

First-principles calculation of interaction between interstitial O and As dopant in heavily As-doped Si

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We investigate the interaction between interstitial oxygen (O_i) and As dopant in heavily As-doped Si using first-principles total-energy calculations. The interaction between O_i and As (substitutional) is found to be short ranged. The most stable configuration is with As and O_i as second nearest neighbors, forming $-\text{Si}-\text{O}-\text{Si}-\text{As}-$ type complexes, with a binding energy of 0.14–0.21 eV. These complexes can trap O_i in their vicinity and thus reduce the O_i mobility. But the magnitude of trapping energy by such complexes is about five times smaller than the value estimated from the experimentally observed retardation of O_i diffusion in heavily As-doped Si. We suggest that structural complexes involving other defects may resolve this discrepancy. © 2007 American Institute of Physics. [DOI: 10.1063/1.2423231]

Heavily doped Czochralski-grown silicon (Si) wafer is the substrate of choice in power discrete devices.^{1,2} Arsenic (As) has been one of the most common doping species used for source and drain in deep submicron complementary metal oxide semiconductor (CMOS) technology. For nodes smaller than 90 nm, the concentration of As in the ultrashallow source and drain is approaching the range of 10^{20} – 10^{21} cm⁻³.^{3,4} Thus, knowledge about the interaction between interstitial oxygen (O_i) and As dopant in such a heavily As-doped Si substrate is very important for helping us to better understand the system, such as the O_i precipitation and formation of extended defects, which are relevant to leakage reduction.^{5–7}

The experimental studies have shown that the diffusivity of O_i decreases substantially in heavily As-doped Si in comparison with that in intrinsic Si.^{8–10} For As concentrations of 4.0×10^{18} cm⁻³ and 1.3×10^{19} /cm³, the diffusion barriers were estimated to increase by as much as 0.64 and 0.68 eV, respectively.⁹ Accordingly, the precipitation of O_i has been shown to be retarded in heavily As-doped Si.¹¹ It has been suggested that these phenomena are possibly caused by the formation of complex structures between dopants and O_i that trap oxygen atoms.^{8,9} However, there is no direct experimental evidence to support the existence of such a complex. Furthermore, no information is available on how such a complex is formed and what are the structure and energy associated with its formation. There remains still a missing link between the retardation of O_i diffusion and the precipitation of O_i in the heavily As-doped Si.

Here, we present first-principles calculations to investigate the interaction between O_i and As in the heavily As-doped Si, in an attempt to find possible complex structures formed by O_i and As in Si and their potential effects on O_i diffusion. Our calculations are performed using pseudopotential plane-wave total-energy method based on density functional theory and local density approximation. We employ ultrasoft pseudopotentials with an energy cutoff of 25 Ry.^{12,13} We use large supercell dimensions of $15.274 \times 16.200 \times 15.274$ Å³ in $[\bar{1}10]$, $[001]$, and $[110]$ directions, respectively, containing 192 Si atoms, and a $(2 \times 2 \times 2)$ special k -point grid for Brillouin zone sampling. Energy minimization is continued until forces on all the atoms are converged to less than 10^{-3} eV Å⁻¹.

Before introducing the effect of As, we determine the configuration of O_i in intrinsic Si. Figure 1 shows the calcu-

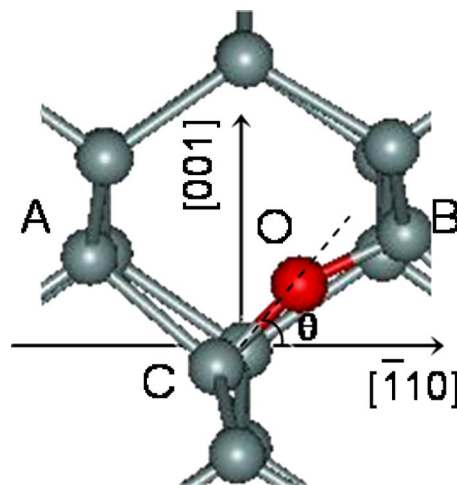


FIG. 1. (Color online) The binding of O_i in intrinsic Si in the (110) plane. Atom positions are energy optimized.

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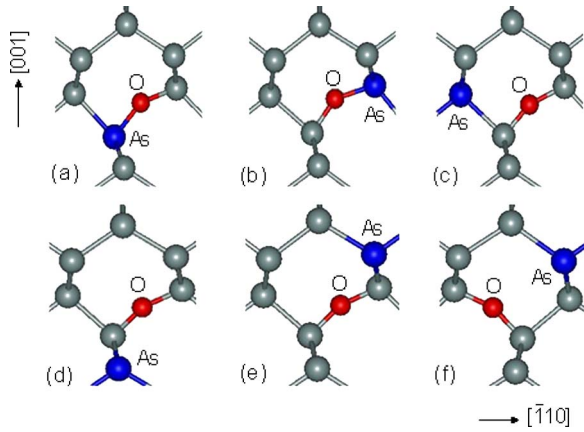


FIG. 2. (Color online) Different configurations with one substitutional As atom interacting with O_i . All the atom positions are energy optimized.

lated equilibrium bonding configuration of O_i in intrinsic Si, occupying a puckered bond-centered interstitial site that bridges two neighboring Si atoms, similar to the bonding configuration in SiO_2 . The bond lengths of Si–O and Si–Si are found to be 1.61 and 3.17 Å, respectively, and the bond angle of Si–O–Si (BOC) is about 161° . These findings agree well with the previous reports.^{14–16}

Next, we investigate how O_i interacts with dopant As atom. We first consider the case with one substitutional As atom in the supercell, corresponding to an As concentration of $\sim 2.6 \times 10^{20} \text{ cm}^{-3}$, within the heavy doping limit. Different substitutional sites for As have been tested to reveal the nature of interaction sites between As and O_i as shown in Fig. 2. The calculated relative energies of these configurations are shown in Table I, in reference to the configuration when As is far away from O_i , which is chosen as the zero point of energy (not included in Fig. 2). Clearly, the direct As–O bonding [Figs. 2(a) and 2(b)] is unfavorable with the highest energy of $\sim 1.15 \text{ eV}$. The most stable low-energy configurations consist of As and O_i being the second nearest-neighbor (2NN) [Figs. 2(c)–2(e)], forming a –Si–O–Si–As– type of complex, in which As and O interact with each other indirectly via a Si in between. Beyond the 2NN distance, there is virtually no interaction between As and O [Fig. 2(f)]; the energy is the same as the reference state when As is far away from O_i . So, the interaction between O_i and As is rather short ranged and effectively attractive at 2NN but repulsive at 1NN (no direct bonding).

Next, we consider the case with two substitutional As atoms in the supercell (As concentration of $\sim 5.2 \times 10^{20} \text{ cm}^{-3}$). We first determine the interaction between the two As atoms themselves. The calculations show that the As atoms are repulsive; their interaction energy decreases from 0.23 eV at the 1NN position to 0.10 eV at the 2NN, and to

TABLE I. Total energy at different configurations with one As interacting with O_i , as shown in Fig. 2. The configuration when As is far way from O_i is set as the reference zero point of energy.

Configuration	Ref.	a	b	c	d	e	f
Energy (eV)	0	+1.15	+1.14	–0.15	–0.14	–0.14	0.00

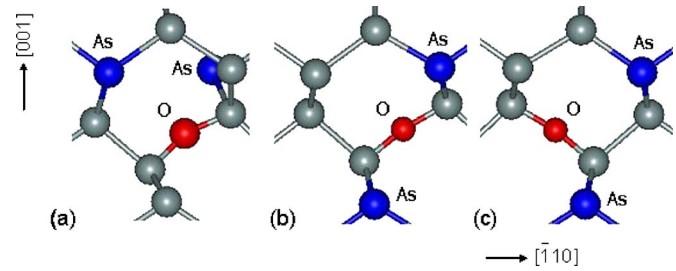


FIG. 3. (Color online) Different configurations with the two substitutional As atoms interacting with O_i . All the atom positions are energy optimized.

zero when they are separated beyond the 2NN distance. Thus, As atoms prefer to be separated without segregation.

Given the repulsive As–As interaction, we consider different configurations of two substitutional As atoms interacting with O_i , as shown in Fig. 3, in two representative extreme cases. One is with both As atoms far away from O_i (not included in the Fig. 3), and the other is with both as the 2NN of O_i forming the –Si–O–Si–As– complex [Figs. 3(a)–3(c)]. Table II shows the calculated relative energies of these configurations. Similar to the case of one As atom, the formation of –Si–O–Si–As– complex is energetically favorable. Comparing the configuration of Fig. 3(b) to those of Figs. 3(a) and 3(c), Table II shows that the energy is further lowered by $\sim 0.10 \text{ eV}$ due to the formation of a complex containing two As atoms [Fig. 3(b)] relative to that containing one As atom as the 2NN of O_i [Fig. 3(a) or 3(c)].

The above calculations indicate that overall the binding energy between O_i and As falls in the range of $\sim 0.10\text{--}0.20 \text{ eV}$. Consequently, O_i can be trapped by the As atom due to the formation of the –Si–O–Si–As complexes, and such trapping effect will be enhanced by increasing the As concentration. This may effectively lead to a retardation of O_i diffusion, because O_i has to overcome a barrier that is equal to its binding energy in the complex in order to escape from As.

In order to understand the physical origin of the formation of energetically favorable –Si–O–Si–As– complex, we plot in Fig. 4 the valence charge density in the bonding plane of Si–O–Si (As) comparing between the case of the intrinsic Si and that of As-doped Si. Figure 4(a) shows the case of intrinsic Si, displaying the two most general bonding nature between the covalent Si–Si bond characterized with charge density concentrated at the center of bond (the left half inside the dashed-line rectangle) and the ionic Si–O bond characterized with high charge density centered only around O (the right half inside the dashed-line rectangle). Arsenic has an extra valence electron, which would fill the antibonding state when forming either an ionic As–O bond with O or a covalent As–Si bond with Si. This is partly reflected by the extra

TABLE II. Relative energies of different configurations with two substitutional As atoms interacting with O_i , as shown in Fig. 3. The configuration with As atoms far away from O_i is set as the reference zero point of energy.

Configuration	Ref.	a	b	c
Energy (eV)	0	–0.10	–0.21	–0.08

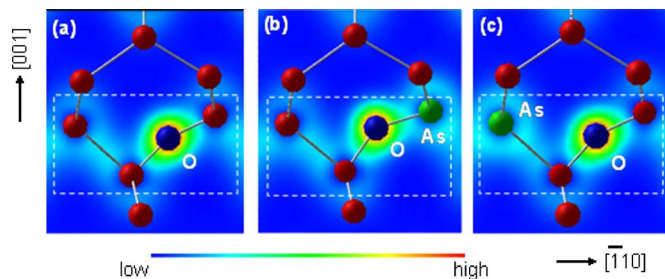


FIG. 4. (Color online) Valence charge density plots in the Si–O–Si (As) bonding plane. (a) O_i in intrinsic Si. (b) O_i in As-doped Si with As as the 1NN of O. (c) Same as (b) with As as the 2NN of O. Atoms in dashed-line rectangles are in the same (110) plane containing Si–O–Si (As) bonds.

high charge density around O and As as well as between As and Si, as shown in Fig. 4(b). This makes the direct O–As bond in the O–As–Si configuration energetically unfavorable. When As sits at the 2NN position of O in the –Si–O–Si–As– complex, as shown in Fig. 4(c), the optimal ionic O–Si is resumed. Also, the O would pull some electrons away from the Si that bonds to the As, which will reduce the charge density between the Si–As bond, compared to that in the intrinsic Si without O. This will improve the covalent bond between Si and As, because the electrons being pulled away are from antibonding state.

The stability of different complexes can also be qualitatively understood in terms of electronegativity difference between Si, As, and O. The ionic O–Si bond is more favorable than O–As bond, because of larger electronegativity difference between O (3.44, Pauling) and Si (1.9) than that between O and As (2.18).¹⁷ Consequently, the direct bonding of O and As is not favored in Si host. Similarly, the covalent Si–Si bond is more favorable than the Si–As bond, because the latter has an electronegativity difference. In forming an O–Si–As complex, O will help to effectively balance the electronegativity difference between Si and As.

Our calculations show that qualitatively, O_i can be trapped by formation of the –Si–O–Si–As– complexes, which reduces the overall mobility of O_i in heavily As doped Si, leading to O_i diffusion retardation as experimentally observed. However, quantitatively, our calculated trapping energies are much smaller than what had been estimated from experiments. We predicted an O_i trapping energy in the range of 0.14–0.21 eV, which is about five smaller than the experimental values of ~ 1.0 eV.⁹ This indicates that the direct binding between O_i and As in Si, as we have determined here, is not sufficiently strong to account for the experimen-

tally observed O_i trapping effects in heavily As-doped Si. We suspect that other types of defects, such as vacancy and/or interstitial, may also participate in forming more complex structures, which provide a much higher trapping energy for O_i . We are currently investigating these possibilities and the results will be published in due course.

In conclusion, we have performed first-principles total energy calculations to study the interaction between interstitial oxygen (O_i) and As dopant in heavily As-doped Si. We found that direct As–O bonding is prohibitive, and the most stable configuration is with As and O_i as second nearest neighbors, forming –Si–O–Si–As– type complexes. Such complexes can trap O_i in their vicinity, which will in turn reduce the overall O_i mobility in qualitative agreement with experiments. Quantitatively, however, the trapping energy of O_i provided by such complexes is found to be too small in comparison with the experimental estimation. Future studies will be directed towards resolving this discrepancy by involving complexes with other defects, such as vacancies and interstitials.

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