Confining P diffusion in Si by an As-doped barrier layer

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The miniaturization of Si-based devices requires control of doping profile, which makes the understanding of dopant interaction and diffusion in Si critical. The authors have studied the effect of As doping on P diffusion in Si using first-principles calculations. The authors found a form of As-vacancy complex is energetically favorable, allowing As to consume the vacancy so as to prohibit the vacancy-mediated P diffusion. Also, in the vicinity of As, the vacancy-mediated P diffusion barrier is increased, decreasing further the P mobility. The results provide useful guidance for designing As-doped barriers to block P diffusion in Si wafer processing and metal oxide semiconductor field-effect transistor device fabrication. © *2007 American Institute of Physics*.
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The continued shrinkage of Si layer thickness in new generations of metal oxide semiconductor field-effect transistor (MOSFET) devices requires ever more accurate control of dopant profiles. For example, in a MOSFET power device made in the Fairchild Semiconductor, the P-doped Si channel is made to approach a small thickness of only a few micrometers. Consequently, one critical issue in Si wafer processing is to design ways to confine P diffusion. One possible method in doing so is by growing another doped layer with a different dopant, such as As, on top of the P-doped channel as a diffusion barrier layer. Previous studies had focused mostly on diffusion of individual dopants, such as P,[1–4] As,[5–8] and Sb;[9] recently, codoping has attracted more and more attention,[10–12] as a promising process to achieve specific dopant profile and concentration. In this letter, we carry out extensive first-principles calculations to investigate the effectiveness of this method and to reveal the underlying physical mechanisms affecting dopant diffusion in the presence of other dopants.

Our calculations are carried out using the density-functional-theory based pseudopotential plane-wave total-energy method within the local density approximation (LDA) and generalized gradient approximation (GGA) as used recently for studying interstitial oxygen in Si.[13] We used a large supercell of 216 atoms to model the Si host lattice, within which vacancies, dopants of P, As, and Sb are introduced in various interacting configurations. We used a plane wave cutoff energy of 12 Ry. and a $(2 \times 2 \times 2)$ k-point mesh for Brillouin zone sampling. All the atoms in the supercell were relaxed with an atomic force convergence of 5×10^{-3} eV/Å. The vacancy-mediated dopant diffusion barriers were determined by exchanging the vacancy and the dopant along constrained pathways, using the nudged-elastic-band (NEB) method.[14]

Considering that P diffusion in Si is assisted mainly by vacancies,[15] here we will focus on the vacancy-mediated P diffusion. (Other diffusion mechanisms, such as interstitial-mediated diffusion, will be considered later.) Our goal is to investigate how the presence of "extrinsic" dopants in the

barrier layer will influence the vacancy-mediated P diffusion in the channel layer. One particular factor is how much the other dopants may consume the vacancies that will in turn affect the availability of vacancies to mediate the P diffusion in Si. We also investigated how the presence of the extrinsic dopants will affect the diffusion barrier of P in Si.

We have first tried "As" as the potential candidate of extrinsic dopant to be used in the barrier layer, because it has been suggested that As forms a stable structure complex with vacancy (Va) in Si.[16,17] We calculated the interaction energy between the As and Va by bringing the two from the faraway position to the nearest-neighbor position in the supercell. Figures 1(a) and 1(b) show the atomic structure of the As–Va complex at the first nearest-neighbor (1NN) position before and after atomic relaxation, respectively. Figure 1(c) shows the interaction energies between the As and Va as a function of their separation from the 1NN to the 6NN position (where the energy is set as the zero point of reference), as calculated using the GGA potential.

The As and Va are found to be attractive with a large binding energy of −0.96 eV (LDA) or −1.07 eV (GGA) at the 1NN and 2NN positions. The energy at the 2NN position is essentially the same as that at the 1NN position, as shown in Fig. 1(c), because starting with either the 1NN or 2NN position the atomic relaxation leads eventually to the same As–Va complex structure, as shown in Fig. 1(b). The large As–Va complex formation energy can be understood in terms of dangling bond energy.

Inspecting the As–Va complex structure shown in Fig. 1(b), one sees that it basically involves formation of one As dangling bond (DB) plus three Si DBs around the vacancy. When the Va is far away from the As, it is surrounded by four Si DBs. Thus, when the Va approaches the As to form the As–Va complex, one Si DB is replaced by the As DB. Because the Si–Si bond is stronger than the Si–As bond and because the Si DB is half-filled with one electron while the As DB is fully filled with two electrons for As being a *p* type of dopant, the As DB energy will be much lower than the Si DB energy. Such DB energy difference has given rise to the large formation energy of the As–Va complex in Si.

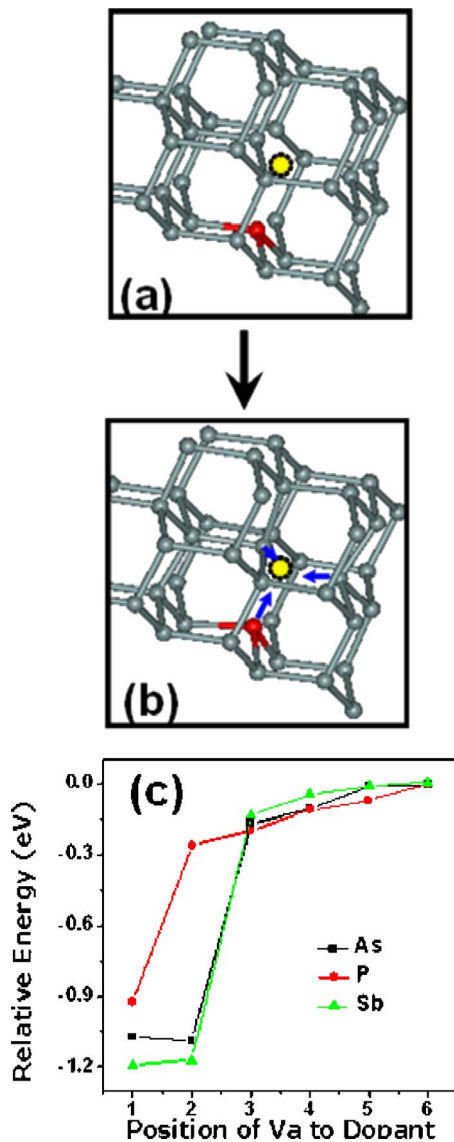a)Electronic mail: fliu@eng.utah.edu

FIG. 1. (Color online) (a) Structure of As (red)–Va (yellow) complex in Si before atomic relaxation. (b) Structure of As–Va complex after atomic relaxation. (b) Formation energies of the As–, P–, and Sb–Va complexes in Si as a function of dopant-Va separation.

For comparison, we performed the similar calculations between P and Va, as shown in Fig. 1(c). The final P–Va complex structure formed at the 1NN position is basically the same as that of the As–Va complex shown in Fig. 1(b). However, the binding energy between P and Va is only 0.78 eV (LDA) or 0.92 eV (GGA), noticeably weaker than that between As and Va. The energy for P at the 2NN position to Va is about 0.64 eV higher than the 1NN position and there is an energy barrier of ~0.51 eV for P to diffuse from the 2NN to the 1NN position. This behavior is different from the case of As, when the 1NN and 2NN positions converge to the same structure without energy barrier. The larger binding energy between As and Va than that between P and Va indicates that when As atoms are introduced, vacancies in the Si lattice will feel a much stronger attraction to As than to P to form more stable As–Va complexes. As a result, if the diffusion of P is primarily mediated by vacancies, it will be slowed down greatly as most vacancies would have been consumed by As. This is consistent with recent experiments by Fairchild Semiconductor.[18]

Again, we can understand the energy difference between the As–Va and the P–Va complex in terms of DB energy. Since the number of Si DBs is conserved for different dopants, the main energy difference for dopant-Va complexes must arise from the DB energy difference between the different dopants. Roughly speaking, the energy scales with the bulk cohesive energy for a given element, i.e., the larger the cohesive energy, the larger the DB energy. Indeed, the above calculated As–Va and P–Va complex energies are in the right order of cohesive energies of GaAs and GaP.[19] The GaAs has a smaller cohesive energy (~6.69 eV/Ga–As bond) than GaP (~7.37 eV/Ga–P bond), so the As has a lower DB energy than P, and hence the As–Va complex is more stable than the P–Va complex.

Based on the above reasoning, it is interesting to realize that if we can find another dopant element that has even a smaller cohesive energy than GaAs, then it will form even a more stable complex with vacancy. For example, one can easily find that the GaSb has a cohesive energy of ~6.06 eV/per Ga–Sb bond, noticeably lower than that of GaAs. Thus, we have repeated the above calculations for Sb–Va interaction in Si, as shown in Fig. 1(c). Indeed, they form a complex with the same structure as shown in Fig. 1(b), but the complex formation energy is even higher at 1.10 eV (LDA) or 1.20 eV (GGA), in comparison to As–Va and P–Va complexes. Although the absolute energy values obtained from LDA versus GGA are different, they exhibit the same quantitative trend and difference from one element to the next. We note that this order is also consistent with the cohesive energies of pure P (3.43 eV/atom), As (2.96 eV/atom), and Sb (2.75 eV/atom) solids, so that their DB energies are in the reverse order from low to high in the order of Sb, As, and P.[20] These calculations suggest that in principle the Sb can possibly work as a more effective extrinsic dopant than As to be used in the barrier layer to block the vacancy-mediated P diffusion. However, experimentally, doping of Sb could be generally harder than doping of As.[18]

As the extrinsic dopants in the barrier layer consume the vacancies by forming stable structural complexes, the next question related to P diffusion is how would P interact with the extrinsic dopant-vacancy complex? As an example, we have calculated the interaction between P and As–Va complex. First, we calculated the interaction between P and As in the Si lattice without vacancy and we found that the two are repulsive with repulsion energies of ~0.30 eV (LDA) or ~0.20 eV (GGA). Now, considering the attractive interaction between P and vacancy as shown above, we expect the interaction between P and the As–Va complex to be highly anisotropic, depending on the direction that P approaches the complex, i.e., toward the As side versus toward the Va side.

Figure 2 illustrates the two situations where we brought P toward the Va side of the As–Va complex from the 4NN to the 1NN position within the (110) plane [Figs. 2(a)–2(d)], in comparison to the case toward the As side of the complex [Figs. 2(e)–2(h)]. In the former case, the two is found attractive with an interaction energy of ~−0.88 eV (LDA) or ~−0.97 eV (GGA), close to that of P–Va without As; while in the latter case, the two becomes only weakly attractive with an interaction energy of ~−0.05 eV (LDA) or −0.09 eV (GGA) due to the repulsion between As and P.

Next, we have studied how extrinsic dopant such as As will affect diffusion of P by calculating the vacancy mediated P diffusion barriers in the vicinity of As, in comparison with
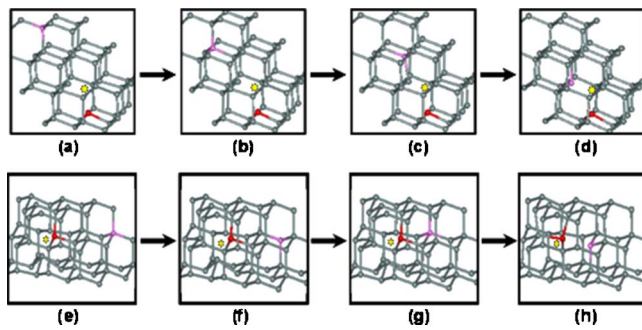
FIG. 2. (Color online) Optimized structural configurations illustrating the anisotropic interaction between P (pink) and As (red)–Va (yellow) complex with P approaching toward the vacancy side (a to d) vs toward the As side [(e)–(h)].

that in the intrinsic Si. We have calculated the energy barriers for exchanging P with Va in the As-doped Si with the P (before exchange) or Va (after exchange) being at the 1NN, 2NN, and 3NN positions to As, as illustrated in Fig. 3 (top panel). The potential energies along the P–Va, exchanging pathways at the different NN positions as determined using the NEB method[14] and GGA potential are shown in Fig. 3 (bottom panel). We used four NEB image points between the initial and final configurations of diffusion. The potential-energy curves are obtained through polynomial fitting to the six data points, as shown in Fig. 3.

We found that in general, the vacancy-mediated P diffusion barriers in Si are increased substantially in the vicinity of As by up to a few hundreds of meV. The closer the P is to As, the larger its diffusion barrier will be. Thus, the P diffu-
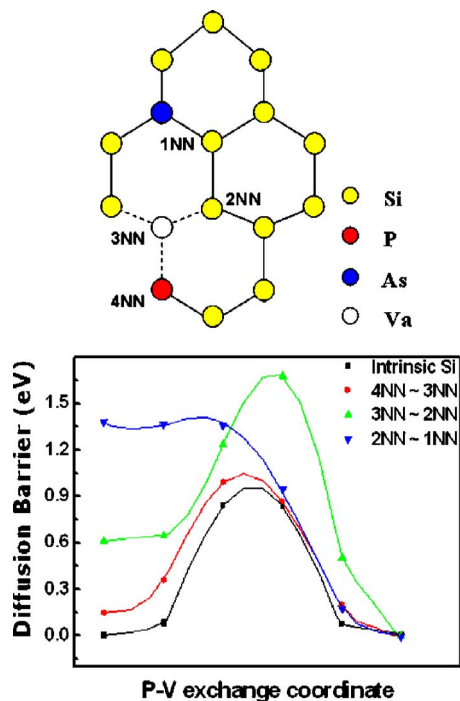
sion in Si will be greatly slowed down if P comes to the vicinity of As. On the other hand, because of the repulsive interaction between As and P as shown above, P is not favored to diffusion toward the As. The potential-energy curves in Fig. 3 become more and more asymmetric when the P is approaching closer to the As from the 3NN, 2NN, to the 1NN position, with the lower energy for P being one lattice site away from As. This is apparently consistent with the attractive interaction between As and vacancy as well as the repulsive interaction between As and P. Therefore, there is a general tendency for P to diffuse away from As.

In summary, we have investigated the effect of As on Va-mediated P diffusion in Si using first-principles total energy calculations. We show that the dopant-Va binding energy in Si scales in general with the DB energy of the dopant. Because As (or Sb) has a much higher binding energy with Va than with P, the As–Va complex formation is energetically more favorable than the P–Va complex. Also, the vacancy-mediated P diffusion barriers in the vicinity of As, is noticeably higher than that in intrinsic Si. We conclude that doping of As will effectively slow down P diffusion in Si via two mechanisms: first by consuming the available vacancies and second by increasing the Va-mediated P diffusion barriers. Our findings point to the possibility of using the heavily As-doped layer as diffusion barriers to confine the P doping profile in Si, as suggested by the experimental results from Fairchild Semiconductor.

FIG. 3. (Color online) Top panel: schematics illustrating the NN positions for P–Va exchange in the vicinity of As. Bottom panel: calculated P–Va exchange barriers for P moving from the 1NN, 2NN, or 3NN to the 2NN, 3NN, or 4NN positions of As, in comparison to that in the intrinsic Si. Symbols are data points of NEB images and lines are polynomial fits.

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