

## Structure and dynamics of the diarsenic complex in crystalline silicon

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(Received 9 May 2005; published 14 November 2005)

Based on first-principles density functional theory (DFT) calculations within the generalized gradient approximation (GGA), we propose a structural model for a diarsenic ( $As_s-As_i$ ) complex in Si and a mechanism for its reorientation, diffusion and dissociation. We find that the lowest-energy structure of  $As_s-As_i$  consists of two As atoms bonded together in a single lattice site with a bond axis which is tilted slightly from the [110] direction. Our study demonstrates the  $As_s-As_i$  pair may undergo reorientations within a lattice site and diffusion, with energy barriers of 1.05 and 1.33 eV, respectively. Dissociation of an  $As_s-As_i$  pair is likely to occur predominantly by the liberation of an  $As-Si_i$  pair to leave behind a substitutional As atom. The dissociation barrier is predicted to be 1.33 eV, and the  $As_s-As_i$  binding energy is calculated to be 1.00 eV relative to dissociation products  $As^0$  and  $AsSi_i^0$ . We also discuss the role of  $As_s-As_i$  pairs in As transient enhanced diffusion and clustering.

DOI: 10.1103/PhysRevB.72.195414

PACS number(s): 61.72.-y, 66.30.Jt, 31.15.Ar

### I. INTRODUCTION

Arsenic is the most common  $n$ -type dopant used in silicon-based device fabrication, by virtue of its high solubility, high activation, and low diffusivity. At high concentrations ( $>10^{20}$  atoms/cm<sup>3</sup>), implanted arsenic atoms may undergo electrical deactivation<sup>1</sup> and transient enhanced diffusion<sup>1-3</sup> (TED) during post-implantation thermal treatment. This could hamper formation of very steep ultrashallow and highly As doped junctions required for the realization of next generation of complementary metal oxide semiconductor (CMOS) devices.

Earlier experimental investigations and theoretical models have suggested that As TED is primarily mediated by vacancies<sup>4-6</sup> while arsenic deactivation is attributed to large arsenic-vacancy complexes.<sup>1,7-9</sup> However, recent experimental observations<sup>10-12</sup> have suggested that interstitials may also play a role in mediating As TED. In addition, recent theoretical studies have predicted the ease of arsenic-vacancy complex annihilation by vacancy-interstitial recombination in the presence of excess interstitials<sup>13</sup> as well as probable low-energy paths for interstitial-mediated As diffusion.<sup>14</sup> Furthermore, recent experimental investigations<sup>15</sup> have revealed that As doping retards the formation of {311} defects, implying that As reacts with interstitials to form stable As-interstitial complexes. This experimental study estimates the dominant As-interstitial complex to be a diarsenic interstitial complex ( $As_s-As_s-Si_i$ , corresponding to a diarsenic substitutional-interstitial pair  $As_s-As_i$ ). The stable  $As_s-As_i$  complex, if it exists, can serve as an important precursor to the formation of larger As-interstitial clusters. Despite its importance, however, little is known about the structure and dynamics of the diarsenic complex.

In this paper we present an *ab initio* study of the atomic structure, energetics, bonding, and dynamics of the  $As_s-As_i$  pair. Using density functional theory calculations we determine the lowest-energy structure of the  $As_s-As_i$  complex, and also predict the pathways and barriers of its reorientation, diffusion, and dissociation.

### II. COMPUTATIONAL DETAILS

All atomic and electronic structures and total energies are calculated using the plane-wave-basis pseudopotential method within the generalized gradient approximation<sup>16</sup> (GGA) to density functional theory (DFT), as implemented in the Vienna *Ab-initio* Simulation Package (VASP).<sup>17</sup> We use Vanderbilt-type ultrasoft pseudopotentials<sup>18</sup> and a plane wave expansion with a cutoff energy of 150 eV. The systems considered 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  $5 \times 10^{-2}$  eV/Å. A  $(2 \times 2 \times 2)$  mesh of  $k$  points in the scheme of Monkhorst-Pack was used for the Brillouin zone sampling.<sup>19</sup> We calculate diffusion barriers and pathways using the nudged elastic band method<sup>20</sup> (NEBM) which reliably finds the minimum energy pathway between two energy minima.

### III. RESULTS AND DISCUSSION

#### A. Structure, bonding, and stability

From an extensive search with several starting configurations, we identified the lowest energy structure of an  $As_s-As_i$  pair. The diarsenic model with  $C_{2v}$  symmetry consists of two bonded As atoms sharing a lattice site with the bond axis aligned slightly off the [110] direction. Figure 1 shows the atomic structure and electron localization function<sup>21</sup> (ELF) isosurfaces of the  $As_s-As_i$  pair, together with those of a neutral  $As-Si_i$  pair and a neutral (110)-split  $Si_i$ . The  $As-Si_i$  pair [Fig. 1(b)] shows a dumbbell structure, aligned parallel to the [110] direction, resembling the most stable single neutral Si interstitial [Fig. 1(c)].

The ELF analysis of  $As_s-As_i$  [Fig. 1(a)] reveals each As is covalently bonded with its two closest Si neighbors as well as the As atom with which it shares a lattice site. The protruding isosurface on each As atom represents an electron lone pair. This suggests that the As atoms tend to have the

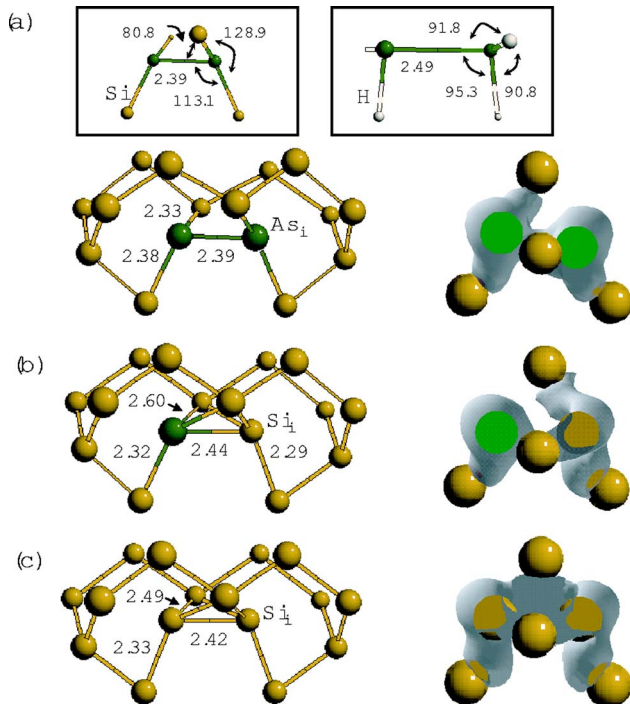


FIG. 1. (Color online) The atomic structure and bonding analysis of (a)  $As_s-As_i$ , (b)  $As-Si_i$ , and (c) (110)-split  $Si_i$ . The grey surfaces represent the isosurfaces of electron localization function (ELF) at the value of 0.7. The bond angles and  $As-As$  bond distance for  $As_s-As_i$  (left) and  $As_2H_4$  (right) are shown in the inset. Bond distances are given in Å. As is depicted with green (dark) atoms and Si is shown with yellow (light) atoms.

$sp^3$  tetrahedral bonding configuration. However, due to the structural constraint in crystalline Si, the  $As_s-As_i$  structure is distorted from the ideal structure. For comparison, we calculated the atomic structure of a  $C_{2v}$   $As_2H_4$  molecule (inset, Fig. 1). For the  $As_2H_4$  molecule, the  $AsAs$  bond length is 2.49 Å, which is slightly longer than 2.39 Å of the  $As_s-As_i$  pair. As expected, there is also a noticeable difference in bond angles between the  $As_2H_4$  molecule and the  $As_s-As_i$  structure. The local strain due to this disparity may undermine the  $AsAs$  interaction.

Figure 2 shows the local density of states (LDOS) on As of the  $As_s-As_i$  pair, with comparison to bulk Si. The donor level is located near the valence band maximum of bulk Si, and it appears to be mainly localized on the As atoms as evidenced by the plot of corresponding decomposed electron densities (Fig. 2, inset). No acceptor level appears within the Si energy gap. The binding energy of the neutral  $As_s-As_i$  pair is predicted to be 1.00 eV relative to the dissociation products substitutional  $As_s^0$  and  $As-Si_i^0$  [Fig. 1(b)] [ $=E(As_2Si_{256})+E(Si_{256})-E(AsSi_{255})-E(AsSi_{256})$ ], where  $E(As_2Si_{256})$ ,  $E(Si_{256})$ ,  $E(AsSi_{255})$ , and  $E(AsSi_{256})$  are the total energies of 216-atom supercells containing a  $As_s-As_i$  pair, no defect, a As substitutional, and a  $As-Si_i$  pair, respectively]. We also calculated the binding energy of the  $As-As_i$  relative to (110)-split  $Si_i^0$  and substitutional  $As_2^0$  and found it to be 1.85 eV [ $=E(As_2Si_{256})+E(Si_{256})-E(As_2Si_{254})-E(Si_{257})$ ], where  $E(As_2Si_{254})$  and  $E(Si_{257})$  are

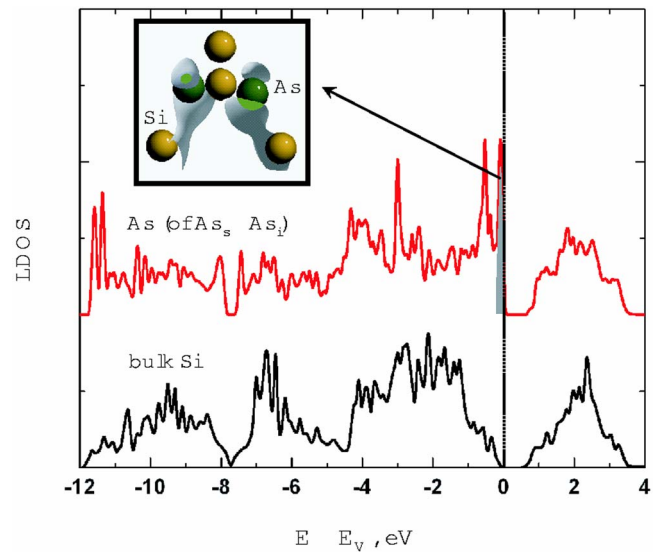


FIG. 2. (Color online) Local density of states (LDOS) on As of the  $As_s-As_i$  pair, with comparison to bulk Si, as indicated. The Si valence-band edge is set at 0 eV. The donor level appears near the Si valence band maximum, and the corresponding decomposed electron densities are displayed in the inset. Green (dark) and yellow (light) balls represent As and Si atoms, respectively.

the total energies of 216-atom supercells containing two As substitutionals and a Si interstitial, respectively]. While these binding energies will vary with the ionization of dissociation products and the position of the Fermi level,  $As_s-As_i$  dissociation to  $As_s^0$  and  $As-Si_i^0$  appears to be more favorable energetically than to  $As_2^0$  and  $Si_i^0$ . A recent theoretical study predicts the barrier for  $As-Si_i^0$  diffusion to be as small as 0.15 eV,<sup>14</sup> indicating  $As-Si_i^0$  mobility can be comparable to  $Si_i^0$  mobility.<sup>22</sup> Given that the dissociation rate of complexes is largely determined by the mobility of departing species and the binding energy, we could expect the most likely result of  $As-As_i$  dissociation is  $As-Si_i$  liberation to leave behind substitutional As.

As shown in Fig. 3, the  $As_s-As_i$  pair has four degenerate states. This complex may rotate between these four equivalent configurations which occupy the same lattice site. The rotation barrier between states which have either the [110] or the  $[1\bar{1}0]$  mirror plane [i.e., (a) and (b) or (c) and (d), respectively,] is only 0.26 eV, while the barrier between states (a) and (c) [or (b) and (d)] is much higher at 1.05 eV. Considering the small activation energy of 0.26 eV, at room temperature we can expect thermal averaging motions between (a) and (b) as well as (c) and (d), leading to the thermal averaged (110)-split state. However, due to the much larger barrier of 1.05 eV [between (a) and (c) as well as (b) and (d)], unlike Si di-interstitial defects in Si (Ref. 23) the symmetry transition to  $D_{2d}$  by the thermal averaging of these four indistinguishable structures appears to be highly unlikely.

## B. Diffusion and dissociation

Figure 4 shows a pathway for  $As_s-As_i$  pair diffusion that occurs through four local minimum states (as labeled A, B,

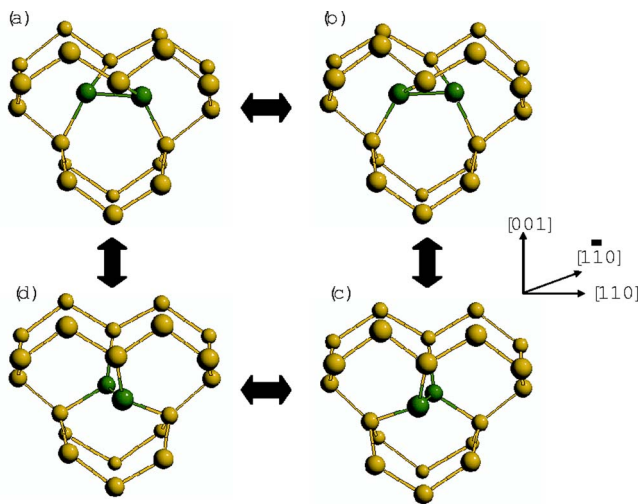


FIG. 3. (Color online) Reorientation of the  $As_s$ - $As_i$  complex within a lattice site. All four configurations are degenerate in energy. Green (dark) and yellow (light) balls represent As and Si atoms, respectively.

C, and D). Here, the lowest energy structure A is depicted in Figs. 1 and 3.

To reach the first transition state  $T_{A-B}$  from the ground-state configuration A, the  $As_{II}$ - $Si_b$  bond as well as the  $Si_d$ - $Si_f$  bond break, which allows the  $As_{II}$  and  $Si_d$  atoms to rotate together and form three new bonds  $As_{II}$ - $Si_e$ ,  $As_{II}$ - $Si_f$ , and  $As_I$ - $Si_d$ . In the resulting local minimum structure B, atoms  $As_I$ ,  $As_{II}$ , and  $Si_d$  all maintain the  $sp^3$  hybrid configuration with  $As_I$  being fourfold coordinated while  $As_{II}$  and  $Si_d$  each occupy their four  $sp^3$  orbitals with three covalent bonds and an unbonded electron pair.

The transformation from local minimum B to local minimum C involves the inversion of  $Si_d$  configuration, with no bond breaking and making. That is, the transition state changes the hybridization about  $Si_d$ . In the transition state, the  $Si_d$  atom is  $sp^2$  hybridized, where the lone pair is held in a  $p$  atomic orbital rather than in a  $sp^3$  atomic orbital. As a result, in the local minimum structure C, the lone pair on  $Si_d$  points in the opposite direction as it does in structure B.

The transition from structure C to D also involves the inversion of  $As_{II}$  configuration, with no bond breaking and making. In structure D, the unbonded electron pair on  $As_{II}$  points in the opposite direction as it does in structure C.

To convert from structure D to  $D'$ ,  $As_I$ ,  $As_{II}$ , and  $Si_d$  must move together to overcome transition state  $T_{D-D'}$  in which  $Si_d$  is fourfold coordinated. In  $T_{D-D'}$ , the  $Si_d$ - $Si_g$  bond is breaking while the  $Si_d$ - $Si_d$  bond is forming. This transition state marks the midpoint in diffusion of the As pair to a new lattice site. The new local minimum structure  $D'$  is an equivalent structure to D with  $As_I$  now possessing an electron lone pair and  $As_{II}$  having fourfold coordination.

Next,  $As_I$  diffuses through  $T_{C'-D'}$  (equivalent to  $T_{C-D}$ ) to arrive at structure  $C'$ , the equivalent of C. Then,  $Si_d$  migrates through  $T_{B'-C'}$  (equivalent to  $T_{B-C}$ ) to achieve structure  $B'$ , the mirror of B. Finally,  $As_I$  and  $Si_d$  migrate simultaneously to overcome transition state  $T_{A'-B'}$  (equivalent to  $T_{A-B}$ ) and arrive at structure  $A'$ , which is equivalent to the original structure A.

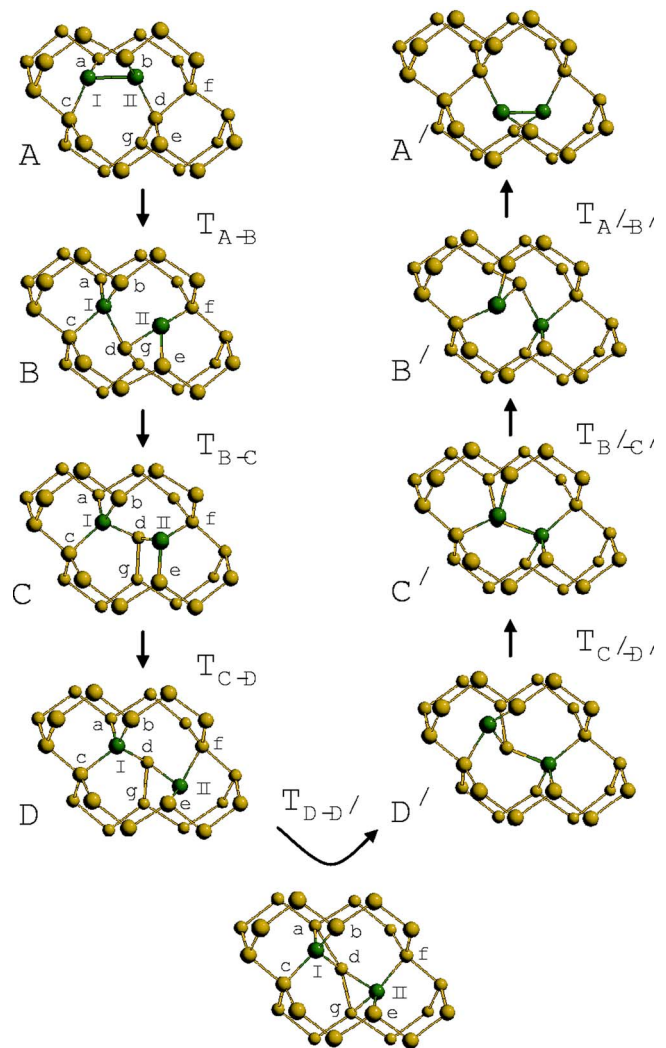


FIG. 4. (Color online) The pathway for  $As_s$ - $As_i$  diffusion in Si. The As atoms are labeled I and II, while relevant Si atoms are labeled (a)–(g). Green (dark) and yellow (light) balls represent As and Si atoms, respectively.

Figure 5 presents the total energy variation along the diffusion path of  $As_s$ - $As_i$ . The initial barrier ( $T_{A-B}$ ) from A to B is estimated to be 1.33 eV. This high activation energy can be attributed to the energy cost of breaking two bonds at this step. B is about 0.55 eV less stable than A. Thus, the barrier for the state B to return to the state A is 0.78 eV. The sizable return barrier implies that B will be a stable structure.

The second barrier from B to C is 0.66 eV, with C being 0.02 eV higher in energy than B. With the return barrier from C to B being 0.64 eV, C is also a stable structure.

Next,  $T_{C-D}$  requires a lower-energy barrier of 0.42 eV to be overcome in order to achieve D, which is 0.08 higher in energy than C. The energy barrier to return to C is 0.34 eV, suggesting that D is also stable.

To achieve the  $T_{D-D'}$  transition state from D, a 0.33 eV energy barrier must be overcome. Since D and  $D'$  are degenerate, the return energy barrier is the same.

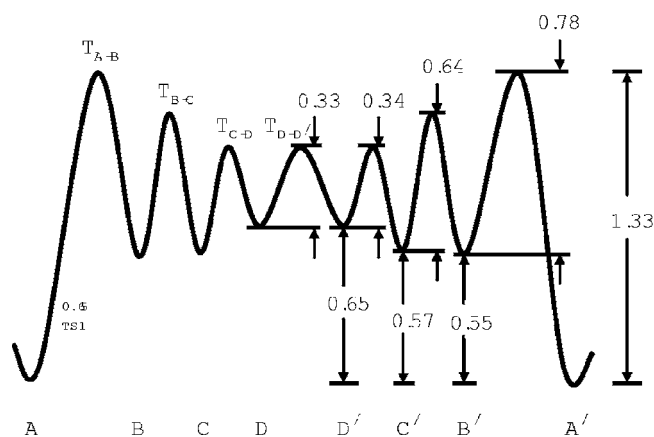


FIG. 5. Energetics along the pathway for  $As_s-As_i$  diffusion in Si.

Since the energy barriers for diffusion are  $\leq 0.66$  eV, we expect the  $As_s-As_i$  complex can transform easily from  $B$  to  $B'$  even at moderate temperatures. The initial step from  $A$  to  $B$  (or  $A'$  to  $B'$ ) requires the highest-energy barrier of 1.33 eV and, assuming steady state kinetics, is the rate limiting overall activation energy required for diffusion.

In addition to identifying the pathway for  $As_s-As_i$  diffusion, we also examined the pathway by which the  $As_s-As_i$  pair dissociates to form a mobile  $As-Si_i$  pair and a substitutional As. The dissociation pathway for  $As_s-As_i$  is shown in Fig. 6. The structures  $A$ ,  $B$ , and  $C$  are the same as those shown in Fig. 4, but from a perspective that is rotated 90° clockwise from that in Fig. 4. The first two steps of dissociation ( $A \rightarrow B$ ,  $B \rightarrow C$ ) are the same as those for diffusion. However, once structure  $C$  is formed,  $As-Si_i$  may separate from the  $As_s-As_i$  complex and diffuse to a neighboring lattice site (structure  $E$ ) by overcoming a 0.60 eV barrier rather than continuing to diffuse as  $As-As_i$  (which would require overcoming a barrier of 0.76 eV). Thus, once the barrier of 1.33 eV is overcome ( $A \rightarrow B$ ), the  $As_s-As_i$  pair is about equally likely to dissociate or continue diffusing. From structure  $E$ , we measure a capture radius of  $>3.60$  Å for the binding of an  $As-Si_i$  pair to form  $As-As_i$ . (Structure  $E$  is 0.30 eV lower in energy than the fully separate  $As-Si_i$  and substitutional As.)

### C. Implication on As TED and clustering

$As-Si_i$ ,<sup>14</sup>  $As-V$ ,<sup>5</sup> and  $As_2-V$  (Ref. 5) complexes have all been predicted to contribute to As TED. A recent theoretical study has shown that arsenic-vacancy complexes are easily annihilated by interstitial-vacancy recombination in the presence of excess interstitials.<sup>13</sup> This suggests that the relative contribution of interstitial- and vacancy-mediated diffusion to As TED depend on which defect is present in excess. Since As implantation will produce an excess of interstitials, we could expect that interstitials would be present in excess during annealing after most vacancy complexes have been annihilated (either by surface annihilation or by interstitial-vacancy recombination). Under these conditions, we expect interstitial-driven diffusion to be important, and we evaluate

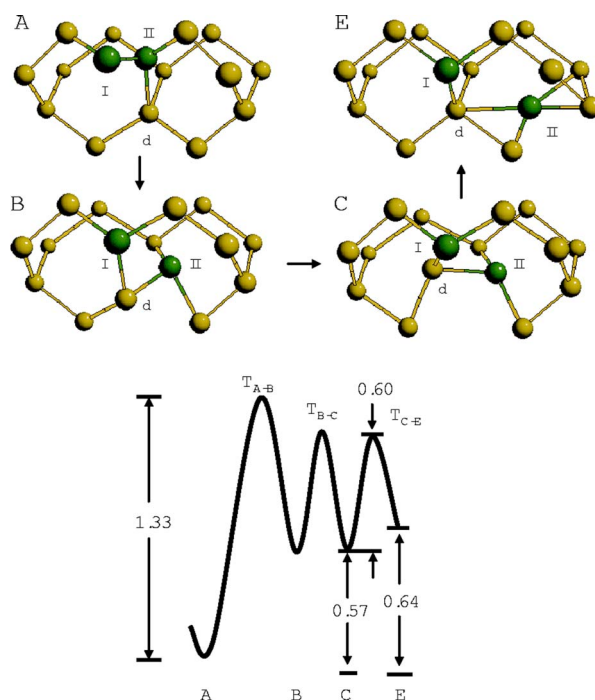


FIG. 6. (Color online) (Upper panel) the pathway for  $As_s-As_i$  dissociation.  $A$ ,  $B$ , and  $C$  are shown from a perspective that is rotated 90° clockwise from the same structures depicted in Fig. 3. (Lower Panel) energetics of  $As_s-As_i$  dissociation. Green (dark) and yellow (light) balls represent As and Si atoms, respectively.

the relative contribution of  $As-Si_i$  and  $As_s-As_i$  to As TED during high-temperature annealing at 1000 °C.

The relative contribution ( $\gamma$ ) of  $As_s-As_i$  and  $As-Si_i$  to As TED can be given by<sup>24</sup>  $\gamma = 2D(As_s-As_i)C_{eq}(As_s-As_i)/D(As-Si_i)C_{eq}(As-Si_i)$ , where  $C_{eq}$  represents the equilibrium concentrations and the factor of 2 is due to the two atoms that  $As-As_i$  carries upon diffusion. Using the Arrhenius equation  $D = D_0 \exp(-E_m/k_B T)$  with  $E_m(As-Si_i) = 0.15$  eV (Ref. 14) and  $E_m(As_s-As_i) = 1.33$  eV,  $D(As-Si_i)$  is approximately five orders of magnitude greater than  $D_m(As_s-As_i)$  at 1000 °C. Therefore,  $C_{eq}(As_s-As_i)$  would have to be equally greater in magnitude than  $C_{eq}(As-Si_i)$  at this temperature for  $As-As_i$  to contribute to As TED. Given no significant difference in the binding energy between  $As-As_i$  and  $As-Si_i^0$  pairs, we suspect that  $C_{eq}(As_s-As_i)$  would not be large enough to make the  $As-As_i$  relative contribution to As TED important.

However, the stable  $As-As_i$  pair may play an important role in As agglomeration. After arsenic ion implantation, an excess population of interstitials is present in the damaged silicon. Upon annealing,  $As_s-As_i$  complexes will likely result from the reaction of  $As-Si_i$  pairs with substitutional As atoms. Subsequently, additional  $As-Si_i$  pairs may bind to  $As_s-As_i$  pairs and form larger arsenic-interstitial complexes. Hence, we expect the  $As_s-As_i$  pair may serve as an important intermediate during the agglomeration process.

## IV. SUMMARY

We present first-principles calculations for the structure,

stability, and dynamics of a substitutional-interstitial diarsenic ( $\text{As}_s\text{-As}_i$ ) pair. The lowest-energy  $\text{As}_s\text{-As}_i$  structure shows  $C_{2v}$  symmetry in which two As atoms share a lattice site and the As-As bond axis is slightly tilted from the [110] direction. The binding energy of this complex is estimated to be 1.00 eV relative to the dissociation products, substitutional  $\text{As}^0$  and  $\text{As-Si}_i^0$ . Our DFT-GGA calculations predict the migration barrier of  $\text{As}_s\text{-As}_i$  to be 1.33 eV. We find the diffusion and dissociation of  $\text{As}_s\text{-As}_i$  involve the same rate-limiting step, making them equally likely. Our theoretical model suggests  $\text{As}_s\text{-As}_i$  diffusion may insignificantly contribute to As TED; however, the  $\text{As}_s\text{-As}_i$  pairs may still

play an important role in As clustering during junction processing.

#### ACKNOWLEDGMENTS

G.S.H. acknowledges the National Science Foundation (Grant Nos. ECS-0304026 and CAREER-CTS-0449373) and the Welch Foundation (F-1535) for their partial financial support. S.A.H. would like to thank the NSF and the University of Texas for financial support. We would also like to thank the Texas Advanced Computing Center for use of their computing resources.

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