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Interaction potentials for vacancy-assisted As diffusion in silicon

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Abstract. A set of interaction potentials for vacancy-assisted As diffusion in silicon have been provided via first-principles pseudopotential calculations. Some important reactions such as $As + V \rightleftharpoons AsV$, $AsV + As \rightleftharpoons As_2V$, $AsV + V \rightleftharpoons AsV_2$, $As + As \rightleftharpoons As_2$ as well as $V + V \rightleftharpoons V_2$ are considered. The results demonstrate that an AsV pair can attract another As due to the binding between the As and the vacancy. It is found that the existence of another As atom nearby greatly reduces the migration barrier for a vacancy moving between the two As atoms. The AsV can also attract another vacancy. The binding force mainly comes from the binding of two vacancies, rather than from that of the AsV pair. The potential energy diagrams obtained provide insight into the dynamical process of As-dopant redistribution in Si and the input for future atomistic diffusion simulations.

1. Introduction

A fundamental factor in diffusion studies is the dopant diffusivity (D). Empirically it is found that D can be described by an Arrhenius equation $D = D_0 \exp(-Q/k_B T)$, where D_0 and Q vary with dopant species but are independent of temperature T. Experimentally D_0 and the activation energy Q are obtained by plotting $\ln D$ versus $1/T$ [1]. The D, D_0 and Q measured in this way include contributions from all possible diffusion mechanisms. It is widely accepted that dopant atoms diffuse in silicon with the assistance of point defects, i.e., vacancies and interstitials [2]. Although the surface thermal oxidation (injects self-interstitials) and nitridation (injects vacancies) provide useful tools for identifying the relative importance of the various atomic-scale diffusion mechanisms, the quantitative results are in fact obtained from fitting the diffusion profile by solving a set of macroscopic diffusion equations via numerical simulations [3]. The input of these numerical simulations relies on the understanding of the dopant–defect interactions. For example, the activation energies of AsV (V denotes a vacancy), AsI (I denotes a self-interstitial of silicon) and the SiI and SiV complexes used in reference [3] are taken from *ab initio* calculations [4]. In a lattice Monte Carlo simulation performed by Dunham and Wu [5], a dopant–vacancy interaction was simply assumed to linearly decrease with dopant–vacancy separation. The binding between dopant and vacancy vanishes at the fourth-nearest neighbours. The second- and third-nearest-neighbour binding were taken as 2/3 and 1/3 of the binding energy at the first-nearest site.

Very recently, List and Ryssel [6] carried out an atomistic analysis of the vacancy mechanism of dopant diffusion in silicon using a Monte Carlo method. They tested several very simple potentials: rectangular shaped, linear and Coulomb shaped ($1/r_{ij}$). It was found that the simulation results were dependent on the shape of potentials. They concluded that

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an assessment of the relative importance of the vacancy mechanism compared to interstitial-related mechanisms for the different dopant atoms required accurate quantitative data on the atomistic potentials.

Ab initio calculations [4, 7] provided some information on As–vacancy interactions such as the formation energy of an AsV pair, the energy barrier for As–V exchange, as well as the binding energy of As and V. These calculations were focused on the single AsV pair. The influence of other As atoms and other vacancies was not considered.

In this paper, we present a set of interaction potential diagrams for vacancy-assisted As diffusion in silicon using an *ab initio* plane-wave method and density-functional theory. The basic reactions for As diffusion in silicon via a vacancy mechanism such as $As + V \rightleftharpoons AsV$, $AsV + As \rightleftharpoons As_2V$, $AsV + V \rightleftharpoons AsV_2$, $As + As \rightleftharpoons As_2$ and $V + V \rightleftharpoons V_2$ are considered. The results demonstrate that an AsV pair can attract another nearby As due to the binding between the As and the vacancy. The existence of another As atom nearby greatly reduces the migration barrier for a vacancy moving between two As atoms, which quantitatively confirms the 'percolation' model [10]. Once an As_2V complex is formed, the corresponding migration barrier for the whole complex is much higher than that of the single AsV pair. The AsV pair can also attract another vacancy. The binding force mainly comes from the binding of two vacancies, rather than from the AsV pair. Two As atoms do not bind with each other in silicon.

The paper is organized as follows. Some computational details are presented in section 2. The accuracy of the calculation has been checked. The results are discussed in section 3, and section 4 concludes the paper with a summary.

2. Computational method

The *ab initio* calculations were based on the Kohn–Sham formulation of density-functional theory (DFT) [11] in the local-density approximation (LDA) to the exchange–correlation energy [12, 13]. We used the nonlocal and norm-conserving Hamann-type pseudopotentials [14] to describe the interactions of the valence electron with the atomic core. Electronic Kohn–Sham wave functions were expanded in a plane-wave basis [15] with a 12 Ryd cut-off. The iterative damped Joannopoulos algorithm [16] was used to obtain the self-consistent one-electron Kohn–Sham equation. The system considered was modelled via a periodic supercell with 64 atomic sites, like in other *ab initio* calculations in this field [7–9]. The integration of $\boldsymbol{k}$-points over the Brillouin zone (BZ) was performed by summing a $2 \times 2 \times 2$ mesh in the first BZ. The Hellmann–Feynman theorem was used to evaluate the forces on all atoms which were allowed to move. Atomic relaxations were considered to the point where the magnitude of the calculated Hellmann–Feynman forces on each atom was smaller than 1 mRyd/Bohr. The convergence of the $\boldsymbol{k}$-point summation and the kinetic energy cut-off were checked by using a $4 \times 4 \times 4$ mesh in the first BZ and a 16 Ryd energy cut-off. The results for the binding energy and the formation energy of the As–V pair differed by less than 0.1 eV, which gives an estimate of the accuracy of the calculation. The defects considered in this paper are in their neutral state. The variation of the calculated properties with the charge state of the defects has not been taken into account.

3. Results and discussion

We first consider the interaction between a substitutional dopant As and a nearby vacancy. Figure 1 shows the distribution of atomic sites in the sixfold rings in silicon. The neighbourhood around a substitutional As atom is denoted as 1, 2, 3 and so on, labelling the first-, second- and

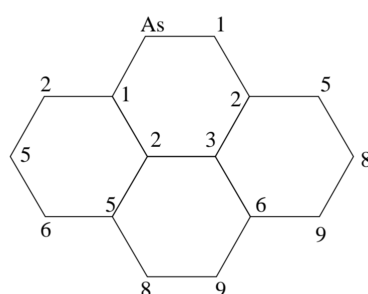

Figure 1. The distribution of atomic sites around As in the sixfold rings. The first-neighbour sites are denoted by 1, the second by 2 and so on.

third-neighbour sites of As, respectively. In the 64-atom unit cell used in this paper, the atomic site furthest from the As which sits at the centre of the cell is its twelfth-neighbour site. The potential energy diagram for an AsV pair is shown in figure 2. For each As–V configuration, the first-neighbour and the second-neighbour atoms around the defects are fully relaxed (for details see reference [17]). It can be seen in figure 2 that the energy barrier for the vacancy moving from the third neighbour of As to the second neighbour of As is 0.23 eV. Once the vacancy is located at the second-neighbour site, it will move quickly to the first-neighbour site of As which experiences a very small energy barrier of only 0.08 eV. The position of this small energy barrier is very close to the second-neighbour site. The exchange barrier between the As and the vacancy is 0.55 eV high. After exchanging position with the As, the vacancy may move away along a different ring which is connected with the As. The vacancy first overcomes an energy barrier of 0.92 eV, arriving at a second-neighbour site of As. Then it moves to the third-neighbour site by passing over another barrier with a height of 0.35 eV. Once the vacancy overcomes the barrier to the third-neighbour site, it can return to the As via a different path. By repeating such a process, long-range diffusion of the As–V complex occurs. The migration barrier $E_m(\text{AsV})$ for the whole As–V complex is 1.19 eV as shown in figure 2, which is close to the experimental result of 1.07 eV [18]. The first-neighbour binding energy of an AsV pair is calculated relative to the infinite As–V separation (here we approximate it as the twelfth-neighbour site). The result obtained is $E_b(\text{AsV}) = 1.21$ eV,

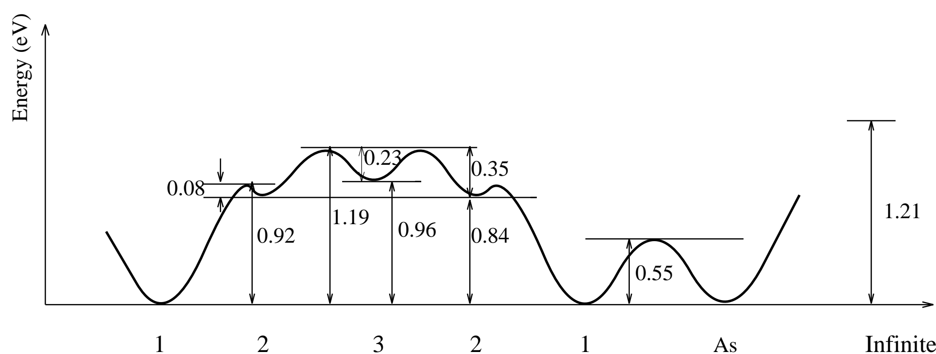

Figure 2. The potential energy diagram for As–V as a function of As–V separation.

which is in good agreement with other *ab initio* calculation findings of 1.20 eV [4] and the experimental measurements of 1.23 eV [19]. The shape of the attractive potential between the As and the vacancy is quite different from that assumed in reference [5].

For comparison, we also studied the migration and the relaxation of a neutral vacancy in the absence of As. The migration barrier obtained for a vacancy is 0.3 eV, which is 0.89 eV lower than the 1.19 eV for As diffusion assisted via a vacancy (see figure 2). The Si atoms surrounding a vacancy relax inward by about 4% with a D_{2d} symmetry. When an As atom is present at the first-nearest-neighbour site of a vacancy, the As atom moves significantly towards the vacancy site. The distance between the As and the vacancy site shrinks by 8.3% compared with the Si–Si bond length in pure Si. On the other hand, the As–Si bond length is 3.4% larger than the Si–Si bond length in pure Si, reflecting the repulsion between As and Si. This geometry possesses C_{3v} symmetry. When the vacancy moves away from the As, atoms neighbouring the vacancy relax inwards and those neighbouring the As relax outwards. The electronic structure of the vacancy is also significantly changed due to the presence of the As nearby. Because of the well-known LDA underestimation of the bandgap (the LDA bandgap of Si is 0.56 eV compared with the 1.17 eV experimental value), we will discuss the electronic structure of the defects qualitatively in the following. When a neutral vacancy is present in Si, there is a doubly occupied defect state located close to the top of the valence band in the gap. The As impurity, on the other hand, generates a singly occupied state close to the conduction band in the gap. When the As and the vacancy bind together, the As reverts to its threefold-coordinated *neutral* state from a fourfold-coordinated state. The single-occupied state at the top of the gap drops to the middle of the gap and the corresponding total energy of the system is lowered. The *extra* valence electron of As in its fourfold-coordinated state becomes localized in the low-energy state of the triple-coordinated As atom. The Fermi level is at the middle of the bandgap.

During the diffusion of As, the AsV pair may interact with another As dopant atom. This is most likely to occur in the heavily doped silicon. One example is in the 'percolation' model proposed by Mathiot and Pfister (MP) [10], in which an 'infinite' network of As atoms in the fifth-neighbour positions with respect to each other exists in a silicon lattice at a high doping level. In this 'percolation' network, the vacancy is assumed to diffuse freely from one impurity atom to another due to the lowering of the migration barrier. The percolation model was used to explain the observed enhanced diffusions of As and P in heavily doped silicon [20]. However, the diffusion was explicitly assumed via the simple vacancy-exchange mechanism without considering any details of the interaction potential of the As and the vacancy. In the present work, we calculate the potential energy diagram for a vacancy migration between two As atoms sitting at the fifth-neighbour sites with respect to each other. As pointed out by MP [10], the third-neighbour site of one As is the second-neighbour site of another As. At the same time, the second-neighbour site of one As can also be the first-neighbour site of another As (see figure 1). The easiest path for vacancy migration is 1–2–5. The calculated potential energy diagram is shown in figure 3. The potential energy for a single AsV pair without another As located at site 5 is also shown for comparison. It can be seen that for a single AsV pair, the vacancy first overcomes an energy barrier of 0.92 eV (0.84 plus 0.08) arriving at a second-neighbour site of As. Then the vacancy should pass over another barrier with a height of 0.46 eV if it moves to site 5. When a second As atom sits at site 5, the total energy is lowered by 0.31 eV compared with that for the single AsV pair due to the binding between the As and V. The migration barrier between site 1 and site 2 is just 0.1 eV, significantly smaller than that of 0.92 eV for a vacancy moving from site 1 to site 2 without another As at site 5. The highest migration barrier for the whole process is 0.45 eV, which is 0.85 eV lower than the 1.30 eV for a single AsV pair shown in figure 3. Therefore, the existence of another As atom

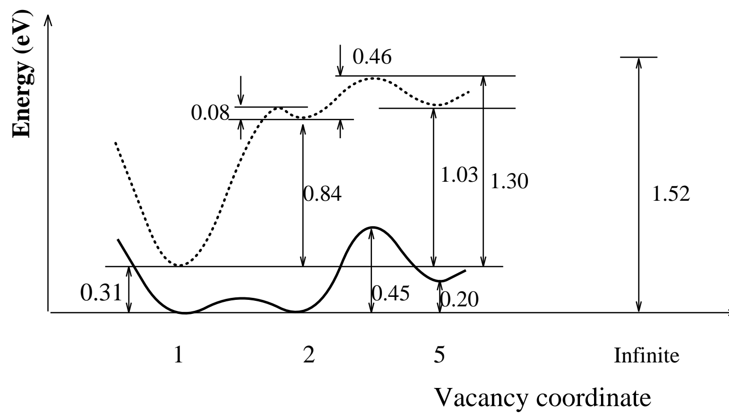

Figure 3. The potential energy diagram for As–V as a function of As–V separation with (solid line) and without (dashed line) another As atom at the fifth-neighbour site with respect to the As.

at site 5 greatly reduces the migration barrier of the vacancy, which quantitatively confirms the 'percolation' model. The potential energy increases by 1.52 eV when the vacancy moves far away from the two As atoms.

The standard 'percolation' model requires that each As atom has another As atom as its fifth neighbour and forms an 'infinite' network. This corresponds to a rather high dopant concentration. Estimations by Ramamoorthy and Pantelides [9] showed that the 'percolation' cannot occur even for dopant concentrations as high as 10^{21} cm^{-3} if the doping of As is uniform. The reported high doping concentration for As in silicon has remained below 3.5×10^{21} cm^{-3} so far [21]. Therefore, it is more likely that As has another partner at atomic sites further away than the fifth neighbours in the doped samples. Figure 4 shows the calculated As–V interaction diagram with and without another As located at the ninth-neighbour site. The diffusion path of the vacancy is through the atomic sites 1–2–3–6–9 shown in figure 1. In this case, the third neighbour of As is also the second neighbour of another As at site 9. It can be seen that the potential energy is 1.21 eV (dashed line) when the vacancy goes to the ninth-neighbour site of As, which means there is in fact no binding between the As and the V when the V goes to site 9

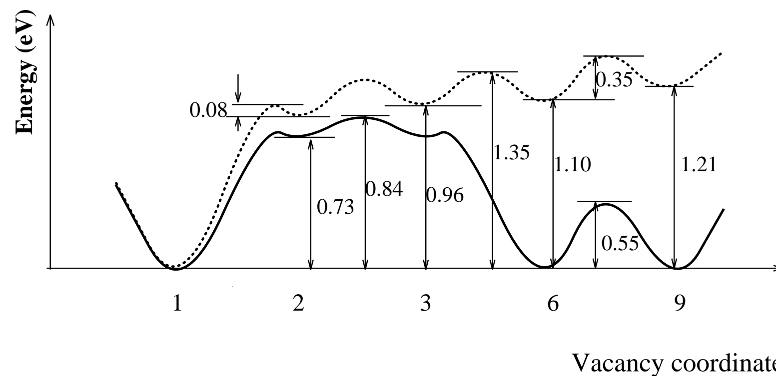

Figure 4. The potential energy diagram for As–V as a function of As–V separation with (solid line) and without (dashed line) another As atom at the ninth-neighbour site with respect to the As.

(compare with figure 2). The highest energy barrier for V moving from site 1 to site 9 is 1.35 eV without another As located at site 9. When there is another As sitting at the ninth-neighbour site of As (solid line), the highest barrier becomes 0.84 eV for V migration between two As atoms, which is 0.51 eV lower than the 1.35 eV barrier without another As atom. Therefore, the influence of another As on the interaction of an As–V pair is still significant even when the As atom is located as far away as at the ninth-neighbour site. Comparing figure 4 with figure 3, one can see that the diffusion of a vacancy is an accelerated process when two As atoms come close, since the diffusion barrier becomes lower.

Due to the attractive nature of As–V interactions, some larger As_nV complexes can be formed during the redistribution of As in silicon. *Ab initio* calculations [9,22] showed that the formation energy of As_nV complexes became negative when $n > 2$. The formation of these As_nV complexes was confirmed by a deactivation experiment [23]. In order to evaluate the contribution of these complexes to the diffusion of As in silicon, we calculated the potential energy diagram for As_2V moving around the sixfold ring. The results are shown in figure 5. The most stable configuration is As–V–As, in which both 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 binding energy of As_2 and V is 2.55 eV, which is slightly larger than twice the AsV binding energy. We calculated the binding energy of two As atoms. The result obtained is −0.13 eV, which means that two As atoms do not bind in silicon. The migration barrier of As_2V shown in figure 5 is 2.0 eV, which is significantly higher than that of a single AsV pair (1.19 eV in figure 2). With such a high migration barrier, an As_2V complex is actually less mobile in silicon. This is in accordance with the experimental observations [21,24].

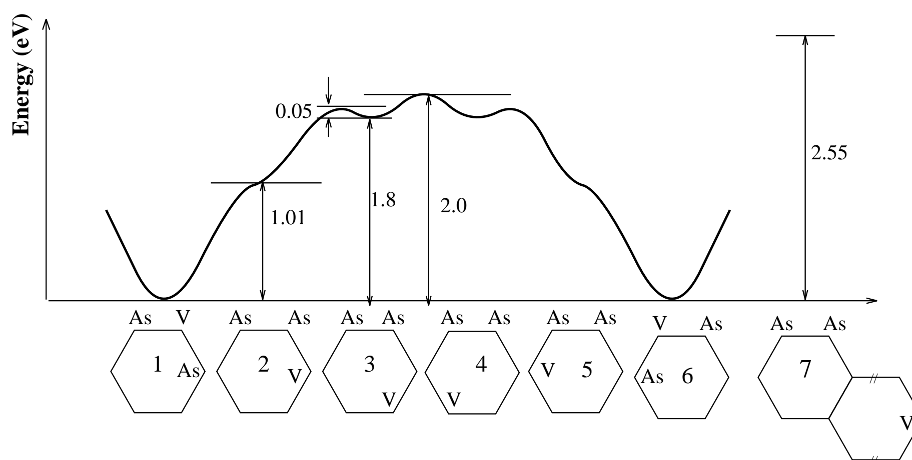

Figure 5. The potential energy diagram for an As_2V complex for vacancy migration around the sixfold ring.

Theoretical calculations [17,25–27] have demonstrated that vacancies can aggregate into larger V_n complexes in silicon, which reveals the property of binding between vacancies. Our calculation gives a 1.84 eV binding energy for two vacancies ($E_b(V_2)$), which is in good agreement with other *ab initio* calculations [26, 27] (1.7–2.0 eV) and experimental measurements [28]. One can easily imagine that an AsV pair will attract another nearby V during its diffusion in silicon, since both As and V are favoured for binding another vacancy. The potential energy diagram for an AsV pair and another V is shown in figure 6. Surprisingly, we find that the binding energy of AsV and V is 1.82 eV (site 6) which is far from the sum

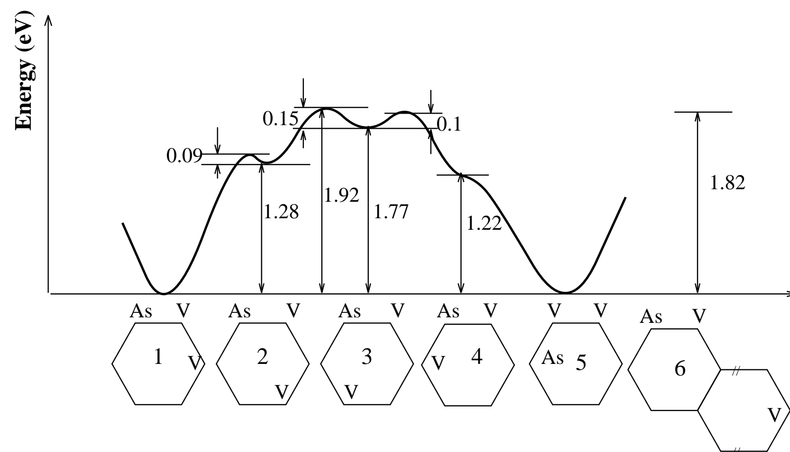

Figure 6. The potential energy diagram for an AsV_2 complex as a function of AsV–V separation.

of E_b(AsV) (1.21 eV) and $E_b(V_2)$ (1.84 eV) but very close to $E_b(V_2)$. It can be seen that the most stable configuration is As–V–V. The energy of the V–As–V configuration is 1.22 eV higher than that of As–V–V. This clearly shows that the binding between an AsV pair and another V mainly comes from the interaction between V and V rather than from that between As and V. The highest energy barrier for V moving around the sixfold ring is 1.92 eV, which means that the AsV_2 complex is less mobile than the AsV pair in silicon.

4. Summary

We have provided a set of detailed potential energy diagrams for As diffusion in silicon via a vacancy mechanism, which can be used in future atomistic diffusion simulations. The results show that the AsV pair can attract another nearby As due to the binding between As and V. The two As atoms, on the other hand, do not bind with each other in silicon. The existence of a nearby As greatly speeds up the diffusion of As dopant by lowering the migration barrier for the vacancy. The enhanced diffusion of As results in the formation of an As_2V complex which has a higher migration barrier than the AsV pair. During the diffusion of the AsV pair, it can attract another nearby vacancy. The binding force mainly comes from the attraction between two vacancies, rather than from that between As and V.

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