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Arsenic defect complexes at SiO_2/Si interfaces: A density functional theory study

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The behavior of arsenic defect complexes at amorphous $SiO_2/Si(110)$ interfaces has been studied using density-functional theory calculation. We find that arsenic defect complexes that are stable in bulk Si show moderate energy gain in SiO_2/Si interface region due to the interface-induced strain effect. We have identified three arsenic defect complex configurations, As_{iI}, As_2I_{2I}, and As_2I_{2II}, which exist only at SiO_2/Si interface. These interface arsenic defect complexes are highly stabilized due to their unique bonding configurations at SiO_2/Si interface. Therefore, they could contribute to arsenic segregation as both initial stage precursor and dopant trapping sites. Our calculation indicates that arsenic atoms trapped in such interface complexes are electrically inactive. Finally, the formation and evolution dynamics of interface arsenic defect complexes are discussed.

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I. INTRODUCTION

The behavior of dopant and defect species at semiconductor interfaces has drawn extensive research attention due to their scientific interest and technological importance.[1–15] A well-known example is the dopant uphill diffusion and segregation in SiO_2/Si interface region.[1–5] As the junction depth of complementary metal-oxide-semiconductor (CMOS) transistors further scales down, this effect may pose more serious technical challenges by increasing dose loss and sheet resistance, leading to device performance degradation.[6–8] Interface-segregation-induced dose loss may also play a key role in the recent emerging nanowire transistors, where nanowires with much larger interface-body ratio are treated with traditional ion-beam doping and thermal anneals.[16–18] For example, a recent experimental study reports that the fraction of active boron atoms could be as low as 15%∼25% in Ge nanowire devices.[18] As an important and practical case, arsenic segregation at SiO_2/Si interface is of great research interest.[5–14] However, while recent experimental studies have characterized the arsenic segregation phenomenon very well, there has been less effort in investigating the underlying mechanism.[9–11] There are several theoretical studies addressing the arsenic segregation issue down to the atomistic level.[12–14] But most of the theoretical studies have focused on the behavior of arsenic in substitutional positions, while disregarding silicon point defects, such as interstitials and vacancies, in SiO_2/Si interface region. However, the importance of point defect in interface region has been clearly recognized in recent studies.[15,19] The interaction between substitutional arsenic and point defects in SiO_2/Si interface region could result in the formation of small arsenic complexes, which may play an important role during the initial stage of arsenic segregation. In addition, due to the unique lattice geometries and strain environment at the SiO_2/Si interface, one would expect significant change in the physics of arsenic complexes close to the interface region. For example, interface arsenic defect complexes may have different configurations and stabilization properties compared with complexes in bulk Si. Therefore, a complete understanding of segregation mechanism requires the consideration of arsenic-point defect complexes, such as arsenic-interstitial pairs (As_i), arsenic vacancy clusters (As_4V), or even new complex species. In addition, despite existing research about realistic SiO_2/Si interface structures,[20,21] most of the previous arsenic segregation studies[12–14] still used tridymite-like SiO_2 in their SiO_2/Si structures. Such artificially constructed structures typically impose unrealistically large stress on both sides of the interface. Therefore, in order to gain a more accurate understanding, an amorphous SiO_2/Si interface is needed since it is the type of interface that exists most commonly in electronic devices.

In this work, we use density-functional theory (DFT) (Refs. 22 and 23) calculation to investigate the mechanism of arsenic pileup and de-activation in SiO_2/Si interface region. First, for the arsenic defect complexes stabilized in bulk Si, the changes of their behavior induced by the proximity of a-SiO_2/Si interface are investigated. Then we identified three energetically favorable arsenic-interstitial complexes which are stabilized only at the SiO_2/Si interface. The configuration, bonding, and electronic properties of the interface arsenic defect complexes are analyzed. Finally, the evolution/diffusion pathways are investigated for the understanding of their formation and migration dynamics.

II. COMPUTATIONAL DETAILS

We use two types of $SiO_2/(110)$ Si interface structures: (1) monolayer crystalline-SiO_2/Si system (c-SiO_2/Si) and (2) amorphous SiO_2/Si system (a-SiO_2/Si), as shown in Fig. 1. The a-SiO_2/Si supercell contains 96 Si atoms and 64 O atoms. The c-SiO_2/Si interface structure contains 144 Si atoms, 24 O atoms, and 48 H atoms. We verified all our major conclusions with larger a-SiO_2/Si and c-SiO_2/Si supercells to remove the effects induced by using small supercells. If we define z direction to be perpendicular to interface plane, x and y directions are contained in this plane. Periodic boundary conditions are applied in all x, y, and z directions for both

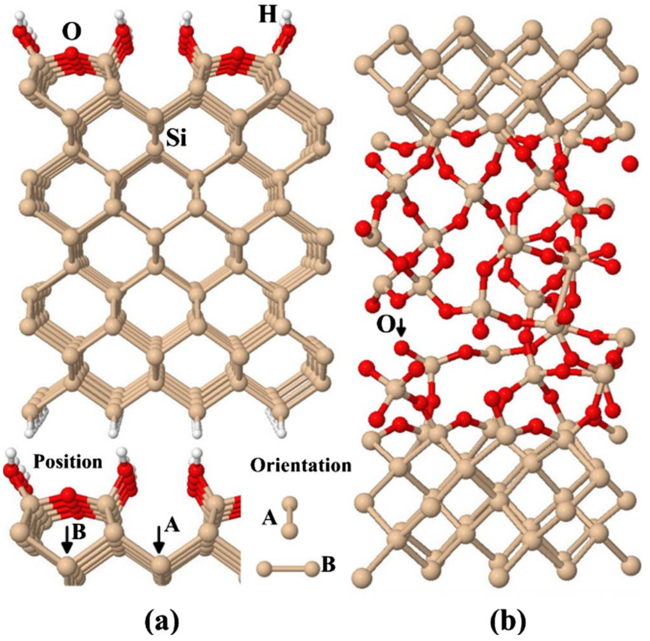

FIG. 1. (Color online) SiO_2/Si interface structures used in this paper: (a) monolayer crystalline-SiO_2/Si interface structure (c-SiO_2/Si) and the definition of position and orientation of As complexes in this system (b) amorphous SiO_2/Si interface structure (a-SiO_2/Si).

a-SiO_2/Si and c-SiO_2/Si structures. For a-SiO_2/Si, the structure is continuous in all directions and supercell-like. For c-SiO_2/Si, the structure is continuous in x and y directions and "slab+vacuum"-like in z direction. The a-SiO_2/Si structure is created by a continuous random network model.[24–26] The construction starts from a periodic tridymite SiO_2/Si structure with nine layers of crystal Si and four layers of tridymite SiO_2. First, the amorphous SiO_2 layer is randomized. Then we relax the entire system at 1500 K via a large number of bond switching, which is performed using the METROPOLIS Monte Carlo method with Keating-like potentials.[27] The a-SiO_2/Si interface structure is later relaxed by DFT calculation to further minimize the total energy. To verify the generated structure, we also constructed amorphous SiO_2 with atomic density consistent with typical amorphous SiO_2 mass density of $2.2\ \mathrm{g/cm^3}$. The average Si-O-Si bond angle and bond angle deviation are 136° and 15°, respectively, which is in good agreement with experimental measurements.[28] The monolayer c-SiO_2/Si structure simplifies tridymite SiO_2/Si structure by using only one monolayer of SiO_2 on top of crystal Si and passivating top oxygen and bottom silicon with hydrogen atoms. The monolayer c-SiO_2/Si system keeps the SiO_2/Si interface topography while avoiding the unrealistic strain induced by a rigid tridymite SiO_2/Si structure. We will show that this simplified system is enough for investigating interface As complexes properties and for estimating their relative stability with respect to As complexes in bulk Si.

For all structure and energetics calculations, we use the plane-wave basis pseudopotential[29] method within the generalized gradient approximation to DFT, as implemented in the Vienna *ab initio* simulation package.[30,31] We use ultrasoft Vanderbilt-type[32] pseudopotentials with a plane-wave cutoff energy of 250 eV. All atoms were fully relaxed using the conjugate gradient method with energy convergence threshold of 1×10^{-3} eV. For formation energies, Γ point sampling is used for the k-space summation and the major results are verified with a $(2\times2\times1)$ Monkhorst–Pack[33] Brillouin-zone sampling. For Fermi-level calculations, a $(4\times4\times4)$ k-space sampling is used.

Diffusion pathways and barriers are extracted by nudged elastic band method (NEBM).[34] This method works by linearly interpolating between two fixed initial and final configurations. Each of the images represents a specific geometry between the initial and final states and the images are connected by a spring interaction. The energy minimization of the string of images gives the minimum-energy pathway.

The bonding mechanisms are analyzed by electron localization function (ELF).[35,36] ELF represents the electron pair localization in terms of the conditional probability of finding an electron in the neighborhood of another electron with the same spin. ELF can take the values ranging from 0 to 1, with $\mathrm{ELF}=1$ corresponding perfect localization and $\mathrm{ELF}<0.5$, suggesting the distribution of delocalized electrons.

III. RESULTS AND DISCUSSION

A. Bulk-stabilized As complexes in interface system

We first construct the As complexes that are most stable in the bulk Si (bulk-stabilized As complexes), such as substitutional arsenic (As_{sub}), As_i, and As_4V, in our SiO_2/Si interface system to check how SiO_2/Si interface would change their stability. After relaxation, we find the proximity to SiO_2/Si interface does not change the lowest energy configurations of these bulk-stabilized As complexes. In order to estimate the stability difference of bulk-stabilized As complexes in SiO_2/Si interface region and in bulk Si, we need to first identify a reference depth in our structures, where the influence of the interface is minimal and As complexes exhibit bulklike properties. We place As_i in split (110) and hexagonal interstitial positions in our interface system and compare the formation energy difference of the two with the difference estimated in bulk Si. We find As_i with split (110) configurations are more stable than those with hexagonal configurations. The formation energy difference of these two configurations is 0.46 eV in the fourth layer from the SiO_2/Si interface, which is very close to the value of 0.42 eV as we calculate in bulk Si. This is in good agreement with a previous study that As_i in split (110) configuration is 0.52 eV more stable than in hexagonal position in bulk Si.[37] Also in Fig. 2, the formation energies of As_4V and split (110) As_i change very little from fourth layer to deeper layers. Therefore in this paper, we treat As complexes in the fourth layer of our structure as in bulk Si, due to the minimal interface effects.

We find that As complexes in the interface layer as well as in SiO_2 side (both with As-O bonds formed) are energetically less stable than those on the Si side. The As-O bonds can cause up to 2.8 eV formation energy penalty. This result is not surprising in that it agrees very well with earlier experimental studies that As resides mainly on the Si side of

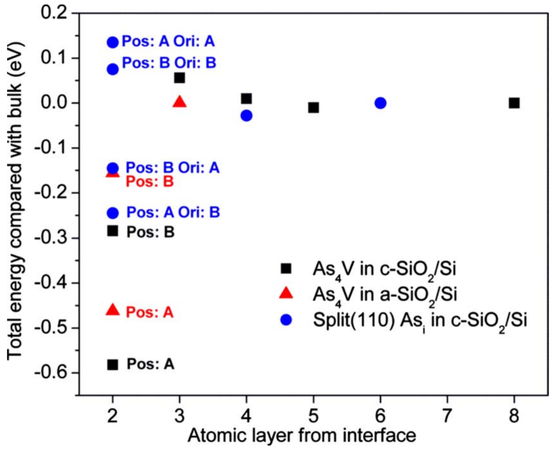

FIG. 2. (Color online) Total energy of As_4V and split (110) As_i in different layers of SiO_2/Si interface structure. The total energy of As complex in deep layers (deep layers are considered to have bulk Si-like properties) are set to be 0 eV reference. The position and orientation associated with interface As complexes are marked, corresponding to the definition in Fig. 1.

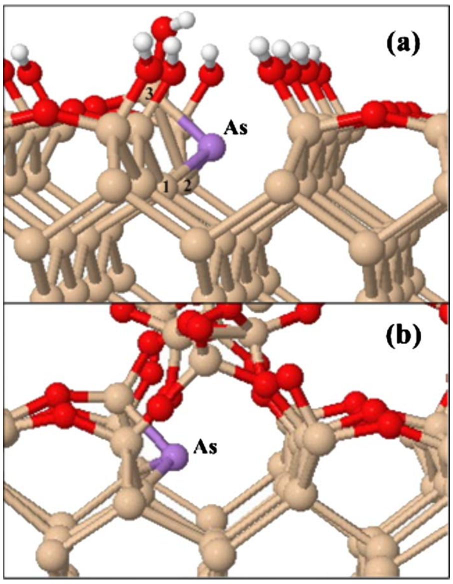

FIG. 3. (Color online) As_{it} configuration at (a) monolayer c-SiO_2/Si interface and (b) a-SiO_2/Si interface.

the interface.[5,11] Previous theoretical studies also indicated that As-O bonds in SiO_2/Si system are energetically unfavorable.[12–14]

Next we consider the stability of As complexes in the second through sixth layers from SiO_2/Si interface. We find the bulk-stabilized As complexes have moderate energy gain in these close-to-interface layers than in bulk Si. In our SiO_2/Si system, As_{sub} has less than 0.3 eV energy gain in the second layer from interface than in bulk Si, and the effect diminishes in deeper layers. As shown in Fig. 2, the formation energy of split (110) As_i in proximity to the SiO_2/Si interface depends highly on the position and orientation of the (110) dumbbell. In certain combinations of position and orientation [e.g., the (110) dumbbell located in the open channel between two Si-O-Si bridges and oriented perpendicular to the channel direction], As_i could be moderately stabilized, while in others, the split (110) As_i at the interface is even less stable than in bulk. As_4V, the major clustering species in bulk Si,[38] is $0.15 \sim 0.6$ eV more stable in the interface layer compared to in bulk Si, and the formation energy also changes with positions. Such a strong position and orientation dependence points to that the stabilization effects can be attributed to geometrical and strain effects rather than to the chemical effects induced by SiO_2. The interface-induced strain depends on position and orientation of As complexes and decreases fast toward deeper layers, corresponding to the flat profiles of formation energy from third to deeper layers in Fig. 2.

B. Interface-stabilized As complexes

Compared with the moderate formation energy gain of bulk-stabilized As complex in SiO_2/Si interface region, we find that arsenic complexes could be deeply stabilized in several configurations that only exist at SiO_2/Si interface(interface-stabilized As complexes). Figure 3 shows an interface arsenic-interstitial configuration (As_{it}). The interstitial arsenic forms bonds with three neighboring silicon atoms by breaking the bond between atom 1 and 3. This structure is energetically unfavorable in bulk Si due to the strain it induces into the crystalline Si lattice. At SiO_2/Si interfaces, however, the As_{it}-induced lattice distortion seems to be well accommodated by the flexibility of Si-O-Si bond angles. We find this As_{it} configuration exists at both c-SiO_2/Si and a-SiO_2/Si interfaces, with comparable bond lengths and bond angles. As_{it} configuration is much more stable than split (110) As_i configuration in bulk Si, with an energy gain of 1.51 eV for c-SiO_2/Si interface and 1.17 eV for a-SiO_2/Si interface. The stabilization could be due to the break of strained interface Si-Si bond and the formation of new bonds in the interface channel space. Due to the randomness of amorphous SiO_2 structure and a-SiO_2/Si interface, this interface stabilization is location dependent. The energy gain of As_{it} depends on local Si-O bonding configurations and may vary in different interface locations. We verified the As_{it} complex in four different locations in a large a-SiO_2/Si supercell with 512 Si atoms and 256 O atoms. The energy gain ranges from 0.50 to 1.86 eV with an average of 1.09 eV, compared with split (110) As_i in bulk Si. This high energy advantage could make As_{it} a trapping site for out-diffusing As_i from bulk Si to SiO_2/Si interface.

It is worthwhile noting that the As_{it} configuration is similar to the split (111) interstitial structure proposed in Ref. 15. The split (111) structure can be viewed as an intermediate trap before silicon interstitial diffuses into SiO_2. In contrast, As_{it} cannot diffuse into SiO_2 due to the energetically unfavorable As-O bonds. The formation energy of As_{it}, as shown in Fig. 4(a), is 0.6 eV lower than that of split (111) interstitial with a neighboring As_{sub}, as shown in Fig. 4(b). This indicates that aside from structural reasons, chemical effects could also be a factor in the stabilization of As_{it}. The less stable split (111) interstitial in a highly arsenic-doped interface may reduce the interstitial out-diffusion into SiO_2 and potentially change the point-defect-assisted dopant diffusion scenario on the bulk Si side.

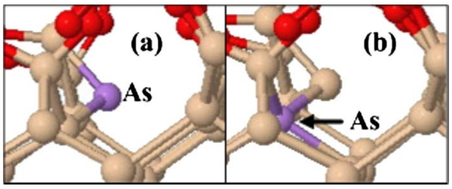

FIG. 4. (Color online) (a) As_{it} structure (b) Split (111) interstitial structure with a neighboring $\mathrm{As}_{\mathrm{sub}}$.

Since As segregation usually results in high-concentration pileup in $\mathrm{SiO}_2/\mathrm{Si}$ interface region, the role of clustered As complexes in this region could be important and interesting. Even if a large amount of arsenic pileup may exist in substitutional sites, one may not deny the role of clustered As-defect complexes, at least as segregation precursors since As atoms can only diffuse to the interface via dopant-defect pairing.[38–41] After checking a variety of clustered As configurations using relatively large c-$\mathrm{SiO}_2/\mathrm{Si}$ structures, we find the most stable ones are those with two As atoms in interstitial positions at the $\mathrm{SiO}_2/\mathrm{Si}$ interface. Figure 5 shows two types of interface stabilized $\mathrm{As}_2\mathrm{I}_2$ complex structures in our $\mathrm{SiO}_2/\mathrm{Si}$ system: $\mathrm{As}_2\mathrm{I}_{2I}$, as shown in (a), (b), and $\mathrm{As}_2\mathrm{I}_{2II}$, as shown in (c), (d). In both structures, two interstitial arsenic atoms are coupled in the interface channel. The difference is in the position and bonding of the underlying silicon atom no. 3. In $\mathrm{As}_2\mathrm{I}_{2I}$, the silicon is in an upper position and forms bond with a first layer silicon atom no. 4. Both of the two arsenic atoms form bonds with first layer silicon, except that one bond (As no. 1 and Si no. 5) is stronger than the other (As no. 2 and Si no. 4). The structure of $\mathrm{As}_2\mathrm{I}_{2II}$ is more symmetric, with two equally strong As-Si bonds. The underlying Si atom no. 3 is in a lower position, forming bonds with a third layer Si atom no. 6. In c-$\mathrm{SiO}_2/\mathrm{Si}$ structure, we find the formation energy of $\mathrm{As}_2\mathrm{I}_{2I}$ is 0.85 eV lower than the stable $\mathrm{As}_2\mathrm{I}_2$ configuration in bulk Si,[42] and is 3.01 eV lower than two separate bulk-stabilized split (110) As_i. The symmetric $\mathrm{As}_2\mathrm{I}_{2II}$ structure is 1.34 eV more stable than $\mathrm{As}_2\mathrm{I}_{2I}$. In a-$\mathrm{SiO}_2/\mathrm{Si}$ structure, $\mathrm{As}_2\mathrm{I}_{2I}$ is 2.80 eV more stable than two separate split (110) As_i in bulk Si, but $\mathrm{As}_2\mathrm{I}_{2II}$ is only 0.61 eV more stable than $\mathrm{As}_2\mathrm{I}_{2I}$. The reduced stability of $\mathrm{As}_2\mathrm{I}_{2II}$ compared with $\mathrm{As}_2\mathrm{I}_{2I}$ in a-$\mathrm{SiO}_2/\mathrm{Si}$ structure is possibly due to the strain induced from SiO_2, since the two coupled arsenic atoms push two interface silicon atom no. 4 and no. 5 upward into SiO_2 side. In c-$\mathrm{SiO}_2/\mathrm{Si}$ structure, such strain is minimal due to the absence of real SiO_2 layers. In bulk Si lattice, such distortion would make these two $\mathrm{As}_2\mathrm{I}_2$ structures highly unstable. We observe that the stabilization of As_{it}, $\mathrm{As}_2\mathrm{I}_{2I}$, and $\mathrm{As}_2\mathrm{I}_{2II}$ is largely due to the unique geometrical properties of $\mathrm{SiO}_2/\mathrm{Si}$ interface itself, instead of chemical interaction with SiO_2. Therefore, these As complexes are still important in systems where SiO_2 layers are defective and incomplete, as long as the $\mathrm{SiO}_2/\mathrm{Si}$ interface topography is maintained.

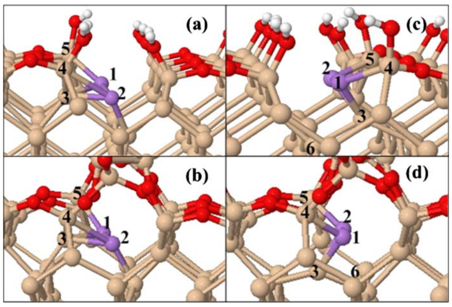

FIG. 5. (Color online) $\mathrm{As}_2\mathrm{I}_{2I}$ configuration at (a) monolayer c-$\mathrm{SiO}_2/\mathrm{Si}$ interface and (b) a-$\mathrm{SiO}_2/\mathrm{Si}$ interface; $\mathrm{As}_2\mathrm{I}_{2II}$ configuration at (c) monolayer c-$\mathrm{SiO}_2/\mathrm{Si}$ interface an d (d) a-$\mathrm{SiO}_2/\mathrm{Si}$ interface. Atoms no. 1 and no. 2 are the two arsenic atoms.

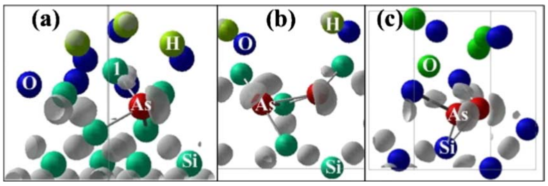

FIG. 6. (Color online) ELF isosurface plot of (a) As_{it} in c-$\mathrm{SiO}_2/\mathrm{Si}$ interface, (b)$\mathrm{As}_2\mathrm{I}_{2I}$ in c-$\mathrm{SiO}_2/\mathrm{Si}$ interface, and (c)$\mathrm{As}_2\mathrm{I}_{2II}$ in a-$\mathrm{SiO}_2/\mathrm{Si}$ interface, with ELF=0.88. The blue balls represent O and green balls represent Si in (a) and (b). In (c), the blue balls represent Si and green balls are O. Red ball represents As in all (a), (b), and (c).

The charge transfer between interface Si and As in As_{it}, $\mathrm{As}_2\mathrm{I}_{2I}$, and $\mathrm{As}_2\mathrm{I}_{2II}$ can be shown by observing the ELF isosurface plot in Fig. 6. Arsenic atoms in all three configurations show electron lone pairs in the interface channel side, which is similar to a previous study[15] for split (111) interstitial at the $\mathrm{SiO}_2/\mathrm{Si}$ interface. For As_{it}, a strong bond exists between arsenic and the interface Si atom no. 1. For $\mathrm{As}_2\mathrm{I}_{2I}$, this strong bond only exists for one arsenic atom, while the other forms a weaker bond with a third layer Si. In $\mathrm{As}_2\mathrm{I}_{2II}$ complex structure, the bonding between arsenic and interface silicon is stronger and exists for both arsenic atoms, which may explain why $\mathrm{As}_2\mathrm{I}_{2II}$ is more energetically stable than $\mathrm{As}_2\mathrm{I}_{2I}$.

The electrical activation properties of As pileup at $\mathrm{SiO}_2/\mathrm{Si}$ interface are of more interest since it matters for ultra shallow junction device performance and dose loss issues. An arsenic complex is considered electrically "active" if it can contribute electrons to conduction band as a donor species. This release of electrons will typically increase the Fermi-level position relative to Si valence-band top ($E_\mathrm{F} - E_\mathrm{V}$). For a given supercell, the $E_\mathrm{F} - E_\mathrm{V}$ should be the lowest when donor species are absent (defect-free system) and should increase when electrically active donors are introduced. Here we evaluate the activation properties of As complexes by examining their $E_\mathrm{F} - E_\mathrm{V}$, as shown in Table I. From the bulk Si test cases, we confirmed that active As complexes, such as $\mathrm{As}_{\mathrm{sub}}$, tend to have higher $E_\mathrm{F} - E_\mathrm{V}$ than the defect-free structure or structure with electrically inactive complexes, such as $\mathrm{As}_2\mathrm{I}$ or $\mathrm{As}_4\mathrm{V}$. If we analysis the Si part of the bandstructure in $\mathrm{SiO}_2/\mathrm{Si}$ systems, we find the interface stabilized As_{it}, $\mathrm{As}_2\mathrm{I}_{2I}$, and $\mathrm{As}_2\mathrm{I}_{2II}$ in both c-$\mathrm{SiO}_2/\mathrm{Si}$ and a-$\mathrm{SiO}_2/\mathrm{Si}$ systems result in comparable $E_\mathrm{F} - E_\mathrm{V}$ in Si band structure compared with that of defect-free systems. And the $E_\mathrm{F} - E_\mathrm{V}$ of these interface-stabilized As complexes are much smaller than the E_F-E_V of structures containing $\mathrm{As}_{\mathrm{sub}}$, which is electrically active. This suggests that electrons are local-

TABLE I. Fermi level of As complexes in bulk Si and SiO_2/Si interface structures. The 0.35 eV and 0.36 eV in parentheses indicate deep donor level positions due to As_{it}.

E_F-E_V (eV)	Bulk *c*-Si(64)	Bulk *c*-Si (216)	*c*-SiO_2/*c*-Si	*a*-SiO_2/*c*-Si
Defect free	0.33	0.35	0.40	0.42
As_{sub}	0.79	0.59	0.87	0.85
Two As_{sub}	0.89	0.65		
Three As_{sub}		0.68		
As_2I	0.53	0.37	0.46	
As_4V		0.35	0.40	
As_{it}			0.43(0.35)	0.43(0.36)
As_2I_{2I}			0.44	0.40
As_2I_{2II}			0.39	0.42

ized in these three interface-stabilized As complexes and very few of them can be released for conduction. Therefore, As trapped in interface As_{it}, As_2I_{2I}, and As_2I_{2II} complexes are most likely inactive, which is very consistent with a previous study of Sai-Halasz *et al.*[8] In a recent experimental paper,[9] the authors found that the segregated As exhibits higher electrical activation with increasing As sheet concentration in SiO_2/Si interface region. This phenomenon was explained by assuming there exists a deep donor state for segregated As. The interaction between donors at high concentration could merge this deep state with the conduction band. The simulation based on this assumption agrees well with their experimental data. In this work, we find As_{it} indeed induces deep donor level in the Si bandstructure of both *a*-SiO_2/Si and *c*-SiO_2/Si systems. The deep donor level is determined at $E_V+0.35$ eV in *a*-SiO_2/Si system and $E_V+0.36$ eV in *c*-SiO_2/Si system (as the computed Si band gap is 0.81 eV for both systems). This deep donor level may result from electrons that are tightly bonded to As_{it}. Such electrons can be released to conduction band upon interactions between neighboring donors. The excellent connection between our theoretical study and experimental results confirms that As_{it} proposed in this work could be one of the major segregation species. The deep donor state also suggests that As_{it} could serve as an electron trap and lead to interface current leakage during device operation.

We also investigated the formation and evolution dynamics of As complexes at SiO_2/Si interface. Figure 7 shows the diffusion pathways from bulk As_i configurations to interface As_{it} configuration. The forward barriers for this process range between 0.36 to 0.57 eV, depending on the initial bulk As_i configurations. The reverse barriers from As_{it} to bulk As_i are between 1.45 to 2.01 eV. The forward diffusion barriers are well below the reverse barriers, which indicates that As_{it} could be created via out-diffusion and interface capture of a bulk As_i. The barrier for As to jump from one interface As_{it} position to a neighboring As_{it} position is around 0.8 eV. This suggest that two As_{it} may diffuse in the interface layer and couple with each other to form a more stable As_2I_2 complex, which could be in either the As_2I_{2I} form or As_2I_{2II} form. While As_2I_{2II} is at least 0.6 eV more stable than As_2I_{2I}, our NEBM calculation shows that it still takes ~0.80 eV barrier for the evolution from As_2I_{2I} to As_2I_{2II} to occur.

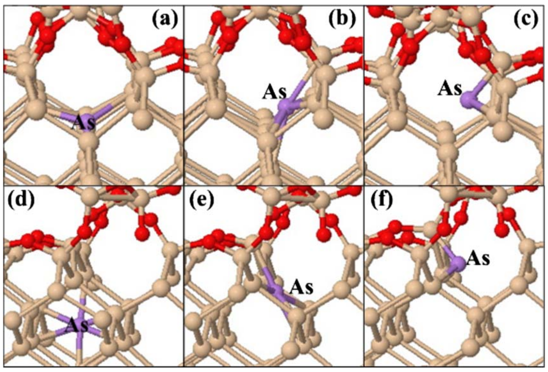

FIG. 7. (Color online) Evolution from As_i in bulk Si to interface As_{it}. (a), (b), (c): from split (110) As_i to As_{it}. (d), (e), (f): from hexagonal As_i to As_{it}.

In a previous study by Dabrovski *et al.*,[12] the authors constructed their interface model by using dopant pairing and dangling-bond sites trapping mechanism at SiO_2/Si interface. Simulation with this interface model agrees well with experimental results except that the concentration of interface trapping site required for this agreement is ten times higher than the realistic dangling-bond density at SiO_2/Si interface. The trapping sites based on interface vacancy complexes were proposed to fill the 10^{13} cm^{-2} density gap. However, in a later study by Ravichandran *et al.*,[14] the vacancy binding energy at interface was found to be too small to support this trapping mechanism. Instead, the author proposed a hydrogen-based interface trapping mechanism to account for the additional trapping sites. The hydrogen effect, however, was experimentally demonstrated to be at most secondary for the As segregation behavior in a recent study.[9] Now we suggest the As_{it}, As_2I_{2I}, and As_2I_{2II} complexes proposed by this work could be the most likely interface trapping sites to explain the previous inconsistency. As described in this paper, the highly stabilized configurations suggest the As-defect complexes could be major candidates for segregation species. The maximum interface density for such complexes is estimated to be at least $1\sim 2 \times 10^{14}$ cm^{-2}, which is enough to hold a large portion of segregation dose. And the trapping in As complexes does not require either dangling-bond sites or hydrogen-passivated interface, and is quite different from the dopant pairing mechanism.

IV. SUMMARY

The configuration, bonding, electrical activation and dynamics of As complexes in SiO_2/Si interface region were investigated using plane-wave-based DFT calculation. We found that bulk-stabilized As complexes [such as As_{sub}, split(110) As_i and As_4V which are stable As complexes in bulk Si] have interface strain-induced energy gain in SiO_2/Si interface region. On the other hand, we discovered three interface-stabilized As complexes, As_{it}, As_2I_{2I}, As_2I_{2II}, that exist only at SiO_2/Si interface layer. The three interface-stabilized complexes are energetically far more favorable than As complexes in bulk Si because they form strong bonds with interface Si and the resulting structural distortion induces minimal strain to the lattice due to the flexible Si-O-Si bond angles at SiO_2/Si interface. The activation properties of the interface-stabilized As complexes are estimated and all of the three complexes are confirmed to be inactive. The experimentally reported increasing electrical activation when segregation dose becomes higher can be attributed to the deep donor level of As_{it}. By analyzing the diffusion/evolution pathways of the As complexes, we suggest interface complexes could be formed by trapping out-diffusing As_i from bulk Si to SiO_2/Si interface, and As_2I_{2I}/As_2I_{2II} may also be created by diffusion and clustering of two neighboring As_{it} defects.

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