

The role of vacancy on trapping interstitial O in heavily As-doped Si

Guang-Hong Lu,^{1,2} Q. Wang,³ and Feng Liu^{2,a)}

¹Department of Physics, Beijing University of Aeronautics and Astronautics, Beijing 100083, People's Republic of China

²Department of Materials Science and Engineering, University of Utah, Salt Lake City, Utah 84112, USA

³Fairchild Semiconductor, West Jordan, Utah 84088, USA

(Received 10 April 2008; accepted 3 May 2008; published online 28 May 2008)

We have investigated the interstitial oxygen (O_i) diffusion in heavily arsenic (As)-doped Si using first-principles calculations. We show that it is not the As *per se* but the Si vacancy (V) that trap O_i to reduce its diffusion. Arsenic actually plays the role of an *arbitrator* to activate thermal generation of As- V pairs, which in turn trap O_i with a large binding energy of ~ 1.0 eV, in quantitative agreement with experiments. Our finding solves a long-standing puzzle on the atomistic mechanism underlying the retardation of O_i precipitation in heavily As-doped Si. © 2008 American Institute of Physics. [DOI: 10.1063/1.2937308]

Interstitial oxygen (O_i) diffusion in silicon (Si) is an important issue in the growth and processing of Si wafers, especially in heavily doped Si wafers, because O_i precipitation mediated by diffusion is one leading cause for the formation of extended defects that are responsible for current leakage.^{1–3} In submicron Si devices based on complementary metal oxide semiconductor technology, the source and drain are heavily doped with arsenic (As).^{4,5} For the node smaller than 90 nm, the concentration of As in the ultrashallow source and drain is approaching a range of 10^{20} – 10^{21} cm⁻³.^{6,7} Therefore, understanding the O_i diffusion in the heavily As-doped Si, especially the atomistic diffusion mechanism underlying the retardation of O_i precipitation, is critical to optimization of Si wafer processing.

Early experiments^{8,9} showed that the diffusivity of O_i is decreased (or the diffusion barrier of O_i is increased) in the heavily As-doped Si relative to that in intrinsic Si. For an As concentration of 4.0×10^{18} and 1.3×10^{19} cm⁻³, the diffusion barrier was estimated to increase by as much as 0.64 and 0.68 eV, respectively.⁹ This is further confirmed by a more recent experiment.¹⁰ The reduced O_i diffusion is believed to be responsible for the retardation of O_i precipitation in heavily As-doped Si.¹¹ These observations have led to the wide speculation that O_i diffusion is reduced in heavily As-doped Si by the formation of certain type of “As- O_i ” complex which traps oxygen atoms,^{8,9} although there is no direct experimental evidence to support the existence of such a complex, and even if it does exist—no one knows its microscopic origin and atomic structure.

Recently, using first-principles calculations, we have studied the O_i -As interaction in the heavily As-doped Si in an attempt to identify such a complex structure.¹² We did find a -Si-O-Si-As- type of complex whose formation is energetically favorable. However, its binding energy is only ~ 0.14 – 0.21 eV, with a trapping energy one order of magnitude too small to account for the experimental observation. Therefore, the question concerning the existence of such complex has not been answered, and the physical mechanism underlying the reduced O_i diffusion and retarded O_i precipitation in the heavily As-doped Si remains unknown.

In this letter, we investigate complex structures containing other defects, in particular, Si vacancy (V) in addition to As and O_i . The reason for choosing V is because it is known that As and V are attractive to each other in Si with a binding energy of ~ 1.2 eV (Refs. 13 and 14) and several defect structures exist in the heavily n -doped Si containing V , such as donor- V complex and donor-pair- V interstitial.¹⁵ We find that the O_i -(As- V) complex can have a large binding energy of ~ 0.9 – 1.4 eV, in quantitative agreement with the experimentally observed O_i trapping energy of ~ 1.0 eV.^{8–11} Thus, we believe we have finally solved the long-standing puzzle on the reduced O_i diffusion and retarded O_i precipitation in the heavily As-doped Si. O_i is not trapped by As alone via the simple O_i -As complex formation as originally suggested, but it is due to a more complicated process that must involve a *vacancy*. Arsenic plays the role of an “arbitrator” in the trapping process by activating the thermal generation of vacancies to form As- V pairs that, in turn, trap O_i .

All the calculations are performed using a pseudopotential plane-wave total-energy method based on density functional theory and local density approximation, as in previous studies of different topics in similar systems.^{12,16} We employ ultrasoft pseudopotentials with an energy cutoff of 25 Ry.¹⁷ We use a large supercell dimension of $15.274 \times 16.200 \times 15.274$ Å³ in the $[\bar{1}10]$, $[001]$, and $[110]$ directions, respectively, containing 192 Si atoms, and a $(2 \times 2 \times 2)$ special k -point grid for Brillouin zone sampling. Energy relaxation is continued until forces on all the atoms are converged to less than 10^{-3} eV Å⁻¹.

Since As cannot effectively trap O_i ,¹² we turned our attention to other possible defects that might affect O_i diffusion. The Si vacancy is of interest because it is one of the most common defects. It has been shown that heavy As doping can activate V formation in Si,¹⁸ and As and V tend to form a stable As- V pair^{13,14} with a binding energy of ~ 1.2 eV.^{13,14,16} Our recent calculations¹⁶ show that, in fact, all the n -type dopants (e.g., As, P, and Sb) are favored to pair up with V in Si because in doing so, a half-filled Si dangling bond of high energy is replaced by a full-filled dopant dangling bond of much lower energy (by ~ 1.0 eV). Also, the As- V pair is stronger than the P- V pair because the dangling-bond energy of As is lower than that of P. Applying

^{a)}Electronic mail: fliu@eng.utah.edu.

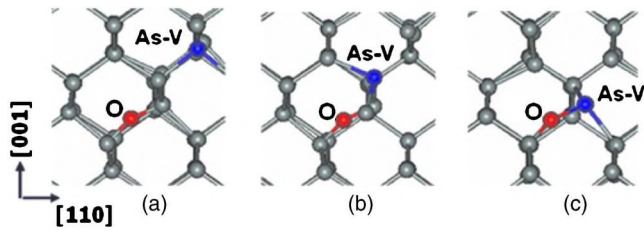


FIG. 1. (Color online) The interaction configurations between O_i and As-V pair with the O_i approaching the As-V pair from the As side. (a) O_i at the 3NN position to As-V. (b) 2NN position. (c) 1NN position.

this principle, we propose to use the As-doped layer as diffusion barriers to confine P diffusion in the P-doped Si.^{16,19}

First, we investigated how V would interact with O_i in the intrinsic Si without As. We found that there exists a strong attraction between the two with a large binding energy of ~ 1.4 eV when they are at the first nearest-neighbor (1NN) position. The binding energy reduces to ~ 0.9 eV when the two move apart to the second NN (2NN) position. When the O_i moves to the V , it forms bonds with two Si atoms that originally surround the V . Consequently, it saturates some of the Si dangling bonds in the vicinity of V giving rise to the strong binding between the O_i and V .

Also, the strong binding between the O_i and V partly stems from the effect of V relaxing the strain induced by O_i in the Si lattice. Far away from V , O_i occupies a puckered bond-centered interstitial site that bridges two neighboring Si atoms.¹² The Si-O bond length is ~ 1.61 Å and the Si-O-Si bond angle is about $\sim 161^\circ$, which are both about the same in SiO_2 . This causes a large compressive strain in the surrounding Si lattice. As O_i moves next to a V , the Si-O-Si bonding configuration (bond length and bond angle) is retained, but in a much easier manner with the O_i occupying the open space around the V site. As a result, the compressive strain in the surrounding Si lattice is partially relaxed.

Encouraged by the above results, next, we further investigate the interaction between O_i and As-V pair in the heavily As-doped Si. The O_i may interact with the As-V pair in two distinct ways: either interacting with the As or with the V in the pair. Figure 1 shows the optimized atomic positions in the first case with the O_i approaching the As-V pair from the As side. The corresponding interaction energies at the different positions are shown in Fig. 2, with the energy of the O_i far away from the As-V pair (not shown in Fig. 1) set as the zero point of energy. One sees that the O_i cannot actually bind with the As-V pair in this manner. As the O_i approaches As, there is a rather weak binding of ~ 0.10 eV (Fig. 2) at the third NN (3NN) [Fig. 1(a)] and 2NN positions [Fig. 1(b)]. However, the direct binding at the 1NN position [Fig. 1(c)] is forbidden with a positive “repulsive” energy of $+0.9$ eV (Fig. 2). It indicates that the O-As bond formation is energetically unfavorable. These results are in good agreement with the previous calculations of interaction between O_i and As in Si without a vacancy.¹² In essence, the O_i cannot bond directly with As in Si, but can bond indirectly with a bridging Si in between by forming a type of $-O_i\text{-Si-As-}$ complex with a moderate binding energy in the order of ~ 0.10 eV.

Figure 3 shows the optimized atomic positions in the second case with the O_i approaching the As-V pair from the V side. Again, the corresponding interaction energies at the different positions are shown in Fig. 2. The results in this

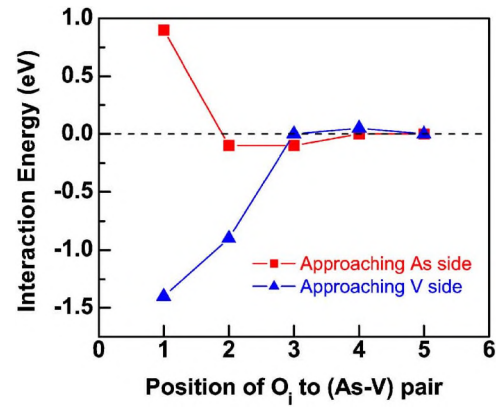


FIG. 2. (Color online) The interaction energy between the O_i and the As-V pair with O_i approaching the As side (red, Fig. 1) or the V side (blue, Fig. 3) as a function their separation. The x axis labels the NN positions of the O_i to the As-V pair. The position far away is set as the reference zero point of energy.

case are qualitatively different from the first case. Most importantly, there exists a strong attraction between the O_i and As-V pair when the O_i approaches the As-V from the V side. When the O_i is at the 3NN [Figs. 3(a) and 3(b)] position to the As-V pair, the binding energy is ~ 0.0 eV (Fig. 2), i.e., there is virtually no binding and the interaction is relatively short ranged. However, the interaction becomes strongly attractive at the 2NN [Fig. 3(c)] and 1NN [Fig. 3(d)] positions with a large binding energy of 0.9 and 1.4 eV (Fig. 2), respectively. At both the 2NN and 1NN positions, the O_i interacts with As via a V in between. At the most stable 1NN position, O_i forms a new bond with a Si atom in another (110) plane next to the As-V (110) plane within which the O_i is originally located [Fig. 3(d)], so that the O_i bridges two Si atoms such as SiO_2 . This results in the formation of an $O_i\text{-As-V}$ complex, with V surrounded by one O_i , one As atom, and several Si atoms.

The optimized binding configuration and binding energies between the O_i and the As-V pair from the V side (Fig. 3) are found essentially identical to those between O_i and V in the intrinsic Si. We believe that the binding energy of $\sim 0.9\text{--}1.4$ eV between the O_i and As-V pair is most likely the physical origin responsible for the experimentally observed ~ 1.0 eV trapping energy of O_i in heavily As-doped Si. Note that without V , As alone can only provide a maximum O_i trapping energy of 0.21 eV.¹² Thus, the vacancy has to be involved to play the critical role in trapping O_i , because O_i binds only to V with a strong enough binding energy in the range of ~ 1.0 eV.

Thus, it is the binding between O_i and V rather than O_i and As that traps the O_i to reduce its diffusion. Then, one would wonder why the reduced O_i diffusion is only observed

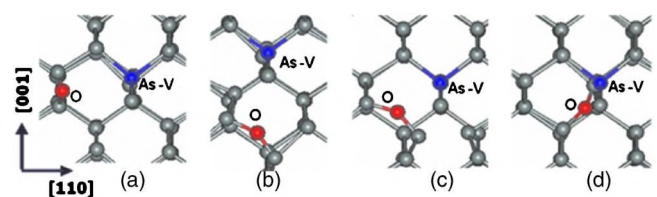


FIG. 3. (Color online) The interaction configurations between O_i and As-V pair with the O_i approaching the As-V pair from the As side. (a) O_i at the 3NN position to As-V. (b) another 3NN position. (c) 2NN position. (d) 1NN position.

in the heavily As-doped Si but not in the intrinsic Si and what is the role that As has played in the process of trapping O_i . Here, we postulate that although vacancies have a large binding energy with O_i , they cannot by themselves effectively trap O_i in the intrinsic Si without other dopants such as As. This is because in the intrinsic Si, there is simply not enough V to trap O_i . It is known that the V concentration in the intrinsic Si is below the detection limit of 10^{16} cm^{-3} even at 1600 K,^{18,20} because of a large V formation energy of $\sim 3.0 \text{ eV}$ as obtained from experiment²¹ and theory.²² Furthermore, in the intrinsic Si, V diffuses very fast with a diffusion barrier less than 0.5 eV ,²³ so that the chance for an O_i to meet with a vacancy and hence be trapped by is very small.

In contrast, in the heavily As-doped Si, the V formation energy is experimentally shown²¹ to be substantially decreased to $\sim 1.1 \text{ eV}$. When a V forms in the vicinity of As (or another dopant, such as P and Sb),¹⁶ its formation energy is reduced by the binding energy of the As– V pairs which is $\sim 1.3 \text{ eV}$.^{13,14,16} In other words, the formation of V creates high-energy Si dangling bonds, while next to As, it creates one low-energy As dangling bond in place of a Si dangling bond.¹⁶ Consequently, the presence of As will activate the thermal generation of vacancies at the typical Si wafer processing temperature,²¹ which in turn trap O_i . Also, the bounded vacancies in the As– V pairs become “stationary” with an increased diffusion barrier of 1.2 eV (Ref. 21) (relative to $<0.5 \text{ eV}$ without As),²³ which may further increase the O_i trapping probability.

We can roughly quantify the role of As played in the trapping process by estimating the local O_i concentration in the vicinity of the As– V pairs in comparison with that in the intrinsic regions in the heavily As-doped Si. According to the Boltzmann distribution, the density of O_i atoms per cm^3 , n_j^O in a particular region (site) j is associated with the site energy E_j^O as

$$n_j^O = \frac{N_O N}{Z} e^{-E_j^O/kT}, \quad (1)$$

where j runs over all N Si lattice sites within a cm^3 , which include positions close to the As– V pair as the 1NNs or 2NNs, denoted as N_{As} with negative site energies of -1.4 and -0.9 eV , and those far away from the As– V pair, denoted as N_{Si} with zero site energies. N^O is the total number of O_i atoms. k is the Boltzmann constant and T is the absolute temperature. Z is the partition function, which can be calculated as

$$Z = \sum_j N_j e^{-E_j^O/kT} = N_{\text{As}} e^{-E_{\text{As}}^O/kT} + N_{\text{Si}} e^{-E_{\text{Si}}^O/kT}. \quad (2)$$

The ratio of O_i atoms trapped in the vicinity of As– V pair over those not trapped away from As is

$$\frac{n_{\text{As}}^O}{n_{\text{Si}}^O} = \frac{N_{\text{As}}}{N_{\text{Si}}} e^{-(E_{\text{As}}^O - E_{\text{Si}}^O)/kT} = \frac{N_{\text{As}}}{N_{\text{Si}}} e^{-\Delta E_{\text{trap}}/kT}, \quad (3)$$

where ΔE_{trap} is the trapping energy of O_i in the vicinity of As– V pair. The concentration of intrinsic Si is $5 \times 10^{22} \text{ cm}^{-3}$, while the typical heavy doping concentration of As is $N_{\text{As}} = 2.6 \times 10^{20} \text{ cm}^{-3}$. Using the calculated trapping en-

ergies of -0.9 to -1.4 eV , as estimated at the typical processing temperature of $900 \text{ }^\circ\text{C}$, the ratio $n_{\text{As}}^O/n_{\text{Si}}^O$ falls in the range of ~ 50 – 5000 . So, 97% to 99.99% of O_i are trapped by the As– V pairs to be immobilized, leading to a substantial reduction of O_i diffusion.

In conclusion, we have performed first-principles total-energy calculations to investigate the nature of the interaction between the O_i and As– V pair in heavily As-doped Si. We reveal the detailed atomistic mechanisms and processes responsible for the reduced O_i diffusivity as observed experimentally, and solve the long-standing puzzle concerning the retarded O_i precipitation in the heavily As-doped Si. We show that O_i is not trapped by As *per se* in the form of O_i –As complex as originally speculated, but instead by the As– V pairs in the form of O_i –(As– V) complex. Arsenic plays the role of arbitrator to activate the thermal generation of vacancies at the typical Si processing temperatures, creating a high V concentration to trap O_i . The typical trapping energy is $\sim 1.0 \text{ eV}$, in good agreement with experiment. Our findings should provide useful guidelines for design strategies to control the defect precipitation and dopant profile in growing and processing heavily doped Si wafers.

This work is supported by Fairchild Semiconductor Corporation and DOE.

¹D. K. Sadana, Mater. Res. Soc. Symp. Proc. **36**, 245 (1985).

²H. Shirai, A. Yamaguchi, and F. Shimura, Appl. Phys. Lett. **54**, 1748 (1996).

³F. Shimura, H. Tsuya, and T. Kawamura, J. Electrochem. Soc. **128**, 1579 (1981).

⁴B. J. Baliga, Power Semiconductor Devices (PWS, Boston, 1995).

⁵D. E. Hill, Defects in Silicon, edited by W. M. Bullis and L. C. Kimerling (Electrochemical Society, Pennington, NJ, 1983) p. 433.

⁶M. C. Arst and J. G. deGroot, J. Electron. Mater. **13**, 763 (1984).

⁷R. A. Craven, Semiconductor Silicon, Proceedings of the Electrochemical Society, edited by H. R. Huff, R. J. Kriegler, and Y. Takeishi (The Electrochemical Society, Pennington, NJ, 1991), Paper No. 18-5, p. 254.

⁸T. Ono, G. A. Rozgonyi, E. Asayama, H. Horie, H. Tsuya, and K. Sueoka, Appl. Phys. Lett. **74**, 3648 (1999).

⁹H. Takeno, K. Sunakawa, and M. Suezawa, Appl. Phys. Lett. **77**, 376 (2000).

¹⁰Q. Wang and I. Ho, Appl. Phys. Lett. **88**, 154107 (2006).

¹¹Y. Zhao, D. Li, X. Ma, and D. Yang, J. Phys.: Condens. Matter **16**, 1539 (2004).

¹²G.-H. Lu, Q. Wang, and F. Liu, J. Appl. Phys. **101**, 026104 (2007).

¹³J. Xie and S. P. Chen, Phys. Rev. Lett. **83**, 1795 (1999).

¹⁴D. C. Muller, E. Alonso, and W. Fichtner, Phys. Rev. B **68**, 045208 (2003).

¹⁵P. M. Voyles, D. J. Chadi, P. H. Citrin, D. A. Muller, J. L. Grazul, P. A. Northrup, and H.-J. L. Gossman, Phys. Rev. Lett. **91**, 125505 (2003).

¹⁶L. Bai, D. Yu, G.-H. Lu, F. Liu, Q. Wang, and H. Yilmaz, Appl. Phys. Lett. **91**, 061926 (2007).

¹⁷F. Liu, S. H. Garofalini, R. D. King-Smith, and D. Vanderbilt, Phys. Rev. Lett. **70**, 2750 (1993).

¹⁸J. Throwe, T. C. Leung, B. Nielsen, H. Huomo, and K. G. Lynn, Phys. Rev. B **40**, 12073 (1989).

¹⁹US Patent No. 7, 132 715.

²⁰R. Wuerschum, W. Bauer, K. Maier, A. Seeger, and H. E. Schaefer, J. Phys.: Condens. Matter **1**, SA33 (1989).

²¹V. Ranki and K. Saarinen, Phys. Rev. Lett. **93**, 255502 (2004).

²²M. I. J. Probert and M. C. Payne, Phys. Rev. B **67**, 075204 (2003).

²³G. D. Watkins, Mater. Res. Soc. Symp. Proc. **469**, 139 (1997), and references therein.