First-principles studies of small arsenic interstitial complexes in crystalline silicon

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We present a first-principles study of the structure and dynamics of small As-interstitial complexes (AsI2, As2I2, AsI3, and As2I3) in crystalline Si. These complexes can be important components of stable As-interstitial clusters or play a key role in interstitial-mediated formation of As-vacancy clusters. Neutral AsI and As2I3 are identified as fast-diffusing species that contribute to As transient enhanced diffusion. We demonstrate that the extended defect configuration As2I3\text{ext} is a stable configuration with a binding energy of 2.64 eV. As2I3\text{ext} can serve as a nucleation site and facilitate the formation of larger As-interstitial clusters in presence of excess Si interstitials and high As concentration. We also discuss the implications of our findings on As transient enhanced diffusion and clustering and highlight the role of small As-interstitial complexes in ultrashallow junction formation.

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I. INTRODUCTION

Aggressive complementary metal oxide semiconductor field effect transistors (MOSFETs) scaling requires both ultrashallow junctions and low sheet resistance to overcome short channel effects and enhance the device performance in MOSFETs.1 It is predicted by the International Technology Roadmap for Semiconductors (ITRS) that ultrashallow junctions less than 5 nm in depth will be necessary to produce the next generation of silicon transistors.1 In order to achieve these challenging goals, the n-type dopant As is a desirable candidate due to its high mass, high solubility, low diffusivity and high activation. However, As also exhibits electrical deactivation and transient enhanced diffusion (TED) during postimplantation thermal annealing.2–7

Earlier experimental and theoretical studies have shown that As TED can be mainly explained by vacancy-mediated As diffusion5–7 and As deactivation might be driven by AsnVn complexes.8–11 However, Kong et al.4,12 and others have reported that interstitial-mediated As diffusion is dominant for As TED under supersaturated interstitial conditions. In the presence of excess Si interstitials, it is predicted that AsnVn complexes are easily annihilated by I-V recombination.13 Hence, from the recent experimental results, it is clear that I-mediated As diffusion can be very important, together with V-mediated As diffusion.2–4 In addition, previous experimental results have shown that As doping affects the size and density of Si (311) extended defects by trapping Si interstitials, suggesting that stable AsnIm complexes are present at intermediate steps of anneal.14

In presence of excess Si interstitials introduced during ion implantation, I2 and I3 clusters can exist in large numbers and be highly mobile under nonequilibrium conditions,15–17 implying a significant contribution to As TED and IIm cluster formation.2–7 Likewise, one can expect that small AsnIm complexes have an important role in As TED and larger AsnIm cluster formation, especially under Si interstitial supersaturation and high As concentrations. Harrison et al.18 have reported a possible formation and binding-energy map of small AsnIm complexes. However, little is known about the detailed structure, stability, and dynamics of the complexes.

In this paper, we present first-principles studies for the structure and dynamics of small AsnIm complexes (AsI2, As2I2, AsI3, and As2I3) in crystalline Si. Using density-functional theory calculations, we determine the ground-state structures and the minimum-energy diffusion pathways/barriers of small AsnIm complexes, elucidating their relative roles in As TED and clustering.

II. COMPUTATIONAL DETAILS

All of our atomic and electronic structure calculations based on density-functional theory (DFT) were done using plane-wave basis ultrasoft pseudopotential (USPP) method with the Vienna Ab-initio simulation package (VASP).19–21 The exchange-correlation energy functional is represented using the generalized gradient approximation (GGA) form of Perdew and Wang (PW91).22 Total-energy calculations were performed on a 2 × 2 × 2 Monkhorst-Pack grid of k points in the simple-cubic cell.23 The optimized Si lattice constant for our system is 5.457 Å. We used a cutoff energy of 200 eV for the plane-wave basis set. A 216-atom supercell was found to sufficiently reduce system size errors in the total energy. All atoms were fully relaxed using the conjugate gradient method to minimize the total energy.

To test convergence with respect to k-point sampling and energy cutoff, we perform calculations with a 4 × 4 × 4 k-point grid and a 300 eV energy cutoff and find that our calculated formation energies vary by less than 0.2 eV, and our energy barriers by less than 0.03 eV. Local density of states (LDOS) are calculated in order to analyze defect characteristics such as the presence of gap states, their location with respect to the Fermi energy (EF), and the presence of resonance states in the conduction band. LDOS calculations are done with a 3 × 3 × 3 k-point sampling of Brillouin zone. LDOS for different supercells are aligned using deep 2s lev-
els of bulk Si atoms, distant from the defect structure. We calculate diffusion pathways and barriers using the nudged elastic band method.\textsuperscript{24} To analyze the electronic structure and characterize bonding properties of stable As\textsubscript{n}I\textsubscript{m} complexes as well as saddle points for diffusion pathways, we have performed a Bader analysis\textsuperscript{25} where the atomic volumes are defined solely from the electronic charge density. For this analysis, core charges are included within the projector augmented wave (PAW)\textsuperscript{26} framework, and the resolution of the charge-density grid is increased to give Bader charges with high accuracy. We calculated an electron localization function (ELF) isosurface at the value of 0.80.\textsuperscript{26} In order to calculate the formation energy in different charged states, we applied a monopole charge correction of 0.11 eV in our 216 atom supercell to compensate for the artificial uniform background countercharge required to maintain charge neutrality.\textsuperscript{27} We used the experimental Si band gap of 1.2 eV to evaluate the chemical potential of electrons since DFT underestimates the gap.\textsuperscript{27}

III. RESULTS AND DISCUSSION

A. Di-interstitials with one arsenic atom (As\textsubscript{I}\textsubscript{2})

We first investigated the lowest energy structure of the neutral di-interstitial with one As atom (As\textsubscript{I}\textsubscript{2}) and its diffusion pathway in crystalline Si. Several theoretical studies have shown that Si di-interstitials (I\textsubscript{2}) are fast-diffusing species with a low migration barrier.\textsuperscript{15,17} In analogy to the Si di-interstitial, As\textsubscript{I}\textsubscript{2} is also expected to be highly mobile. The lowest energy configuration identified is shown in Fig. 1.\textsuperscript{15} While I\textsubscript{2} has equilateral triangular shape as the ground state, the overall triangular shape of As\textsubscript{I}\textsubscript{2} is slightly distorted with the addition of an As atom to the structure. As a result, the Si-Si (I–III) bond length is 2.41 Å and the As-Si (I–IV) bond length is 2.51 Å in the relaxed structure.

We assessed the stability of neutral As\textsubscript{I}\textsubscript{2} in crystalline Si by its relative formation energy.\textsuperscript{28} The formation energy in

FIG. 1. (Color online) The ground-state structure of As\textsubscript{I}\textsubscript{2} viewed from the (110) and (111) directions. Yellow (light) and purple (dark) represent Si and As atoms, respectively.

FIG. 2. Formation energy as a function of Fermi level for the minimum-energy configuration of As\textsubscript{I}\textsubscript{2}.

FIG. 3. (Color online) Local density of states (LDOS) of (a) substitutional As (red color) in crystalline Si. LDOS for interstitial As (red color) in crystalline Si. LDOS for interstitial As (red color) in transition states of As\textsubscript{I}\textsubscript{2}: (c) $\Gamma_{\text{AB}}$ and (d) $\Gamma_{\text{BC}}$ shown in Fig. 4. The zero in horizontal axis ($E-E_F$) corresponds to the calculated Fermi level associated with the structure. The corresponding decomposed electron densities are displayed in the inset with the ELF isosurface with a value of 0.80. Blue and red represent Si and As atoms, respectively.
the neutral state is 4.91 eV for the relaxed configuration shown in Fig. 1. In Fig. 2, the formation energy is calculated as a function of Fermi level, which shows that neutral and negatively charged AsI₂ are stable in lightly and heavily n-doped regions in Si, respectively. The binding energy of AsI₂ is estimated to be 0.56 eV with reference to the dissociation products of neutral I₂ and substitutional As by \( E_b(\text{AsI}_2)=E_f(I_2)+E_f(\text{As})-E_f(\text{AsI}_2) \). We also calculate the binding energy with reference to the dissociation products of neutral AsI and split-(110) interstitial (I) and find it to be 1.88 eV by \( E_b(\text{AsI}_2)=E_f(I)+E_f(I)-E_f(\text{AsI}) \). Although the “I₂ and As dissociation” route is more favorable than the “AsI and I dissociation” route, the most probable result of AsI₂ dissociation is expected to be I and AsI in the Si lattice because both I and AsI are highly mobile. It should be noted that it is challenging to show a complete dissociation dynamics for given arsenic-interstitial clusters. For example, the dissociation for AsI₂ pair can be the combinatorial constituents of I and AsI. In the arguments for AsI₂ dissociation, we would like to show two possible dissociated pairs while the binding energies for two cases are shown. Although I₂ (+As) itself is known for fast diffusers, I⁺AsI seems to be more promising due to their higher concentrations and configurational entropy effect. Moreover, readers can pick up the binding energy with their own discretion based on our discussions.

In order to characterize the bonding of stable AsI₂, we calculated the LDOS for the As atom in the cluster structure and compared it with that of substitutional As. Figures 3(a) and 3(b) show the band-gap portion of the LDOS for an As atom in a substitutional position and in the cluster, respectively. The LDOS in Fig. 3(b) has a high intensity peak close to the valence-band edge, corresponding to a lone electron pair from the ELF. A Bader analysis, summarized in Table I, shows 5.6 valence electrons for stable AsI₂ in the neutral state when a substitutional As has 5.7 valence electrons. No significant charge transfer to As is found in the positively and negatively charged states of AsI₂ as compared to the neutral state.

Next we propose a diffusion pathway for AsI₂ that occurs through three local minima, labeled as A, B, and C, in Fig. 4. Du et al. suggested a novel diffusion pathway of I₂ with a migration barrier of 0.30 eV, with a mechanism consisting of a translation and/or rotation and then a reorientation step. The diffusion pathway of AsI₂ might follow a similar trajectory to I₂ because the structures of AsI₂ and I₂ are very similar. In Fig. 4, the ground-state configuration A is rotated roughly by 60 degrees with respect to the axis connecting both Si (I) and Si (II) atoms in order to reach another local minimum B. At the transition state \( T_{AB} \), the rotational and translational movements of both Si(III) and As(IV) atoms are made from one Si lattice site to another. The reorientation mechanism of the As atom is shown from B to C through the transition state \( T_{BC} \). The As(IV) atom is rotated roughly by 60 degrees about an axis connecting the Si(I) and Si(II) atoms, without affecting the atomic position of Si(III).

The LDOS of the As atom in the saddle-point structures reveals some interesting features of the diffusion pathway. Figure 3(c) is from the saddle point of AsI₂(\( T_{AB} \) in Fig. 4) and Fig. 3(d) is from the saddle point of AsI₂(\( T_{BC} \) in Fig. 4).

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**TABLE I. Number of valence electrons obtained from Bader decomposed charge analysis on As-interstitial atom of AsI₂ and As₂I₂ in the neutral state. If (−1) and (+1) are specified, they are representing negatively and positively charged state, respectively.**

<table>
<thead>
<tr>
<th>Number of valence electrons</th>
<th>As substitutional</th>
<th>As interstitial</th>
</tr>
</thead>
<tbody>
<tr>
<td>As</td>
<td>5.7</td>
<td></td>
</tr>
<tr>
<td>AsI₂“A”</td>
<td>5.6[5.6(−1), 5.6(+1)]</td>
<td></td>
</tr>
<tr>
<td>AsI₂”T₂”</td>
<td>6.2</td>
<td></td>
</tr>
<tr>
<td>AsI₂”T₃”</td>
<td>5.6</td>
<td></td>
</tr>
<tr>
<td>As(II)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>As₂I₂“A”</td>
<td>5.8[5.8(−1), 5.8(+1)]</td>
<td>5.9[5.9(−1), 5.9(+1)]</td>
</tr>
<tr>
<td>As₂I₂”B”</td>
<td>5.4</td>
<td>5.4</td>
</tr>
<tr>
<td>As₂I₂”C”</td>
<td>5.4</td>
<td>5.4</td>
</tr>
</tbody>
</table>
B. Di-interstitials with two arsenic atoms (As$_2$I$_2$)

We next investigated the structure of the neutral di-arsenic interstitial (As$_2$I$_2$) in crystalline Si. Starting with several stable configurations of I$_2$, we performed an extensive search of energetically favorable configurations of As$_2$I$_2$ in order to identify the global minima. We assessed the stability of neutral As$_2$I$_2$ in Si by the relative formation energy. Based on the structural configurations in Fig. 6, the formation energies for (a), (b), and (c) are given by 3.90, 4.07, and 4.15 eV in the neutral state, respectively. Our identified atomic structure of As$_2$I$_2$ in Fig. 6 is more energetically favorable by 0.52 eV in terms of formation energy, as compared to previous calculations. In Fig. 7, the formation energy is calculated as a function of Fermi level, which shows that neutral As$_2$I$_2$ is stable in both lightly and heavily $n$-doped Si.

Consideration of the two local minima [(b) and (c) in Fig. 6] helps us identify the relative roles of chemical bonding and symmetry for the stabilization of As$_2$I$_2$ structures. Starting with the global minimum configuration [Fig. 6(a)], we can clearly observe that the most stable structure is highly symmetric and well bonded. A possible reason for the stabilization is that both the Si and As atoms in the global minimum have formed highly symmetric, $sp^3$-like bond configurations. The $sp^3$-like hybridization is supported by the fact that the sum of bond angles between the As atom and its three neighboring Si atoms is 324.3; close to the sum of angles ($3 \times 109.5 = 327$). As is evident from the absence of sharp peaks near or in the band gap in Fig. 8, this pair is fully involved in bonding with neighboring atoms.

Next, we consider the local minimum As$_2$I$_2$ configurations of (b) and (c) in Fig. 6. The bonding of the Si atoms in Fig. 6(b) preserves $sp^3$-like hybridization, while that of the As atoms starts to deviate from it, resulting in a sharp peak in the LDOS close to the valence band, with corresponding antibonding resonance level in the conduction band, and a total energy increase of 0.17 eV. In the local minimum structure [Fig. 6(c)], which is next highest in energy to structure Fig. 6(b), the symmetric bonding is lost for both Si and As atoms, increasing the occupation of nonbonded states, and the total energy to 0.25 eV above the global minimum structure [Fig. 6(a)]. From the Bader analysis in Table I, the As atoms in the two configurations in Fig. 6(b) and Fig. 6(c) are locally donating their valence electrons into the neighboring Si atoms.

For the sake of completeness, we estimate the binding energy of the neutral As$_2$I$_2$. The ground state Fig. 6(a) binding is estimated to be 1.90 eV with respect to the dissociation
products of neutral AsI and I by $E_b(\text{As}_2\text{I}_2) = E_b(\text{AsI}) + E_b(\text{I}) - E_b(\text{As}_2\text{I})$. We also calculate the binding energy of $\text{As}_2\text{I}_2$ with reference to two neutral AsI and find it to be 2.19 eV by $E_b(\text{As}_2\text{I}_2) = E_b(\text{AsI}) + E_b(\text{AsI}) - E_b(\text{As}_2\text{I})$. With the assumption that the dissociation rate of $\text{As}_2\text{I}_2$ is highly dependent on both the mobility of the leaving species and the binding energy, dissociation products of two neutral AsI are expected since AsI is highly mobile. In addition, there are four degenerate states [Fig. 6(c)], which participate in the reorientation mechanism shown in Fig. 9. With an energy barrier of 0.32 eV, $\text{As}_2\text{I}_2$ can translate among these four degenerate configurations.

We propose a diffusion pathway for $\text{As}_2\text{I}_2$ that occurs through three local minima, labeled as A [Fig. 6(a)], B [Fig. 6(b)], and C [Fig. 6(c)], in Fig. 10. The lowest energy structure of $\text{As}_2\text{I}_2$ is given by A (and the equivalent A'). In order to reach the first transition state $T_{AB}$ from the ground-state configuration A, As(I) and As(II), which are closely aligned along [110], are slightly rotated around the axis connecting the two As atoms. Rotation and translation of the two As atoms results in a reduction in the distance between them, from 3.18 to 2.62 Å. The final state of this process is the next local minimum B in Fig. 10.

To reach the second transition state $T_{BC}$ from the local minimum B, one of two Si atoms that are bonded together with two As atoms, is shifted into the (111) direction, allowing them to share the lattice site. During the transition of $T_{BC}$, As(I) and As(II) are rotated into the [110] direction to form a triangular shape with a Si atom in the direction of the displacement. With a transformation into B, two As atoms are rotated by almost 90 degrees with respect to original ground-state position A, aligning them in the [110] direction. In the local minimum B, the bond distance of As(I) and As(II) is 2.41 Å, which is smaller than for any other configuration.

In local minimum C, there are four degenerate states as depicted in Fig. 9. In order to reach one of these degenerate states, C', the Si atom just below two As atoms is required to be shifted into the opposite [110] direction with a slight translational movement of these atoms. Next, As(I) and As(II) diffuse through $T_{BC}^{B\rightarrow C}$ (equivalent to $T_{BC}$) to reach the local minimum B' (equivalent to B). Then they migrate through $T_{AB}^{A\rightarrow B}$ (equivalent to $T_{AB}$) to get to the global minimum A'.

The diffusion mechanism of $\text{As}_2\text{I}_2$ is identified with translation and rotation in their structures with a migration barrier, as shown in Fig. 11. The initial barrier from A to B configurations is calculated as 1.03 eV. The barrier from B to C is 0.42 eV. Then, reorientation occurs with a migration barrier.
of 0.32 eV. Although the local minimum B has a slightly higher relative energy by 0.16 eV than the ground state A, the partial diffusion pathway can be composed of B (B') and C (C') with low energy barrier of 0.42 eV.

C. Tri-interstitials with one and two arsenic atoms

We obtained structural configurations and formation energies for As$_{1}$ and As$_{2}$I$_{3}$ clusters. Figure 12 shows that the lowest energy configuration for neutral compact type tri-interstitials with one As atom (As$_{1}$) in crystalline Si. The ground state As$_{1}$ in Fig. 12(a) has a bond length of 2.37 and 2.43 Å for the Si-Si(III–IV) and As-Si(III–V) bonds, respectively. The transition state of As$_{1}$, shown in Fig. 12(b), has a similar configuration to I$_{3}$ with comparable As-Si and Si-Si bond lengths of 2.56 and 2.51 Å, respectively. We assessed the formation energy of As$_{1}$ to be 6.71 eV in Fig. 12(a). The stable As$_{1}$ structure is formed by displacing the two silicon atoms in the I$_{3}$ cluster away from the base of equilateral triangle in (111) direction. The binding energy of As$_{1}$ is estimated to be 1.96 eV with respect to the dissociation products of neutral I and AsI$_{2}$ by $E_{b}(\text{AsI}_{3}) = E_{b}(\text{I}) + E_{b}(\text{AsI}_{2}) - E_{b}(\text{AsI}_{3})$.

When an As atom replaces one of the Si interstitial atoms in I$_{3}$ it does not distort the bond configurations significantly, as shown in Fig. 12, and As$_{1}$ exhibits a similar reorientation behavior as I$_{3}$, as shown in Fig. 13. We find that the rotation barrier for As$_{1}$ is 0.39 eV while a reorientation barrier is just 0.10 eV (see Fig. 14). The 60 degree rotation of As$_{1}$ occurs by a screw motion between two local minima which are labeled A and B in Fig. 13. The ground state A and B can move into a nearest-neighbor lattice site by the transition state “R$_{A}$” and “R$_{B}$,” respectively. However, As(V) has limited space to reorient its position while maintaining the overall atomic configuration of As$_{1}$, which, unlike I$_{3}$, implies anisotropic diffusion. Hence our calculations show that the dynamics of compact As$_{1}$ will be dominated by dissociation as well as reorientation of the cluster. Next, we consider an extended As$_{2}$I$_{3}$ configuration. The lowest energy configuration of As$_{2}$I$_{3}$ is found to have a formation energy of 6.00 eV, as shown in Fig. 15(a). The binding energy is calculated to be 2.67 eV with respect to the dissociation products of neutral I and AsI$_{2}$ by $E_{b}(\text{AsI}_{3}) = E_{b}(\text{I}) + E_{b}(\text{AsI}_{2}) - E_{b}(\text{AsI}_{3})$. 

FIG. 11. (Color online) Atomic configurations and bond lengths of As$_{1}$ in (110) and (111) directions: (a) the lowest energy configuration, (b) the transition-state configuration. As is depicted with purple (dark) atom and Si is shown with yellow (light) atom.

FIG. 12. (Color online) Atomic configurations and bond lengths of As$_{2}$I$_{3}$ in (110) and (111) directions: (a) the lowest energy configuration, (b) the transition-state configuration. As is depicted with purple (dark) atom and Si is shown with yellow (light) atom.
Finally, we investigate the relative stability of tri-interstitials with two As atoms within both compact (As$_3$I$_3^c$) and extended structures (As$_3$I$_3^{ext}$). The lowest-energy configuration of As$_3$I$_3^c$ is shown in Fig. 16 with a formation energy of 5.95 eV. The binding energy of As$_3$I$_3^c$ is estimated at 2.05 eV with respect to the dissociation products of neutral AsI and AsI$_2$. The propensity of As$_3$I$_3^c$ to easily dissociate is explained by the relatively large distance of 2.98 Å between As(V) and As(VI).

The lowest-energy configuration of As$_3$I$_3^{ext}$ is shown in Fig. 15(b) with a formation energy of 5.36 eV. The binding energy of As$_3$I$_3^{ext}$ is estimated to be 2.64 eV with respect to the dissociation products of neutral AsI and AsI$_2$. The bond length between the As atom and the three neighboring Si atoms is 2.31 Å, which shows highly symmetric bonding characteristics. The As atoms and their neighboring Si atoms have a stable bonding geometry in As$_3$I$_3^{ext}$, which is similar to the extended type I$_3^{ext}$.

D. Implications on interstitial-mediated arsenic diffusion and clustering

Harrison et al. suggested the easy annihilation of arsenic-vacancy complexes due to interstitial-vacancy recombination in the presence of excess interstitials. Depending on which defect is in excess, the relative role of interstitial- and vacancy-mediated diffusion in As TED can be determined. Kong et al. suggested that interstitial-mediated As diffusion could be predominant with excess Si interstitials, controlling initial interstitial and vacancy concentrations. Moreover, Brindos et al. showed that the number and size of ̅311 extended defects is reduced as As doping concentration is increased, suggesting the existence of stable arsenic-interstitial complexes at 750 °C.

In order to investigate the implications of arsenic-interstitial complexes for As TED and clustering, ab-initio density-functional theory calculation results for formation, binding, and migration energy of arsenic-interstitial complexes are summarized in Table II. Here, we have calculated the formation energy of each cluster with respect to three reference states; $E_f^1$ has a reference state of substitutional As atoms and a perfect Si lattice, $E_f^2$ has a reference state of substitutional As and $n$ interstitial Si atoms in the Si lattice, and $E_f^3$ has a reference state of substitutional As and $n$ interstitial Si atoms in the extended defects whose formation energy per atom is approximately 2 eV. $E_f^1$ describes the energetic cost to form clusters from a perfect crystal—these energies are very high because of the high cost of forming interstitials. $E_f^2$ does not include the cost of forming the interstitials, which is appropriate in the limit where there is a high concentration of interstitials in the lattice. In this

FIG. 13. (Color online) AsI$_3^c$ diffusion pathway in crystalline Si. The local minimum structures (A and B) are shown with intermediate transition states.

FIG. 14. (Color online) Migration barrier along with AsI$_3$ diffusion pathway in crystalline Si.

FIG. 15. (Color online) Lowest energy structure of (a) AsI$_3^{ext}$ and (b) As$_3$I$_3^{ext}$. As is depicted as purple (dark) atom and Si is shown as yellow (light) atom.
limit. As$_n$I$_m$ clusters are increasingly stable with cluster size. Since experimental conditions will lie somewhere between these two limits ($E_{f1}$ and $E_{f2}$), $E_{f3}$ considers the energetic cost of available interstitials from {311} extended defects which are formed by excess Si interstitials under nonequilibrium conditions during thermal annealing.

Even though As$_n$I$_m$ clusters are energetically stable in the presence of excess interstitials, there is an entropic cost to forming these clusters. At high temperatures and low As and/or interstitial concentrations, entropy will favor smaller clusters. This configurational entropy can be estimated from the equilibrium concentration of Si-free interstitials ($C_I^*$), taken to be $7.95 \times 10^{27} \exp(-4.002/kT)$ cm$^{-3}$. Because the defect concentrations in Si after ion implantation are not explicitly known and they highly depend on implant process conditions, the equilibrium concentrations are assumed as an extreme case in order to demonstrate a configurational entropy effect in the clusters. Here, we are assuming that the As concentration is higher than that of the Si interstitials under the high As dose ($>5 \times 10^{14}$ cm$^{-2}$) conditions used for junction formation. Then, the configurational entropy ($S$) of bringing each additional interstitial into a cluster will be dominated by $k \ln(C_I^*/C_{Si})$. At 1000 K, this configurational entropy increases the free energy of formation of the clusters by 1.22 eV per interstitial; the values ($E_{f3} - TS$) are shown in Table II. Therefore, larger clusters are less favorable due to the configurational entropy.

The compact configurations of As$_2$I$_2$ and As$_3$I$_3$ are expected to dissociate instead of diffuse as a cluster. The neutral AsI$_2$ can be easily formed with excess Si interstitials and high As concentrations, and AsI has a low migration barrier of ($<0.2$ eV). The relative contribution of AsI$_2$ and AsI to As TED can be found by evaluating $D$(AsI$_2$)C(AsI$_2$)/$D$(AsI)C(AsI), where C is the defect concentration. Using $D = D_0 \exp(-E_m/kT)$ with $E_m$(AsI) = 0.15 eV and $E_m$(AsI$_2$) = 0.36 eV, $D$(AsI$_2$) is approximately one order of magnitude greater than $D$(AsI$_2$) at 1200 K. If C(AsI$_2$) is greater in magnitude than C(AsI) at 1200 K with excess Si interstitials under nonequilibrium conditions after ion implantation, AsI$_2$ (and AsI) could be expected to make a large contribution to As TED. For As$_n$I$_m$ clustering, the most likely key intermediate states are As$_2$I$_2$ and As$_3$I$_3$. Since the migration barrier of AsI is extremely low ($<0.2$ eV), neutral As$_2$I$_2$ can be easily formed under excess Si interstitials and high As concentrations. While neutral As$_2$I$_2$ is highly mobile and has relatively strong binding energy, it can also evolve into the larger As$_3$I$_3$ by reacting with an additional Si interstitial.

Neutral As$_3$I$_3$ has a formation energy of 5.36 eV ($E_{f1}$) and a strong binding energy of 2.64 eV when there are three additional atoms (Table II). This result implies that the neutral As$_3$I$_3^{ext}$ is a very stable configuration and a likely key nucleation state for larger arsenic-interstitial clusters. The high migration barrier of As$_2$I$_2^{ext}$ is required to support it. Unfortunately the diffusion pathway and barrier of As$_3$I$_3^{ext}$ is hard to determine explicitly due to its complex structure. To

![FIG. 16. (Color online) Lowest energy structure of As$_3$I$_3^{ext}$. As is depicted as purple atom and Si is shown as yellow atom.](image)

| TABLE II. Formation energy ($E_{f1}$, $E_{f2}$, and $E_{f3}$), formation free energy ($E_{f3} - TS$) at 1000 K, binding energy ($E_b$), and migration energy ($E_m$) of neutral mono-, di-, and tri-interstitials with arsenic-interstitial complexes. $E_{f1}$ describes the energetic cost to form clusters from a perfect crystal while $E_{f2}$ does not include the cost of forming the interstitials. $E_{f3}$ considers the energetic cost of available interstitials from {311} extended defects which are formed by excess Si interstitials under nonequilibrium conditions during thermal annealing. Energy unit is [eV]. All of them are calculated in [216+n] atom supercell (Refs. 15–18, 29, 31, 37, and 38). |
|---|---|---|---|---|---|
| [216+n] atoms | Clusters | $E_{f1}$ | $E_{f2}$ | $E_{f3}$ | $E_{f3} - TS$ | $E_b$ | $E_m$ |
| n=1 | I | 3.74 | | | | 0.29 |
| | AsI | 3.07 | −0.67 | 1.33 | 1.33 | 0.67 | 0.15 |
| | As$_2$I | 2.00 | −1.63 | 2.37 | 2.37 | 1.07 | 1.33 |
| | I$_2$ | 5.49 | −1.97 | 2.03 | 3.25 | 1.99 | 0.30 |
| | AsI$_2$ | 4.91 | −2.50 | 1.50 | 2.72 | 1.88 | 0.36 |
| | As$_2$I$_2$ | 3.90 | 3.51 | 0.49 | 1.71 | 2.19 | 1.03/0.42 |
| n=2 | I$_3$ | 6.93 | −4.25 | 1.75 | 4.18 | 2.30 | 0.49 |
| | I$_3^{ext}$ | 6.28 | −4.91 | 1.09 | 3.53 | 2.95 |
| | AsI$_3$ | 6.71 | −4.50 | 1.50 | 3.93 | 1.96 | 0.39 |
| | As$_2$I$_3$ | 6.00 | −5.21 | 0.79 | 3.22 | 2.67 |
| | As$_3$I$_3$ | 5.95 | −5.27 | 0.73 | 3.17 | 2.05 |
| | As$_3$I$_3^{ext}$ | 5.36 | −5.85 | 0.15 | 2.58 | 2.64 |
exclude the possibility of a low diffusion barrier for neutral As$_2$I$_3$ we performed ab-initio molecular dynamics (MD) with a 2 fs time step for 50 ps, using a Nose-Hoover thermostat to maintain the temperature at 1000 K. We did not observe a single diffusion event for the entire duration of MD run. In contrast, Estreicher et al.\textsuperscript{17} have shown by ab-initio MD simulation that the diffusion event for I$_2$ and I$_3$ can happen within few ps at 100 K. In addition, an adaptive kinetic Monte Carlo simulation (aKMC) (Ref. 39) was used to extensively search for low energy saddle points, find possible diffusion pathway for As$_2$I$_3$, and calculate the dynamics of this cluster over long time scales. In our aKMC dynamics, As$_2$I$_3^{\text{ext}}$ is seen to exchange rapidly between conformers, crossing a low migration barrier (<1 eV), before breaking up into As$_3$I+AsI by crossing a higher barrier (>1 eV). Thus, As$_2$I$_3^{\text{ext}}$ is unlikely to diffuse with low migration barrier less than 1 eV and the energy cost of breaking its bond network configuration should be high.

IV. SUMMARY

We present a first-principles study of the structure and dynamics of small As-interstitial complexes (As$_2$I, AsI$_2$, As$_2$I$_3$, and As$_2$I$_2$) in Si. The compact type configurations of AsI$_2$ and As$_2$I$_3$ are expected to dissociate easily and the extended configuration, As$_2$I$_3^{\text{ext}}$, forms a stable bonding network and has a strong binding energy of 2.64 eV. In presence of excess Si interstitials and high As concentration, As$_2$I$_3$ could be a key intermediate state, and As$_2$I$_3^{\text{ext}}$ could provide a key nucleation site in the formation of larger As-interstitial clusters. A diffusion mechanism for neutral As$_2$I$_2$ is proposed with an overall migration barrier of 0.36 eV. Our results show that As$_2$I may significantly contribute to As TED for excess Si interstitials. A diffusion mechanism for neutral As$_2$I$_3$ is suggested with an overall migration barrier of 1.03 eV and an intermediate reoriented configuration with an energy of 0.42 eV. This detailed understanding of the relative roles of small As-interstitial complexes can provide valuable guidance for ultrashallow junction engineering.

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32 $E_{f1}(\text{As}_{m}\text{I}_n) = E(\text{As}_{m}\text{I}_n) - (216+n-m) \times \mu_{\text{Si}} - n \times \mu_{\text{As}}$

33 $E_{f2}(\text{As}_{m}\text{I}_n) = E(\text{As}_{m}\text{I}_n) - (216+n-m) \times \mu_{\text{Si}} - n \times \mu_{\text{As}}$

34 $= E(Si_{217}) - 216 \times \mu_{\text{Si}}$

35 $E_{f3}(\text{As}_{m}\text{I}_n) = E_{f2}(\text{As}_{m}\text{I}_n) + E_f(311)$ per atom.


