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# First-principles studies of di-arsenic interstitial and its implications for arsenic-interstitial diffusion in crystalline silicon

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**Abstract**

We propose new structural configurations and novel diffusion mechanisms for neutral di-arsenic interstitial ($As_2I_2$) in silicon with a first-principle density functional theory simulation within the generalized gradient approximation. With an assumption of excess silicon interstitials and high arsenic concentrations, neutral $As_2I_2$ is expected to be favorable and mobile with low-migration barrier. Moreover, because the diffusion barrier of arsenic interstitial pairs (AsI) is very low ($< 0.2$ eV) under the same conditions, $As_2I_2$ can be easily formed and likely intermediate stage of larger arsenic interstitial clusters.


*Keywords:* Silicon; Arsenic; Interstitial; Transient enhanced diffusion

## 1. Introduction

By the year 2012, it is predicted by the International Technology Roadmap for Semiconductors (ITRS) that ultrashallow junction (USJ) less than 5 nm in depth will be necessary to produce the next generation of silicon transistors [1]. At high concentrations ($>10^{20}$ atoms/cm$^3$), implanted As atoms may undergo electrical deactivation and transient enhanced diffusion (TED) during post-implantation thermal annealing [2–8]. In order to form sub-10 nm junctions with high As activation, a detailed atomic-level understanding of arsenic-defect interactions during USJ formation is necessary. Electrical deactivation of As is believed to be due to the formation of As-vacancy complexes [9,10], while As TED is thought to be mediated by both vacancy and interstitial defects in crystalline silicon [11]. Although vacancies are thought to play a large role in diffusion and clustering processes, it is silicon interstitials that exist in excess at the onset of annealing following dopant implantation [12]. Recent experimental and theoretical results have showed that As interstitials may also play a significant role in mediating As TED [13–17]. Furthermore, experimental studies have considered that the As doping may decrease the size and density of {3 1 1} extended defects, suggesting that As reacts with interstitials to form stable arsenic interstitial complexes [18]. A detailed understanding of arsenic interstitial complexes would provide valuable guidance to efforts to minimize the impact of junction depth and dopant activation in MOSFET ultrashallow junctions.

## 2. Computational details

All atomic and electronic calculations were performed with the Vienna Ab-initio Simulation Package (VASP), which performs first-principles calculations based on density functional theory (DFT) [19–21]. The exchange-correlation energy functional is represented using the generalized gradient approximation (GGA) form of Perdew and Wang [22]. The simulations were performed on a uniform grid of $k$ points equivalent to a $2\times2\times2$ Monkhorst and Pack grid in the diamond cubic cell [23]. A 216-atom supercell is used here. The optimized Si lattice constant for our system is 5.457 Å. We used a cut-off energy of 200 eV for plane-wave expansion. All atoms are fully relaxed using conjugate gradient method to minimize

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the total energy until all residual forces on the atom are less than $5 \times 10^{-2}$ eV/Å. We calculate the diffusion barriers using the nudged elastic band method [24].

## 3. Energetics of di-arsenic interstitials

We propose the structural configurations for neutral di-arsenic interstitials ($As_2I_2$) in silicon with a first-principles density functional theory simulation within the generalized gradient approximation. Starting with several initial configurations of silicon di-interstitials [25], extensive search of energetically favorable configurations of $As_2I_2$ was done in order to identify the local minimum structures. We identified that the lowest energy structure of $As_i$–$As_i$ is composed of two As atoms bridging three neighboring Si atoms in ['A', Fig. 1a] while there are additional two local minima, ['B', Fig. 1b] and ['C', Fig. 1c]. We assessed the stability of these neutral $As_i$–$As_i$ pairs in silicon by the relative formation energy, which is defined by

$$E_f = E[Si_{216}As_2] - 216\mu_{Si} - 2\mu_{As},$$

where $E[Si_{216}As_2]$ is the total energy of arsenic interstitial complexes in the supercell, $\mu_{Si}$ is the energy per atom ($= E[Si_{216}]/216$) in bulk Si and $\mu_{As}$ is the relative energy per substitutional As atom in defect-free bulk Si. Based on the structural configurations in Fig. 1, the formation energies for 'A', 'B', and 'C' are 3.95, 4.11 and 4.19 eV, respectively. Our identified atomic structures of $As_2I_2$ in Fig. 1 seem to be more favorable compared with previous theoretical results [16].

Moreover, the binding energy of neutral $As_i$–$As_i$ ($As_2I_2$) of ground state 'A' is estimated to be 1.90 eV with reference to the dissociation products of neutral $As_s$–$As_i$ ($As_2I$) and neutral split-(1 1 0) $Si_i$ (I) [$E_b(As_2I_2) = E_f(As_2I) + E_f(I) - E_f(As_2I_2)$]. We also calculated the binding energy of $As_2I_2$, 'A' with reference to two $As_i$ (AsI) and found it to be 2.19 eV [$E_b(As_2I_2) = E_f(AsI) + E_f(AsI) - E_f(As_2I_2)$]. The formation energies of $As_2I$, AsI, I is given by 2.11, 3.07, and 3.74 eV, respectively [13,17].

The dissociation of $As_2I_2$ to $As_2I$ and I seems to be more energetically favorable than to AsI and AsI, depending on the ionization of dissociation products and the position of Fermi level. However, the recent theoretical study shows that the diffusion barrier of $As_2I$ is 1.33 eV, which is much larger than that of AsI, 0.15 eV [13]. Suppose that the dissociation rate of $As_2I_2$ is highly dependent on both of the mobility of leaving species and the binding energy, both dissociation pathway for $As_2I_2$ could be comparably expected. As shown in Fig. 2, there are four degenerate states ('C') which can serve as a reorientation mechanism for whole diffusion pathway. $As_i$–$As_i$ pair may translate between these four degenerate configurations with energy barrier of 0.32 eV, as shown in Fig. 3.

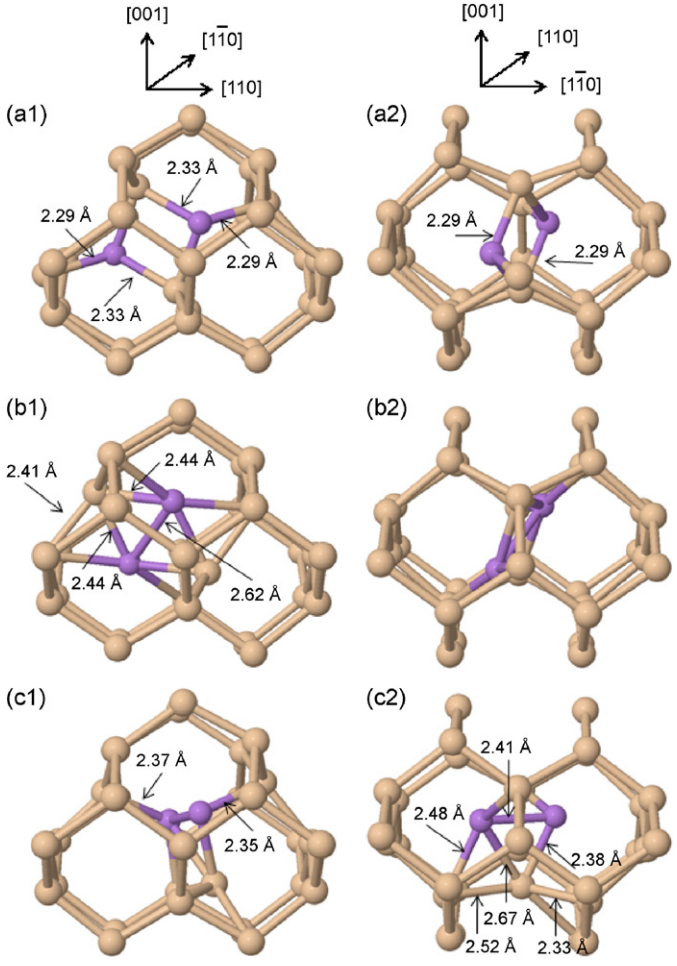


Fig. 1. Atomic configurations of front view (left) and side view (right) of $As_2I_2$. The lowest energy configuration is (a1). (b1) and (c1) are local minimum. Arsenic is depicted with purple (dark) atom and silicon is shown with yellow (light) atom.

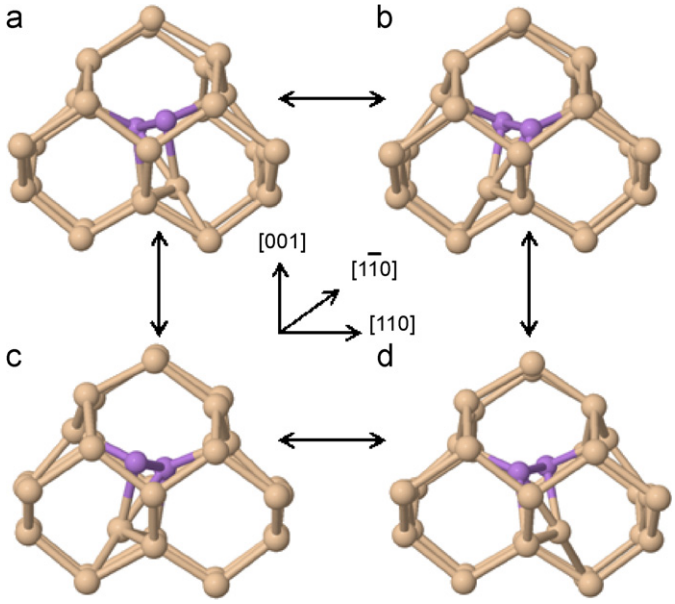


Fig. 2. Reorientation of $As_2I_2$ complex within a lattice site. All four configurations are degenerate in energy.