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First-Principles Study of Interaction of As-Vacancy and Ring Mechanism of Diffusion under Presence of Ge in Si

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***Abstract*—We performed first-principles calculation to study the interaction of As-vacancy and ring mechanism of diffusion under presence of Ge in Si in neutral and positively charged state respectively, in which it is found that the vacancy barrier decreased substantially when it hops around the ring. We believe it indicates that existence of As atom can lower the vacancy migration barrier. The vacancy migration barrier also decreased with existence of Ge atom in vicinity. We also calculate As-vacancy ring mechanism in the crystalline Ge. It is found that the formation energy of the vacancy and migration barrier was obviously smaller than that in crystalline Si. All these results support the suggestion that As diffusion can be enhance with presence of Ge, and provide physical insight of As diffusion in $Si_{1-x}Ge_x$.**

Keywords-As; vacancy; Ge; ring mechanism

I. INTRODUCTION

The characterization of dopant diffusion in Si1-xGex is important because $Si_{1-x}Ge_x$ is increasingly being used to produce devices such as heterojunction bipolar transistors and heterojunction meta-oxide-semiconductor transistors. High performance strained Si/relaxed SiGe MOSFETs demand he fabrication of shallow source/drain junctions. However, the formation of n^+p junctions suffers from the dramatically enhanced diffusion of As in SiGe [1][2][3]. Therefore knowledge about the diffusion mechanism of As in Si and SiGe is of extreme importance to the semiconductor industry. We are motivated to understand the influence of Ge on the behavior of As diffusion mechanism in atom level.

It is known that As diffuses in Si mainly by vacancy-assisted diffusion[4]. And 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 neighbor attraction exists, the As atom and vacancy usually just exchange their positions repeatedly, and will make no contribution to long range migration. The attractive interaction extends to at least the third nearest neighbors, thus allows 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 [5] [8]. Figure 1. [5] is a schematic figure demonstrating the impurity-vacancy ring mechanism., We studied the influence of Ge atoms on As-V interaction and ring mechanism of diffusion in Si using *ab initio* density functional calculations.

II. METHOD

In our calculations, we adopted the CASTEP [9] density functional electronic structure package, and the PBE [10] 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. And we used a Vanderbilt ultra-soft pesudopotential [10] for Si with a supercell of 64 atoms and a plane-wave-basis set with a kinetic-energy cutoff of 330 eV for all calculations. A 2^3 Monkhorst [12] set was applied to k-point sampling. It is found that such criteria can converge total energy differences to better than 0.01eV/atom. In order to minimize the electronic energy, a density mixing scheme is utilized [13], whereas for minimization of ionic energy, Hellmann-Feynman theorem is utilized to calculate forces as well as a conjugate gradient scheme [14]. The relaxation of all configurations used in these calculations proceeds until the Hellmann-Feynman force is not greater than 0.03 eV/Å, which was found to converge atomic positions to better then 0.01 Å. Linear Synchronous Transit (LST) and Quadratic Synchronous Transit (QST) [15] are also adopted to inspect for migration barriers.

III. RERSULTS AND DISCUSSION

A. *As-V pair Ring Mechanism of Diffusion without Ge Atom in Crystalline Si*

Multiple rounds of calculation were performed to handle As-V ring mechanism without Ge in the neutral charged state [5] [6] [7]. We also performed the calculation to our results, and consider them as basis for comparison with results of the As-V system under presence of Ge atom. The results on As-V ring mechanism in positively charged state is also presented, which to our knowledge, was not studied before.

The formation energy of a neutral vacancy is 3.56eV in neutral charged 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[5][6][7]. The binding energy drops to 0.47eV and 0.34eV respectively when the vacancy moves to the 2nd and 3rd nearest site. The barrier for the exchange of As atom and the vacancy is 0.98eV. The binding energy between neighboring As and Ge atoms is only 0.07eV, indicating that there is no strong interaction between them. The barrier for migration of neutral vacancy in Si is 0.36eV. The energy

profile along the diffusion pathway is specified by "Cry-Si" in Figure 3. A difference between our results and previous calculations is: the migration barrier of the vacancy between the 2nd and 3rd nearest site to the As atom is much smaller than that when As atom is not there, revealing a quite different behavior of the effective As-vacancy potential of Dunham and Wu's model[8]. Our results demonstrates that the As atom makes the vacancy more likely to make ring migration than to move far away from the As atom, which is consistent with Pankratov et. al.'s conclusion[5], but with values much larger than theirs.

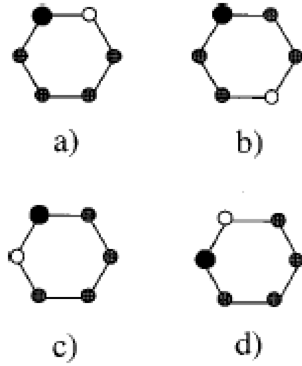

Figure 1. The impurity-vacancy migration on a dimond lattice. The figure shows the ring process that enables the impurity displacemnt in the direction of "downwards". The black dots represents the impurity, while the little empty circle indicates the vacancy. Panel(a) shows the starting configuration of the impurity-vacancy pair. (b) shows the vacancy on a third-nearest-neighbor site while moving along the ring path. In (c), the vacancy approaches the impurity from the new direction, which enables the impurity to jump to the position as depicted in (d).

In positively charged state, the energy difference between the vacancy moving to the 1st and the 2nd nearest site is 0.57eV, about 0.22eV smaller than that in neutral state. Also, the energy difference between the vacancy on the 2nd and the 3rd nearest sites to the As atom is smaller than 0.03eV. It indicates that ring mechanism is more likely to happen in positively charged state. The vacancy can migrate in Si with barrier of 0.44eV, which is a little larger than that in the neutral state. The energy profile along the diffusion pathway is specified by "Cry-Si" in Figure 4. It can be found that the vacancy migration barrier from the 2nd and the 3rd nearest sites to As is about 0.34eV, lower than that when no As atom exists, indicating that existence of As atom can facilitate the vacancy's ring mechanism. It is consistent with the conclusion from the neutral state.

B. As-V pair Ring Mechansim of Diffusion in the Presence of a single Ge atom in Crystalline Si

To study the influence of Ge on As-V ring mechanism diffusion, a Ge atom is 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 neighboring to the diffusion ring of vacancy (see Figure 2. (a)); (2) one of the substitutional locations on the diffusion ring (see Figure 2. (b) and (c)). The Ge atom does not involve into exchanging position with vacancy in the first location, but it does when in the second. Three diffusion paths are schematically defined in Figure 2. . The interstitial Ge atom is not taken into account, for we presume it may easily recombine with the neighboring vacancy.

Figure 3. shows the energy profile along the three diffusion paths, which are specified by "Ge-a", "Ge-b" and "Ge-c" respectively, in the condition of neutral charge state. In case (a), when the Ge atom is at least 2 lattice positions away from vacancy, and the migration barrier profile is almost the same with that when the Ge atom is not there. The exchange barrier between the vacancy and the As atom decreases by 16% when the vacancy approaches to the Ge atom. In case (b), the migration barrier between position 1 and 2 also decreases, indicating that the vacancy is more likely to exchange position with Ge than with Si atom. But the migration barrier profile between 3 and 5 is greater than that without Ge. If the zero point is at position 5, the migration barrier profile between 3 and 5 is the same as when no Ge exists. In case (b), configuration with the vacancy at position 1 is the most stable. It acts like a trap, and the migration barrier will increase when vacancy moves away from it. For case(c), the migration barrier profile is obviously smaller than that when no Ge exists. The difference is especially obvious then Ge is in the vicinity, namely position 2 and 3. Aforementioned phenomenon shows that the exchange barrier of the vacancy to the neighboring atom will be lowered when Ge atom appear in the vicinity. We suppose that the increased barrier in case (b) can be eliminated by adding more Ge atoms into the system.

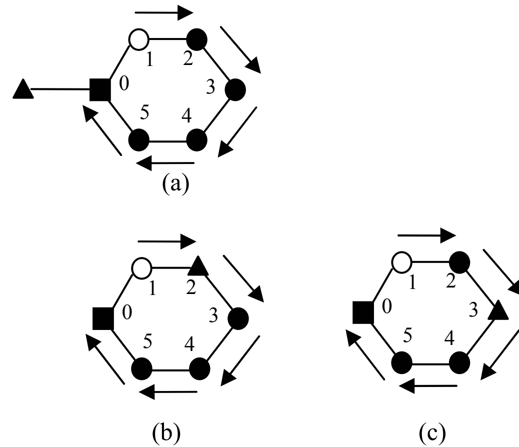

Figure 2. Schematically shows the three Ge atom position involving into the As-V ring mechanism: (a) the Ge atom locates near the ring, (b) and (c) the Ge atom locates in the sbustitutional position of the ring, where ▲, ■, ● and ○ denote Ge, As, Si atoms and V respectively. The numbers show the different lattice position and arrows show the direction of vacancy hopping.

Figure 4. shows the energy profiles along the diffusion pathway in positively charged states. It shows the similar tendencies as can be found in the neutral state The migration barriers are lowered when there is Ge atom in the vicinity of

the vacancy, but the barriers rises when the vacancy moves away from Ge and As atom. The difference is that, in the positively charged state, the migration barriers are higher than those in neutral charged state.

C. As-V Ring Mechanism of Diffusion in the Crystalline Ge

In order to understand the ring mechanism when more Ge atoms involve with the As-V system, we performed ring mechanism calculation in the crystalline Ge. The results can be considered as the approximation of large component of Ge in $Si_{1-x}Ge_x$. In neural charged state, the formation energy of a vacancy falls to 2.59eV, indicating that the equilibrium concentration of vacancy may increase substantially, and thus enhance As diffusion. The binding energies of As-V are 0.97eV, 0.58eV and 0.41eV when the vacancy is at the 1st, 2nd and 3rd nearest site to As respectively. The exchange barrier of the As atom and the vacancy is 0.72eV. Compared with the corresponding values in Si, it shows that the vacancy in Ge is more likely to follow a ring migration. The migration barrier of the vacancy in Ge is 0.26eV, also weaker than that in Si, but comparable with the value when the vacancy and Ge atom exchanges in Si. The energy profile along the diffusion pathway is specified by "Cry-Ge" in Figure 3. . It is obvious that the energy profile along the diffusion pathway is much lower than that in Si.

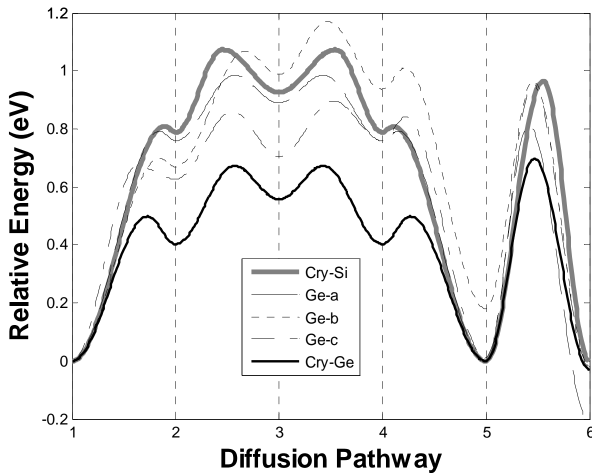

Figure 3. The vacancy migration energy profile along the diffusion pathway in neutral charged state. X axis shows the positions along the ring specified in Figure 2. . The barrier between position 5 and 6 is the exchanging barrier between As and vacancy. The zero point of the energy is that the vacancy locates at the 1st nearest lattice site of As atom.

In positively charged state, the energy difference between the vacancy locating on the 1st and 2nd nearest site respectively to the As atom is 0.25eV, about 0.35eV smaller than that value in neutral state. Also, the energies of the vacancy locating on the 2nd and 3rd nearest sites to the As atom are almost the same. The behavior is similar to that in Si, indicating that ring mechanism is more likely to happen in positively charged condition. In Ge without the As atom, the vacancy migrates with barrier of 0.26eV, almost the same as that in neutral state. The energy profile along the diffusion pathway is specified by "Cry-Ge" in Figure 4. It can be found that the vacancy migration barrier from the 2nd and the 3rd nearest to the As atom is about 0.20eV, a little lower than that when without As atom. It is obvious that the energy profile along the diffusion pathway is much lower than that in Si.

D. Discussion

Eguchi et al. discussed the As continnum model in Si and $Si_{1-x}Ge_x$ in detail[3][16]. The effective diffusivities of As in $Si_{1-x}Ge_x$ can be written as

$$D_{eff}^{As}(SiGe) = h_{As} \times \left(f_i \left\{ D_i^0 + D_i^- \left[\frac{n}{n_i(SiGe)} \right] \right\} + f_v \left\{ D_v^0 + D_v^- \left[\frac{n}{n_i(SiGe)} \right] \right\} \right).$$

where $n_i(SiGe)$ is the intrinsic carrier concentration in $Si_{1-x}Ge_x$. The concentration differed from that in Si by a factor $\exp(\Delta E_g/(2kT))$ decribing 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 by the neutral and single nagatively charged intersitial (vacancy) defects, respectively, and were set equal to those in Si. The factor f_i and f_v represent the fractions of intersitial- 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 varied in the simulations to fit the observed SIMS data.

Compared with our first-principles calculations, the neutral charged As-V pair in our calcuation is composed of the positively charged substitutional As and negatively charged vacancy, corresponding to the diffusion part in Eguchi model with coeffficent D_v^-. And for the same reason, the positvely charged As-V corresponding to D_v^0. In Eguchi's model, two factors contribute to As enhancment diffusion in $Si_{1-x}Ge_x$: one is energy gap reduction responsible for the intrinsic carrier concentration; and the other is a fitting parameter h_{As} to describe the As enhancement diffusion. In our calculation, we foucsed on atomstic level describption of the seond reason in Eguchi model. We suppose there are three reasons that can explain the h_{As}: The first one is the weakened migration barrier when vacancy exchanges position with the neighboring Si atom during As –V ring mechanism. The second is the reduction of barrier in exchanging of the As atom and the vacancy position. The mechanism takes effect not only in ring mechansim, 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[17]. The third is the increase of the vacancy equilibrium concentration and decrease of the vacancy migration barrier, which provides the vacancy greater opportunity to bind with the As atom.

In Figure 3. and Figure 4. 0, the migration barriers profile under the presence Ge in some positions are greater than that without Ge. We attibute it to only a single Ge atom introduced

into the As-V system. For the As and Ge atom both have attraction to the vacancy, they can act as the trap of vacancy. Therfore, compared with without Ge, the migration barrier of a vacancy will increase a little when the vacancy move far away both of As and Ge atom. We suppose that the increased barrier can be eliminated by adding more Ge atoms into the system. The results of As-V ring mechanism in crystalline Ge can be considered as the approximation of large component of Ge in $Si_{1-x}Ge_x$.

Our calculation also show some differences in neutral and positively charged state. The vacancy migration barriers in neutral state are generally smaller than those in positively charge state. But in positively charged state, the energy difference between the vacancy moving to the 1st and the 2nd nearest site is much smaller than that in neutral state. Also, the energy difference between the vacancy on the 2nd and the 3rd nearest sites to the As atom is almost the same, much smaller than that in the neutral state.

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

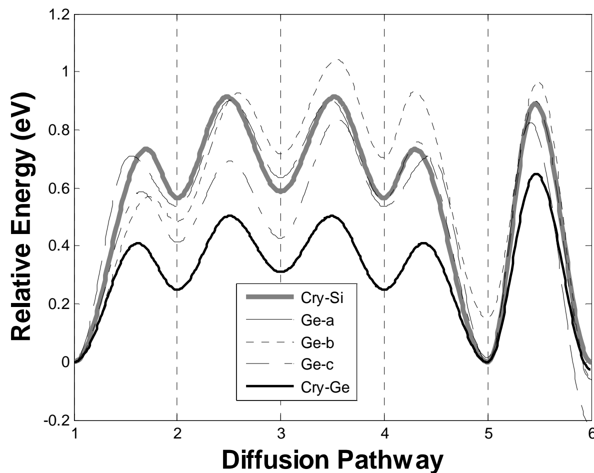

Figure 4. The vacancy migration energy profile along the diffusion pathway in positively charged conditions. X axis shows the positions along the ring specified in Figure 2. . The barrier between position 5 and position 6 is exchanging barrier between As and V. The zero point of the energy is that V locates in the 1st nearest lattice site of the As atom.

IV. SUMMARY

In summary, this paper examines the mechanism of As-V ring diffusion under presence of Ge. We found the vacancy migration barrier profile in ring mechanism is different from traditional picture. The exchange barrier for the vacancy to the neighboring atom (As and Si) will be lowered in the vicinity of Ge atom. In crystalline Ge, the enhancement of As diffusion in $Si_{1-x}Ge_x$ can be contributed to smaller formation energy of vacancy and migration barriers. Our results provide the microscopic physical insight to the continuum model of As diffusion in $Si_{1-x}Ge_x$.

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