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Jinyu Zhang[1]**, Yoshio Ashizawa**[2] **and Hideki Oka**[2]

[1] Fujitsu R&D Centre Co. Ltd, Room B306, Eagle Run Plaza No 26 Xiaoyun Road, Chaoyang District, Beijing 100016, People's Republic of China
[2] Fujitsu Laboratories Ltd, Japan

E-mail: zhangjy@cn.fujitsu.com

Abstract
We performed first principles calculations to study the As–vacancy interaction and the ring mechanism of diffusion in the presence of Ge in Si in neutral and positively charged states. We discovered that the vacancy barrier decreases substantially when the vacancy hops around the ring. We believe that this indicates that the existence of As atoms can lower the vacancy migration barrier. The vacancy migration barrier is also decreased when Ge atoms are present in the vicinity. We made calculations on the As–vacancy ring mechanism in crystalline Ge and found that the formation energy and migration barriers of the vacancy are smaller than those in crystalline Si. These results support our conclusion that As diffusion can be enhanced by the presence of Ge, and provide physical insight into As diffusion in $Si_{1-x}Ge_x$.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

The characterization of dopant diffusion in $Si_{1-x}Ge_x$ is important because $Si_{1-x}Ge_x$ is increasingly used in producing devices such as heterojunction bipolar transistors and heterojunction metal–oxide–semiconductor transistors. High performance strained Si/relaxed SiGe MOSFETs demand the fabrication of shallow source/drain junctions. However, the formation of n^+p junctions suffers from the dramatically enhanced diffusion of As in SiGe [1–3]. Therefore, knowledge about the diffusion mechanism of As in Si and SiGe is extremely important to the semiconductor industry. We were motivated to understand the influence of Ge on the behaviour of the As diffusion mechanism at atomistic levels.

Vacancy-assisted diffusion plays an important role in As diffusion [4]. In crystalline Si, As is known to diffuse via self-interstitials and vacancies in similar shares [5]. But in crystalline
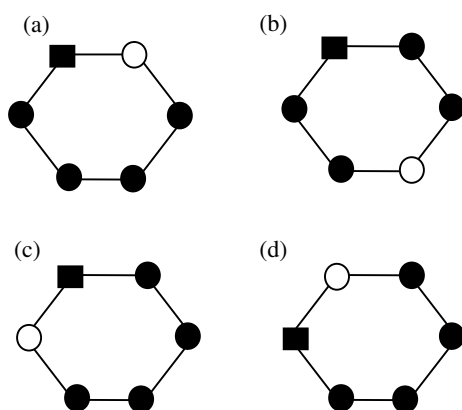
Figure 1. The impurity–vacancy migration on a diamond lattice. The figure shows the ring process that enables the impurity displacement in the 'downwards' direction, where ■, ● and ○ denote impurities, Si atoms and vacancies respectively. Panel (a) shows the starting configuration of the impurity–vacancy pair. Panel (b) shows the vacancy on a third nearest neighbour site while moving along the ring path. In (c), the vacancy approaches the impurity from a new direction, which enables the impurity to jump to the position depicted in (d).

Ge, As diffuses mainly via vacancy-assisted diffusion [6]. The vacancy-mediated diffusion of substitutional As in Si is strongly dependent on the character of the As–vacancy (As–V) interaction. When strong first nearest neighbour attraction exists, the As atom and vacancy usually exchange positions repeatedly, and will make no contribution to long range migration. The attractive interaction extends to at least the third nearest neighbours, thus allowing a vacancy to move along a ring of Si sites around the As atom. This process enables the As–V pair to move, and underlies the 'ring mechanism' of diffusion [7, 11]. Figure 1 is a schematic figure showing the impurity–vacancy ring mechanism [7]. We studied the influence of Ge atoms on As–V interaction and the ring mechanism of diffusion in Si using *ab initio* density functional calculations.

2. Computational method

In our calculation, we adopted the CASTEP [12] density functional electronic structure package, and the PBE [13] generalized gradient approximation (GGA) for the exchange–correlation functional (which has been proven to be able to generate very accurate structures in many previous defect studies) with a plane wave basis set. We used a Vanderbilt ultrasoft pseudopotential [14] for Si with a supercell of 64 atoms and a plane wave basis set with a kinetic energy cut-off of 330 eV for all calculations. A 2^3 Monkhorst [15] set was applied in k-point sampling. Numerical convergence was verified by performing test calculations for supercell size between 64 atoms and 128 atoms, plane wave cut-off between 330 and 400 eV and Brillouin zone sampling between 2^3 and 3^3. It is found that such criteria can converge total energy differences to better than 0.01 eV/atom. In order to minimize the electronic energy, a density mixing scheme was utilized [16], whereas for minimization of the ionic energy, the Hellmann–Feynman theorem was utilized for calculating forces and as a conjugate gradient scheme [17]. The relaxation of all configurations used in these calculations proceeds until the Hellmann–Feynman force is not greater than 0.03 eV Å^{-1}, which was found to converge atomic positions to better than 0.01 Å. Linear synchronous transit (LST) and quadratic synchronous transit (QST) [18] were adopted to inspect for migration barriers.

3. Results and discussion

3.1. As–V pair ring mechanism of diffusion without Ge atoms in crystalline Si

Multiple rounds of calculation were performed to handle the As–V ring mechanism without Ge in the neutral state [7, 9, 10]. We also performed calculations to verify our results, and consider them as a basis for comparison with results of the As–V system in the presence of Ge atoms. The results on the As–V ring mechanism for the positively charged state are also presented; to our knowledge, this mechanism has not been studied before.

The formation energy of a neutral vacancy is 3.56 eV in the neutral state. The As–V pair has a strong binding energy of 1.26 eV relative to a neutral substitutional As atom and a vacancy, which is in good agreement with previous *ab initio* calculations [7, 9, 10, 20]. The binding energy drops to 0.47 and 0.34 eV respectively when the vacancy moves to the second and third nearest sites. The barrier for the exchange of the As atom and the vacancy is 0.98 eV. The binding energy between neighbouring As and Ge atoms is only 0.07 eV, indicating that there is no strong interaction between them. The barrier for migration of a neutral vacancy in Si is 0.36 eV. The energy profile along the diffusion pathway is labelled 'Cry-Si' in figure 3. A difference between our results and previous calculations is that the migration barrier of the vacancy along the path between the second and third nearest sites with respect to the As atom is much smaller than that when the As atom is not there, revealing a behaviour different to that of the effective As–vacancy potential of Dunham and Wu's model [11]. Our results demonstrate that the As atom makes the vacancy more likely to undergo ring migration than to move far away from the As atom. This is consistent with the conclusion of Pankratov *et al* [7], but uses values much larger than theirs. Pankratov *et al* found that the migration barriers on the path 1–2–3, are remarkably small (less than 0.1 eV). However, they are still finite, in contrast to the completely smooth potential suggested by Sugino and Oshiyama [8].

For the positively charged state, the energy difference between the vacancy moving to the first and the second nearest sites is 0.57 eV, about 0.22 eV smaller than that for the neutral state. Also, the energy difference between the vacancy on the second and the third nearest sites with respect to the As atom is smaller than 0.03 eV. This indicates that the ring mechanism is more likely to arise for the positively charged state. The vacancy can migrate in Si with a barrier of 0.44 eV, which is a little larger than that for the neutral state. The energy profile along the diffusion pathway is labelled 'Cry-Si' in figure 4. We found that the barrier to vacancy migration from the second to the third nearest site with respect to As is about 0.34 eV lower than that when no As atom exists, indicating that the existence of As atoms can facilitate the vacancy's ring mechanism. This is consistent with the conclusion for the neutral state.

3.2. As–V pair ring mechanism of diffusion in the presence of a single Ge atom in crystalline Si

To study the influence of Ge on the As–V ring mechanism diffusion, a Ge atom was introduced into the As–V system. Normally a Ge atom may occupy one of the following positions and influence the As diffusion: (1) a substitutional location neighbouring the diffusion ring of the vacancy (see figure 2(a)); (2) one of the substitutional locations on the diffusion ring (see figures 2(b) and (c)). The Ge atom does not involve exchanging position with the vacancy in the first location, but it does for the second. Three diffusion paths are defined schematically in figure 2. The interstitial Ge atom is not taken into account, for we presume it may easily recombine with the neighbouring vacancy.

Figure 3 shows the energy profile along the three diffusion paths, which are labelled 'Ge-a', 'Ge-b' and 'Ge-c', for the condition of a neutral charge state. In case (a), when the Ge atom
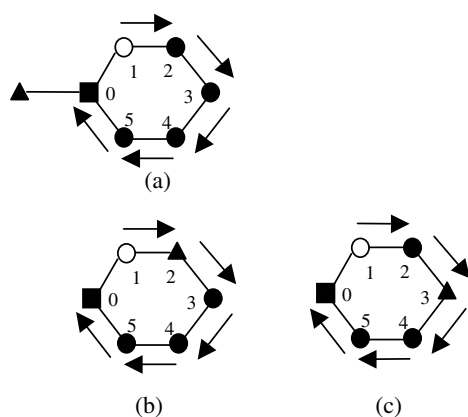
Figure 2. Schematic diagram of the three Ge atom positions involved in the As–V ring mechanism: (a) the Ge atom locates near the ring; ((b), (c)) the Ge atom locates in a substitutional position of the ring, where ▲, ■, ● and ○ denote Ge, As, Si atoms and the vacancy respectively. Numbers specify different lattice positions and arrows show the direction of vacancy hopping.
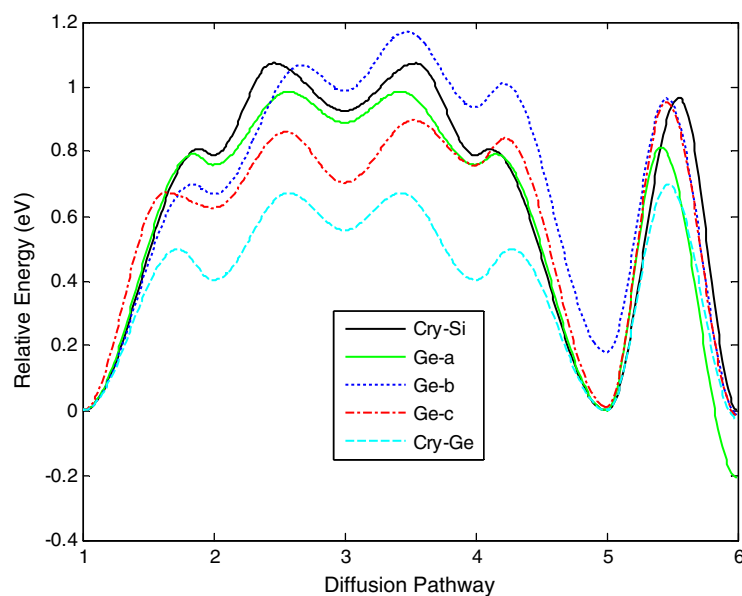

Figure 3. The vacancy migration energy profile along the diffusion pathway in the neutral state. The x axis shows the positions along the ring specified in figure 2, where position 6 is equivalent to position 0. The energy profile from position 1 to 5 represents the exchange barrier between vacancy and neighbouring Si or Ge atoms. The barrier between positions 5 and 6 is the exchange barrier between As and the vacancy. The vacancy at position 1 is taken to define the origin of the energy scale.

is at least two lattice positions away from the vacancy, the migration barrier profile is almost the same when the Ge atom is not there. The exchange barrier between the vacancy and the As atom decreases by 16% when the vacancy approaches the Ge atom. In case (b), the migration barrier between positions 1 and 2 also decreases, indicating that the vacancy is more likely to exchange position with Ge than with a Si atom. But the migration barrier increases by about
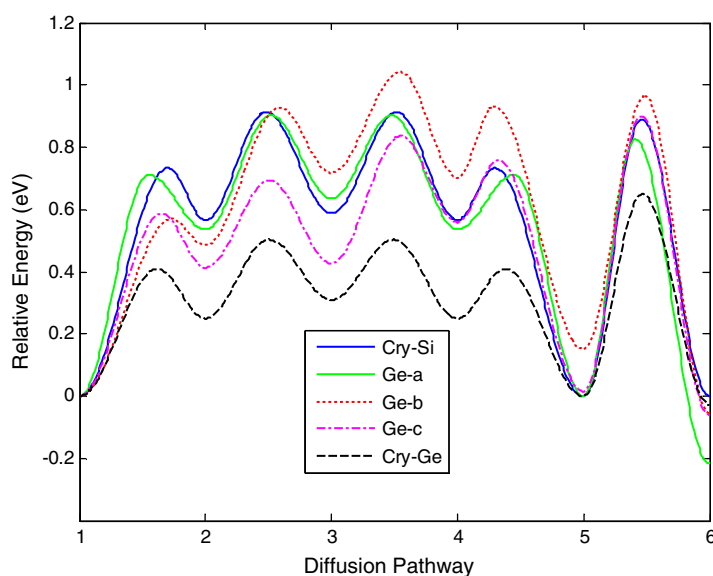
Figure 4. The vacancy migration energy profile along the diffusion pathway for the positively charged states. The x axis shows the positions along the ring specified in figure 2, where position 6 is equivalent to position 0. The energy profile from positions 1 to 5 represents the exchange barrier between the vacancy and neighbouring Si or Ge atoms. The barrier between position 5 and position 6 is the exchange barrier between As and the vacancy. The vacancy at position 1 is taken to define the origin of the energy scale.

0.12 eV when the vacancy moves from position 2 to 3, which shows that the energy profile between positions 3 and 5 is greater than that without Ge. If the system with the vacancy at position 5 is taken to define the origin of the energy scale, the migration barrier profile between 3 and 5 is the same as when no Ge exists. When a vacancy is at position 2, the corresponding As and Ge positions are at position 0 and position 1 respectively. When both As and Ge atoms are attracted to a vacancy, the configuration acts like a 'trap' of the vacancy, providing more attraction than without a Ge atom. Therefore the migration barrier will increase when the vacancy moves away from it, namely, from position 2 to 3. For case (c), the migration barrier profile is obviously smaller than that when no Ge exists. The difference is especially obvious when Ge is in the vicinity, namely at position 2 and 3. The aforementioned phenomenon shows that the exchange barrier for the vacancy and a neighbouring atom will be lowered when a Ge atom appears in the vicinity. We suppose that the increased barrier in case (b) can be eliminated by adding more Ge atoms into the system.

Figure 4 shows the energy profiles along the diffusion pathway for the positively charged state. It shows tendencies similar to those found in the neutral state. The migration barriers are lowered when there is a Ge atom in the vicinity of the vacancy. The difference is that, in the positively charged state, the migration barriers are higher than those in the neutral state.

3.3. As–V ring mechanism of diffusion in crystalline Ge

In order to understand the ring mechanism when more Ge atoms are involved with the As–V system, we performed ring mechanism calculations for crystalline Ge. The results can be considered as the approximation of large components of Ge in $Si_{1-x}Ge_x$. In the neutral state, the formation energy of a vacancy falls to 2.59 eV, indicating that the equilibrium concentration

of vacancies may increase substantially, and thus enhance the As diffusion. The As–V binding energies are 0.97, 0.58 and 0.41 eV when the vacancy is at the first, second and third nearest sites with respect to As respectively. The exchange barrier of the As atom and the vacancy is 0.72 eV. Compared with corresponding values for Si, this shows that the vacancy in Ge is more likely to follow a ring migration. The migration barrier of the vacancy in Ge is 0.26 eV, weaker than that in Si, but comparable with the value when the vacancy and Ge atom exchange in Si. The energy profile along the diffusion pathway is labelled 'Cry-Ge' in figure 3. It is obvious that the energy profile along the diffusion pathway is much lower than that in Si.

For the positively charged state, the energy difference between the vacancy locating on the first and second nearest sites with respect to the As atom is 0.25 eV, about 0.35 eV smaller than the value for the neutral state. Also, the energies of the vacancy locating on the second and third nearest sites with respect to the As atom are almost the same. The behaviour is similar to that for Si, indicating that the ring mechanism is more likely to arise for the positively charged state. For crystalline Ge without As atoms, the vacancy migrates with a barrier of 0.26 eV, almost the same as that for the neutral state. The energy profile along the diffusion pathway is labelled 'Cry-Ge' in figure 4. It can be found that the barrier to vacancy migration from the second to the third nearest site with respect to the As atom is about 0.20 eV, which is a little lower than that without As atoms. It is also obvious that the energy profile along the diffusion pathway is much lower than that in Si.

3.4. Discussion

Eguchi *et al* discussed the As continuum model for Si and $Si_{1-x}Ge_x$ in detail [3, 19]. The effective diffusivities of As in $Si_{1-x}Ge_x$ can be written as

$$D_{\text{eff}}^{\text{As}}(\text{SiGe}) = h_{\text{As}} \times \left(f_{\text{i}} \left\{ D_{\text{i}}^0 + D_{\text{i}}^- \left[\frac{n}{n_{\text{i}}(\text{SiGe})} \right] \right\} + f_{\text{v}} \left\{ D_{\text{v}}^0 + D_{\text{v}}^- \left[\frac{n}{n_{\text{i}}(\text{SiGe})} \right] \right\} \right) \qquad (1)$$

where $n_{\text{i}}(\text{SiGe})$ is the intrinsic carrier concentration in $Si_{1-x}Ge_x$. The concentration differed from that in Si by a factor of $\exp(\Delta E_{\text{g}}/(2kT))$ describing the energy gap reduction in $Si_{1-x}Ge_x$. The parameters D_{i}^0 (D_{v}^0) and D_{i}^- (D_{v}^-) represent the contributions from the neutral and singly negatively charged interstitial (vacancy) defects respectively, and were equal to those for Si. The factors f_{i} and f_{v} represent the fractions of interstitial- and vacancy-mediated diffusion respectively. The factor h_{As}, which is an enhancement factor, was utilized to account for the faster diffusion in SiGe, and it was varied in the simulations to fit the observed SIMS data.

Unlike in our first principles calculations, the neutral As–V pair in our calculation is composed of a positively charged substitutional As and a negatively charged vacancy, corresponding to the diffusion part in the Eguchi model with coefficient D_{v}^-. For the same reason, the positively charged As–V corresponds to D_{v}^0. In Eguchi's model, two factors contribute to the As enhancement of diffusion in $Si_{1-x}Ge_x$: one is the energy gap reduction responsible for the intrinsic carrier concentration and the other is a fitting parameter h_{As} used to describe the As enhancement of diffusion. In our calculations, we focused on atomistic level description of the second factor in the Eguchi model. We propose three reasons that may explain the h_{As}. The first one is the weakening of the migration barrier when the vacancy exchanges position with the neighbouring Si atom in the As–V ring mechanism. The second is the reduction of the barrier to exchange of the As atom and the vacancy position. The mechanism takes effect not only in the ring mechanism, but also in As simple diffusion, that is, the As atom can exchange position with the vacancy, and continue to hop by exchanging with another vacancy [19]. The third is the increase of the vacancy equilibrium concentration and decrease of the vacancy migration barrier, which provides the vacancy with a greater opportunity to bind with the As atom.

In most cases, the barrier to migration of the vacancy will be lowered when a Ge atom appears in the vicinity. But as shown in figures 3 and 4, the migration barrier profiles in the presence of Ge in some positions are greater than those without Ge. We attribute this to having only a single Ge atom introduced into the As–V system. As mentioned in section 3.2, As and Ge atoms are both attracted to the vacancy if they locate at a neighbouring lattice site. This configuration acts like a 'trap' for the vacancy. Without Ge, a vacancy may overcome a higher barrier to move away from them. We suppose that the increased barrier could be eliminated by adding more Ge atoms into the system. The results on the As–V ring mechanism in crystalline Ge can be considered as the approximation of a large component of Ge in $Si_{1-x}Ge_x$, and it is obvious that the energy profile along the diffusion pathway is much lower than those in all other cases.

Our results show some differences between the neutral and positively charged states. The vacancy migration barriers for the neutral state are generally smaller than those for the positively charged state. But for the positively charged state, the energy difference between the vacancy moving to the first and the second nearest sites is much smaller than that for the neutral state. Also, the energy difference between the vacancy on the second and the third nearest sites with respect to the As atom is almost the same, much smaller than that for the neutral state. This indicates that the ring mechanism is more likely to arise for the positively charged state.

On the basis of these new physical insights, it is possible for us to improve the As diffusion continuum model for $Si_{1-x}Ge_x$. We are still investigating this model.

4. Summary

In summary, this paper examines the mechanism of As–V ring diffusion in the presence of Ge. We found that the vacancy migration barrier profile in the ring mechanism is different to that of the traditional view. In most cases, the vacancy to neighbouring atom (As and Si) exchange barrier will be lowered in the vicinity of a Ge atom. In crystalline Ge, the enhancement of As diffusion in $Si_{1-x}Ge_x$ can be attributed to the smaller formation energy of vacancy and migration barriers. Our results could provide microscopic physical insight into the continuum model of As diffusion in $Si_{1-x}Ge_x$.

Acknowledgment

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