

Structure, stability, and diffusion of arsenic-silicon interstitial pairs

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Recent experimental studies [A. Ural, P. B. Griffin, and J. D. Plummer, *J. Appl. Phys.* **85**, 6440 (1999); R. Kim, T. Hirose, T. Shano, H. Tsuji, and K. Taniguchi, *Jpn. J. Appl. Phys.* **41**, 227 (2002); S. Solmi, M. Ferri, M. Bersani, D. Giubertoni, and V. Soncini, *J. Appl. Phys.* **94**, 4950 (2003)] have suggested the importance of Si interstitials in As transient enhanced diffusion during *pn* junction formation in silicon. Using density functional theory calculations within the generalized gradient approximation, we have examined the structure, stability and diffusion of As–Si_i pairs. For the negatively charged As–Si_i pair, we find a minimum energy structure in which the As atom bridges two approximate lattice Si atoms, while for the neutral and positively charged As–Si_i we find the lowest energy structure is comprised of an As and Si_i pair that is aligned in the [110] direction while sharing a lattice site. Our results suggest that in *n*-type extrinsic regions the diffusion of –1 charged As–Si_i pairs will be prevailing with an overall activation energy of 3.1–3.4 eV, while under intrinsic conditions the neutral and –1 charged pairs will both contribute to arsenic diffusion. The predicted activation energies are similar to experimental observations for As diffusion and previous calculations for As-vacancy complex diffusion. These results clearly support that interstitials can contribute significantly to As transient enhanced diffusion, particularly in the region where interstitials exist in excess. © 2005 American Institute of Physics. [DOI: 10.1063/1.2130398]

As device dimensions scale down to nanometer scales, the formation of ultrashallow junctions (<20 nm in depth) is required to avoid short-channel effects. At present, the junctions are widely synthesized by using low energy ion implantation to introduce dopant impurities into the silicon substrate. This step is followed by thermal annealing to repair the ion-bombardment induced substrate damage and electrically activate the implanted dopants. During postimplantation annealing, the dopant impurities often exhibit significant transient enhanced diffusion (TED). The resulting dopant profile spreading poses a great challenge in forming ultrashallow *pn* junctions required for nanometer scale device structures. It is therefore necessary to elucidate the underlying mechanism of dopant TED, and in turn find a means to minimize the TED while maximizing the electrical activity of injected dopant impurities.

At high concentrations ($>3 \times 10^{20}$ atoms/cm³) and high temperatures (≥ 750 °C), arsenic (As) has been found to exhibit significant TED during postimplantation thermal treatment.^{1–5} Previous theoretical studies have proposed that Si vacancy (V) mediated diffusion in the form of mobile As–V and As₂–V complexes may be primarily responsible for the As TED.^{6–8} However, recent experimental observations have suggested that Si interstitials (Si_i) may also promote As TED,^{1–3} warranting further study of the TED mechanism. Moreover, in a recent theoretical study, we showed that mono- and di-vacancy arsenic complexes (As_mV, As_nV₂) can easily be annihilated in the presence of interstitials with an annihilation barrier of ≤ 0.21 eV.⁹

In this paper, we present the structure and diffusion of As–Si_i pairs based on first principles calculations. We identify the lowest energy structure and binding energies of As–Si_i pairs, as well as calculate the pathways and barriers

for As–Si_i pair diffusion in the negative, neutral, and positive charge states. Based on computed activation energies, we predict dominant mobile As–Si_i pairs under intrinsic and extrinsic conditions. We also discuss the relative role of vacancies and interstitials in As TED.

All atomic and electronic structures and total energies are calculated using the plane-wave basis pseudopotential method within the generalized gradient approximation (GGA) (Ref. 10) to density functional theory (DFT), as implemented in the Vienna *Ab-initio* Simulation Package (VASP).¹¹ We use Vanderbilt-type ultrasoft pseudopotentials¹² and a planewave cutoff energy of 12 Ry. The defect systems computed here are modeled using a 216-atom supercell with a fixed lattice constant of 5.457 Å. All atoms were fully relaxed using the conjugate gradient method until residual forces on constituent atoms become smaller than 5×10^{-2} eV/Å. A (4 × 4 × 4) mesh of *k* points in the scheme of Monkhorst-Pack was used for the Brillouin zone sampling.¹³ We calculate diffusion barriers and pathways using the nudged elastic band method (NEBM),¹⁴ which reliably finds the minimum energy pathway between two energy minima.^{9,15}

From a search using various initial configurations, we identified the lowest energy As–Si_i structures in the negative, neutral, and positive charge states. In the negatively charged As–Si_i[–] structure, the As atom bridges two approximate lattice Si atoms as depicted in Fig. 1(a). For As–Si_i⁰ and As–Si_i⁺, the lowest energy structure is comprised of As and Si_i atoms that are aligned in the [110] direction while sharing a lattice site [Figs. 2(a) and 3(a)].

We assessed the relative stability of these neutral and charged As–Si_i pairs by computing defect ionization levels (μ_i). At a given Fermi level (ϵ_F), the relative formation energy of a charged defect in charge state $q = \pm 1$ to a neutral defect is given by $E_f^q - E_f^0 = q(\epsilon_F - \mu_i)$, where ϵ_F is given relative to the valence band maximum (E_V). Thus, the defect

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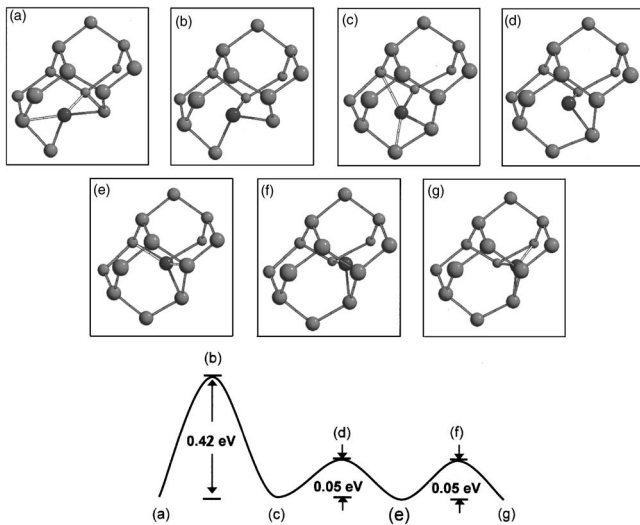


FIG. 1. (Upper Panel) The As-Si_i⁻ pair diffusion pathway. The green (dark-colored) and yellow (light-colored) balls represent As and Si atoms, respectively. The white outlined bonds indicate the orientation of the As atom and are not actual bonds. (Lower Panel) Corresponding diffusion barriers for the As-Si_i⁻ pair.

levels can be approximated by $E_D^q + q(E_V^q + \mu_i) = E_D^0$, where E_D^q and E_D^0 are the total energies of the defects in q and neutral charge states, and E_V^q is the position of the valence band maximum in supercell E_D^q . In calculating a charged defect, a homogeneous background charge is included to maintain the overall charge neutrality in the periodic supercell. To account for the Coulomb energy between the charged defect and the background charge, a monopole correction is made to the total energy of the charged system.¹⁶ Assuming a pointlike +1 charge defect in the 216-atom supercell, the monopole correction is estimated to be approximately 0.11 eV. This correction may overestimate the required adjustment if the charge on the defect is significantly delocalized.¹⁷ From the calculations, we determined the positions of As-Si_i⁰ acceptor and donor levels at $E_V + 0.10$ eV and $E_V + 0.19$ eV, respectively (for the computed Si band gap of 0.63 eV). According to the defect levels, the positive charge state (As-Si_i⁺) is energetically most favorable up to 0.14 eV, after which the negative charge state (As-Si_i⁻) becomes the most stable.

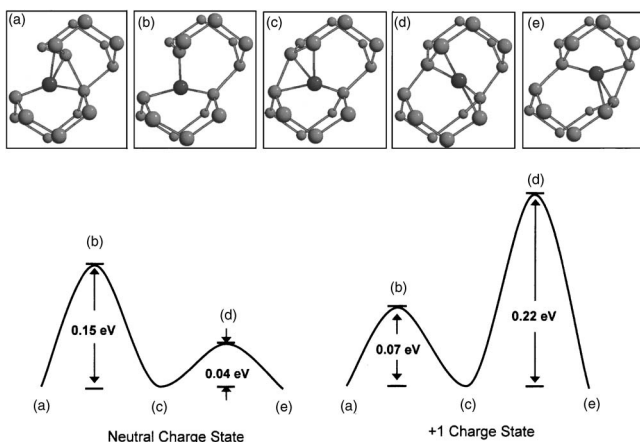


FIG. 2. (Upper Panel) As-Si_i pair diffusion pathway for mechanism A. The green (dark-colored) and yellow (light-colored) balls represent As and Si atoms, respectively. The atomic configurations of As-Si_i⁰ and As-Si_i⁺ cases are indistinguishable. (Lower Panel) Corresponding diffusion barriers for As-Si_i⁰ and As-Si_i⁺ pairs, as indicated.

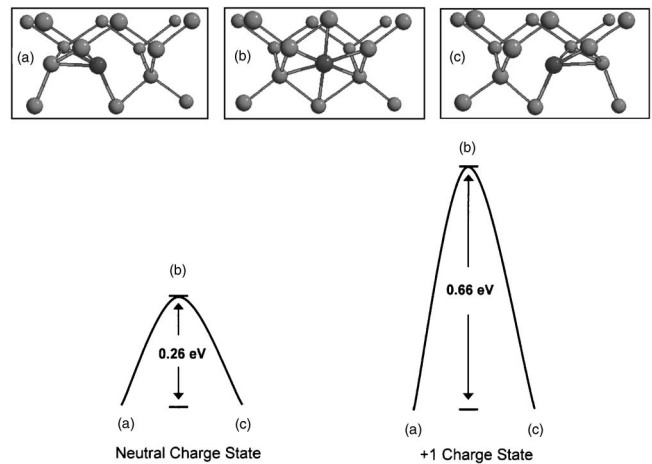


FIG. 3. (Upper Panel) As-Si_i pair diffusion pathway for mechanism B. The green (dark-colored) and yellow (light-colored) balls represent As and Si atoms, respectively. The atomic configurations of As-Si_i⁰ and As-Si_i⁺ cases are indistinguishable. (Lower Panel) Corresponding diffusion barriers for As-Si_i⁰ and As-Si_i⁺ pairs, as indicated.

The formation energy of As-Si_i⁰ is calculated to be 3.11 eV ($=E[\text{AsSi}_{216}] - E[\text{AsSi}_{215}] - E[\text{Si}_{216}]/216$, where $E[\text{AsSi}_{216}]$, $E[\text{AsSi}_{215}]$, and $E[\text{Si}_{216}]$ are the total energies of As-Si_i⁰, substitutional As⁰, and crystalline Si). This leads to formation energies of 2.98 eV and 3.33 eV, respectively for As-Si_i⁻ and As-Si_i⁺ in intrinsic regions. Under intrinsic conditions, the binding energies of As-Si_i⁻, As-Si_i⁰, and As-Si_i⁺ are approximated to be 0.72 eV, 0.59 eV, and 0.37 eV, respectively, relative to the dissociation products of substitutional As⁰ and (110)-split Si_i⁰. {Here, the As-Si_i binding energy is determined by $E_b(\text{As-Si}_i^q) = E_f(\text{As}^0) + E_f(\text{Si}_i^0) - E_f(\text{As-Si}_i^q)$, where the Si interstitial formation energy [$E_f(\text{Si}_i^0)$] is calculated to be 3.70 eV}. Note that these relative formation and binding energies are determined using the computed Si band gap of 0.63 eV, leaving room for improvement in the values.

Figure 1 shows the diffusion pathway for the negatively charged As-Si_i⁻ pair, involving three steps. In the first step, an As-Si bond breaks and a new As-Si bond forms as the As atom migrates over a barrier of 0.42 eV from one bridged As site to another. The next two steps involve As reorientation within the same bridged site by overcoming barriers of 0.05 eV. The low barrier for As reorientation ensures that As-Si_i⁻ diffusion will occur in a random direction.

We also identified two diffusion mechanisms for the neutral As-Si_i⁰ and positively charged As-Si_i⁺ pairs. One mechanism (A) involves two transition states TS_{A1} and TS_{A2} [Figs. 2(b) and 2(d)], while the other (B) involves one transition state TS_B [Fig. 3(b)]. The atomic structures at the local minima and saddle points for mechanisms A and B, along with corresponding energy diagrams, are depicted in Figs. 2 and 3.

In mechanism A, the two steps involved in As-Si_i pair diffusion include: (i) the As and Si_i atoms switching their positions at the same lattice site through the transition state T_{A1} and (ii) the As atom moving to an adjacent lattice site through the transition state T_{A2} while pushing a neighboring Si lattice atom in the [110] direction to form a As-Si_i pair at the adjacent lattice site. The energy barriers for the two steps are respectively predicted to be 0.15 eV (0.07 eV) and 0.04 (0.22 eV) eV for the neutral (positively charged)

As–Si_i pair. Note that the second step becomes the limiting step in the positive charge state in contrast to the neutral charge state, where the first step was the limiting step.

Mechanism B predicts As–Si_i pair diffusion via a hexagonal interstitial site. In this case, the As atom migrates from a (110)-split state to another (110)-split state via the hexagonal As interstitial state (which turns out to be the transition state, TS_B). This diffusion jump requires overcoming a barrier of 0.26 eV in the neutral state, while 0.66 eV in the positive charge state.

Here it is worthwhile to note the diffusion directions associated with mechanisms A and B. In mechanism A (Fig. 2), the As diffusion is restricted to the [110] direction, while it can occur in a random direction through mechanism B (Fig. 3). However, considering the small barrier difference (of approximately 0.1 eV) between mechanisms A and B, it can be expected that the neutral As–Si_i pair may undergo diffusion by both pathways.

The computed formation energies and diffusion barriers yield the overall activation energies of 3.40(=2.98+0.42) eV, 3.26(=3.11+0.15) eV, and 3.55(=3.33+0.22) eV for As–Si_i pair diffusion in the negative, neutral, and positive charge states, respectively, under intrinsic conditions (where the Fermi level is positioned at midgap). The comparable diffusion activation energies of the negatively charged and neutral complexes indicate that both may contribute to interstitial-mediated As diffusion under intrinsic conditions. Under highly *n*-type doped regions, the formation energy of the anionic As–Si_i[−] pair will decrease, making it the dominate diffusing species. At midgap and above, the As–Si_i[−] pair will have an approximate activation energy of 3.1–3.4 eV based on the computed band gap.

The computed activation energies we present are comparable to activation energies obtained from both recent computations of arsenic-vacancy complex diffusion^{7,8} and experimental observations of overall defect-mediated As diffusion.⁴ For instance, based on DFT calculations, Ramamoorthy and Pantelides predicted activation energies of 3.9 eV and 2.7 eV for As–V and As₂–V complexes, respectively.⁷ Subsequently, Xie and Chen estimated As–V activation energies of 2.51–3.59 eV, depending on As concentration.⁸ Experimental work by Larsen *et al.*⁴ places the activation energy for As diffusion between 2.65 eV and 3.89 eV.

In addition to diffusion activation energies, the relative density of interstitials and vacancies will also determine the relative contribution of As–Si_i and As–Si_v to As TED. A recent theoretical study⁹ has shown that in the presence of silicon interstitials, arsenic-vacancy complexes are easily annihilated by interstitial-vacancy recombination. Therefore, we would expect that the relative contribution of vacancy- and interstitial-mediated diffusion will depend on which native defect is present in excess. Since As implantation usually produces an excess of interstitials, interstitials can be expected to play a vital role in As TED (except at the early stages of annealing in which vacancies can also exist in ex-

cess near the surface). This is consistent with recent experimental observations^{1–3} that suggest interstitial-mediated As TED. Our results provide more support that interstitials will also be a determining factor in understanding the kinetic behavior of implanted As species during postimplantation thermal annealing.

In summary, we have performed plane-wave basis, pseudopotential total energy calculations to determine the structure, stability, and diffusion of As–Si_i pairs. Under intrinsic conditions, we estimate the binding energies of 0.72 eV, 0.59 eV, and 0.37 eV for As–Si_i[−], As–Si_i⁰, and As–Si_i⁺, respectively, relative to the dissociation products of substitutional As⁰ and (110)-split Si_i⁰. Our results also suggest that As–Si_i[−] and As–Si_i⁰ will both contribute to As diffusion under intrinsic conditions with As–Si_i[−] diffusion dominating under extrinsic conditions. The overall diffusion activation energies of As–Si_i[−] and As–Si_i⁰ pair are computed to be approximately 3.3–3.4 eV at midgap, consistent with 2.7–3.9 eV as determined by experiments. Furthermore, since As–V complexes can be easily annihilated by interstitial-vacancy recombination we can expect that interstitials will play an important role in As TED when Si interstitials exist in excess. The mechanistic understanding we present in this work will greatly contribute to developing an improved physical model for formation of highly As doped ultrashallow junctions required for future generations of Si-based electronic devices.

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