.19 eV, respectively. Here E_m is different from the migration barrier of 1.30 eV shown in Fig. 2 since the diffusion of As will take place once the vacancy overcomes the third neighbor site of As (for details, see Refs. [9,10,15,18]). The corresponding activation energy Q for the AsV pair is 3.56 eV. When another As atom is located at site 5, the formation energy for this AsV-As(5) complex is 2.06 eV. The obtained activation energy is 2.51 eV which is 1.05 eV lower than that of 3.56 eV for a single AsV pair. The 1.05 eV decrease of the activation

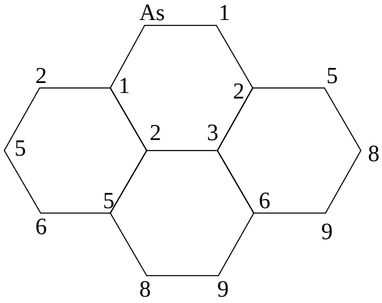

FIG. 1. The distribution of atomic sites around As in the sixfold rings. The first neighbor sites are denoted by 1, second by 2, and so on. The fourth and seventh neighbor sites are out of the plane.

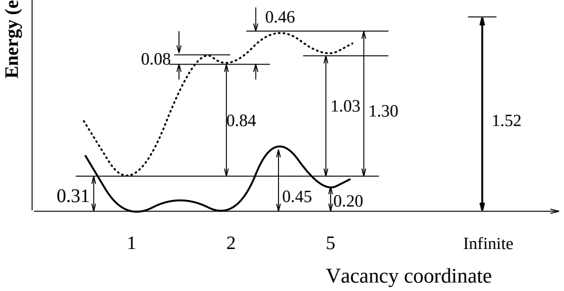

FIG. 2. Potential energy diagram for As-V as a function of As-V separations with (solid line) and without (dashed line) another As atom at the fifth neighbor site of As.

energy is in excellent agreement with the value of 1 eV obtained by Larsen *et al.* [2] from fitting the experimental results. The activation energy is also very close to the 2.7 eV of the formation energy of an As_2V complex calculated by RP who attributed the enhanced diffusion of As to the fast migration of As_2V. Later, we will show that As_2V is less mobile in Si because of its high migration barrier.

The standard percolation model requires that each As atom has another As atom at its fifth neighbor and forms an infinite network. This corresponds to a rather high dopant concentration if the distribution of As is uniform. Estimation of RP showed that the percolation cannot occur even for dopant concentration as high as 10^{21} cm^{-3}, while the reported threshold for the steep increase of the diffusivity is 2.5×10^{20} cm^{-3}. In real cases, the fluctuation of doping makes percolation possible in some high concentration patches. However, it is more likely that As has another partner at atomic sites farther than fifth neighbor. Figure 3 shows the calculated As-V interaction diagram with and without another As at sites 6. The diffusion path of vacancy is along the atomic sites 1-2-3-6. Once the vacancy overcomes site 2, it goes quickly to site 3, which is the first neighbor of As at site 6 and the third neighbor of original As. The total energy for vacancy at site 3 is 0.10 eV lower than that of site 1. As-V exchange occurs when the vacancy passes over another barrier of 0.50 eV to site 6. The energy is increased by 1.41 eV if the vacancy goes infinitely away (here we take it as the twelfth neighbor of As). The highest energy barrier for this process is 0.61 eV, which is 0.74 eV lower than the 1.35 eV of no As atom at site 6 (dashed line) and 0.58 eV lower than the 1.19 eV migration barrier of a single AsV pair [10]. At the same time, the formation energy of such an AsV-As(6) complex is 2.17 eV and the activation energy is 2.88 eV, which are 0.20 and 0.68 eV lower than the corresponding value of an AsV complex, respectively. We also calculated the diffusion of vacancy along paths of 1-2-5-8 and 1-2-3-6-9. The highest energy barrier is 0.62 and 0.85 eV with another As siting at site 8 and site 9, respectively. Both are significantly lower than the 1.19 eV migration barrier of an AsV pair. Therefore, the diffusion of an As atom in Si will be greatly accelerated via vacancy mechanism once it sees its partner nearby. This can easily happen at the initial stage of annealing in heavily doped samples. As a consequence, more and more As_2V (or even larger As_mV) complexes will be formed since they have lower formation energies [5,19].

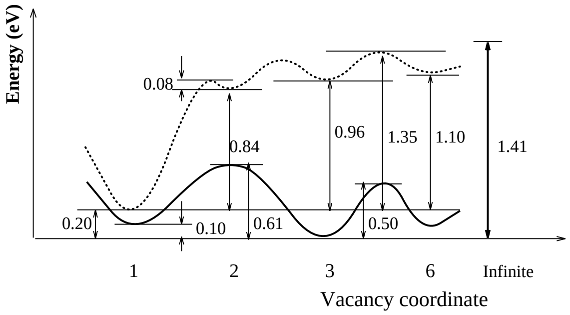

FIG. 3. Potential energy diagram for As-V as a function of As-V separations with (solid line) and without (dashed line) another As atom at the sixth neighbor site of As.

Ramamoorthy and Pantelides calculated the activation energy Q of As_2V by summing the formation energy (E_f) and the migration barrier (E_m) and found that it was 1.2 eV lower than that of AsV pair. They concluded that these As_2V complexes can migrate fast through the sample which resulted in the observed enhanced diffusion. However, a smaller activation energy does not definitely mean a fast diffusion due to the following reasons: (i) In equilibrium state, the diffusivity $D = D_0 \exp(-Q/k_BT) = D_0 \exp(-E_f/k_BT) \exp(-E_m/k_BT)$. The prefactor D_0 is determined by the jump frequency of the complex and the changes of entropy of the system. A different complex has a different D_0. (ii) It is easily shown that $Q(\mathrm{As}_4V) < Q(\mathrm{As}_3V) < Q(\mathrm{As}_2V) < Q(\mathrm{As}V)$ since the formation energy of the As_mV complex decreases about $E_b(\mathrm{As}V)$ whenever one more As atom joins the complex (in the case of $m < 4$). Here $E_b(\mathrm{As}V)$ is the first neighbor binding energy of an AsV pair. The formation energy of the As_mV complex becomes negative when $m > 2$ [5,19]. While the increase of the migration barrier is less than $E_b(\mathrm{As}V)$ because the vacancy needs only to move to the third nearest neighbor site of As in the same ring during diffusion. The net effect is that As_mV has a lower activation energy than $As_{m-1}V$ in the case of $m \leq 4$. The conclusion that the As_4V moves faster than As_3V, As_2V, and AsV derived from the value of activation energy is obviously not consistent with the diffusion experiments [1,3], where the $As_mV (m \geq 2)$ complexes were considered less mobile. *In fact, the smaller formation energy corresponds only to a high concentration at the equilibrium, while the mobility is determined by the migration barrier.*

In order to evaluate mobility of the As_2V complex, we calculate the potential energy diagram for vacancy moving around the sixfold ring. The results are shown in Fig. 4. The most stable configuration is As-V-As, in which both

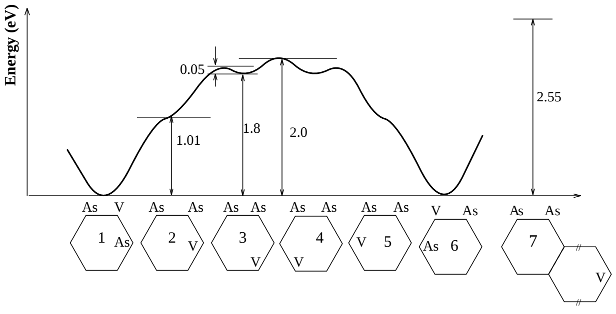

FIG. 4. Potential energy diagram of As_2V complex for vacancy migration in the sixfold ring.

As atoms are at their neutral threefold sites. The As-As-V configuration is not a stable state, the total energy is 1.01 eV higher than that of As-V-As. The migration path shown in Fig. 4 is equivalent to the migration sequence (abcd) in Fig. 2 of Ref. [5]. It can be seen in Fig. 4 that the migration barrier of the As_2V complex is 2.0 eV which is significantly higher than that of a single AsV pair (1.19 eV). With such a high migration barrier, the As_2V complex actually moves slowly in Si. This is in accordance with the conclusions of Refs. [1,3].

Up to now, we have obtained such a picture of As diffusion and clustering in heavily doped Si: At the initial stage of annealing, the diffusion of As is an accelerating process as more and more As dopants find their partners locating at the fifth or sixth neighbor sites. This process would not last for a long time since the As_2V complex will be formed quickly. Checking the reported enhanced diffusion [2], we find that the corresponding annealing time is 10 sec. This is fully consistent with our analysis. In the early experiment of FW [1], the annealing lasted for several hours. There will be a large number of existing As_2V, As_3V, or even As_4V complexes. The higher doping gives more of such less-mobile complexes, therefore, the diffusivity decreases when the doping concentration exceeds a maximum value. In the very recent experiment performed by SN [3], the annealing time was from 15 minutes to 1 hour for a heavily arsenic-doped Si sample [Fig. 1(a) in Ref. [3]]. During this period of time, the dominant defects would be As_2V complexes. That is why they did not observe the enhanced diffusion reported by Larsen *et al.* [2]. Although the As_2V complex moves slowly, it can still contribute to the diffusion of As at elevated temperature. Therefore, the observed diffusivity of As keeps constant when the doping concentration exceeds 3.5×10^{20} cm^{-3} at 1050 °C. When the temperature is lower, the diffusion of the As_2V complex is reduced due to its high migration barrier. That is the reason why the observed diffusivity of As undergoes a reduction for As concentrations exceeding 2×10^{20} cm^{-3} at 900 °C. The deactivation experiment of As [20] in heavily doped Si showed the average number of As atoms per complex (As_nV), $\overline{n} = 2.5 \pm 0.7$ after 15 sec of annealing and $\overline{n} = 3.2 \pm 0.8$ after 2 h of annealing. This clearly showed the *time dependence* of the clustering process. The time dependence of the diffusion and clustering also explains why Dunham and Wu [6] got the enhanced diffusion, using a short simulated diffusion time, while List and Ryssel [7] did not, using a long diffusion time. By looking at the potential diagrams of Figs. 2 and 3, it can be seen that vacancy actually experiences a "nonattractive" potential during its diffusion along 1-2-5 and 1-2-3-6. This explains why List and Ryssel got the observed enhanced diffusion using a nonattractive potential after a long simulation time. We note that the early experiment of FW [1] used an As-doped SiO_2 layer as the diffusion source to Si, while the later work of Larsen *et al.* [2] used Si samples doped by ion implantation. However, the very recent experiment of SN [3] also used Si samples doped by ion implantation, yet the observed diffusion behavior was quite different from that of Larsen *et al.* Therefore, it is the time dependence of the diffusion process and the dopant-defect interaction discussed above which play the essential roles.

In conclusion, we have provided extensive first-principles studies on the As-V interactions in Si. By checking the As-V interaction potential and the specific experimental conditions, we get a consistent picture with different diffusion experiments as well as atomistic simulations. The diffusion and clustering of As in heavily doped Si are *time-dependent* processes. The enhanced diffusion lasts a short period of time, then it slows down due to the manifestation of clustering. In contrast with the previous work of RP, we have found that the As_2V complex does not accelerate As diffusion in Si, the driving force comes from the extended percolation effect. Higher dopant concentration increases the diffusivity at the initial annealing stage, but also increases the possibility of forming less-mobile clusters. Therefore, a different annealing time gives a different concentration dependence of dopant diffusivity.

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