Ab initio calculation of As-vacancy deactivation and interstitial-mediated As diffusion in strained Si

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Abstract—We investigate As-vacancy deactivation and interstitial-mediated As diffusion in strained Si by using density functional theory calculation. First, we find that biaxial tensile strain will not have a significant effect on the binding energies of As-vacancies. Second, tensile strain increases the stability of the diffusing As-Si_i pairs. Our results could be one of the reasons that explain why As activation/deactivation and interstitial-mediated As TED has a weak dependence on biaxial tensile strain experimentally.

Keywords- silicon; arsenic; strain; diffusion ; deactivation

I. INTRODUCTION

By the year of 2012, it is predicted by the 2005 International Technology Roadmap for Semiconductor (ITRS) that shallow junctions less than 5 nm in depth will be necessary to produce the next generation of silicon transistors [1]. To create ultra-shallow junctions (USJ), dopants are implanted into silicon, which damages the silicon and creates a large number of defects. Following dopant implantation, the silicon is thermally annealed in order to re-crystallize the silicon and electrically activate the dopants. However, it is difficult to obtain shallow junction depths and high dopant activation as the interaction of silicon defects and dopants during annealing results in enhanced dopant diffusion as well as dopant deactivation. In order to form sub-10 nm junctions with high dopant activation, a detailed atomic-level understanding of dopant-defect interactions during USJ formation is necessary. Dopant deactivation and dopant transient enhanced diffusion (TED) both present obstacles for meeting USJ requirements in the coming years. Electrical deactivation of As is believed to be due to the formation of As-vacancy complexes [2,3], while As TED is thought to be mediated by both vacancy and interstitial defects in crystalline silicon [4]. 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 [5].

Recently, the strain effect on junction processing has received much attention due to the enhanced mobility of carriers for developing high performance strained-silicon metal oxide semiconductor field effect transistors (MOSFETs). At high concentrations (> 10^{20} atoms/cm³), implanted arsenic (As) atoms may undergo electrical deactivation and TED during post-implantation thermal annealing [6-11]. While

experimental studies have focused on As deactivation and TED in strained Si on $Si_{1-x}Ge_x$ substrates, they showed that As diffusivity shows little change under a certain range of tensile strain and there is no evidence for a difference in electricallyactive As concentration a as function of tensile strain [12, 13]. However, the effect of strain on As diffusion and activation/deactivation is relatively unstudied theoretically [14]. A detailed understanding of the strain effect on As TED and deactivation would provide valuable guidance to efforts to minimize the impact of strain on junction depth and dopant activation in MOSFET ultrashallow junctions.

II. COMPUTATIONAL DETAILS

All calculations were performed with the Vienna Ab-initio Simulation Package (VASP) which performs first principles calculations based on density functional theory (DFT) [15-17]. The exchange-correlation energy functional is represented using the generalized gradient approximation (GGA) form of Perdew and Wang [18]. The simulations were performed on a uniform grid of k points equivalent to a $2 \times 2 \times 2$ Monkhorst and Pack grid in the diamond cubic cell [19]. A 216-atom supercell is used here. The optimized Si lattice constant for our system is 5.457 Å. We used a cutoff energy of 12 Ry for plane-wave expansion. All atoms are fully relaxed using conjugate gradient method to minimize the total energy until all residual forces on the atom are less than 5×10^{-2} eV/Å. We calculate the diffusion barriers under the static approximation using the climbing nudged elastic band method [20].

In order to induce a biaxial strain in Si, we applied the lattice constant (a_{||}) of relaxed Si_{1-x}Ge_x to the two crystallographic directions on the (001) plane. Then we optimized the lattice constant (a_⊥) in the other direction perpendicular to the strain plane in a 216-atom supercell. According to elastic theory, the "in-plane" biaxial strain ε_{\parallel} can change the "out-of-plane" strain ε_{\perp} by the equation

$$\boldsymbol{\varepsilon}_{\parallel} / \boldsymbol{\varepsilon}_{\parallel} = -2(C_{12} / C_{11}), \tag{1}$$

where C_{11} (167 GPa) and C_{12} (65 GPa) are elastic constants of Si [21]. We used a "in-plane" lattice constant of 5.500 Å and a "out-of-plane" lattice constant of 5.426 Å in order to induce a 0.79 % biaxial tensile strain (equivalent to the relaxed "in-plane" lattice constant of Si₈₀Ge₂₀). The calculated $\mathcal{E}_{\perp}/\mathcal{E}_{\parallel}$ are in excellent agreement with the experimental values obtained from (1).

III. ARSENIC DEACTIVATION IN STRAINED SILICON

We investigated the thermodynamic energetics of Asvacancy complexes in unstrained and strained Si in order to understand how a biaxial tensile strain can affect the stability of As-vacancy complexes. It is widely accepted that the deactivation of As is due to the formation of As_nV_m clusters [9-11]. At concentrations greater than 3×10^{20} atoms/cm², arsenic (As) impurities have been observed to deactivate at temperatures as low as 400 °C [10]. Theoretical studies have suggested that AsV, As₂V, As₃V, As₄V, As₂V₂, and As₃V₂ all may play a role in As deactivation. This deactivation model has been supported by results from positron annihilation and Hall effect experiments [22-24].

We calculated the formation energies and binding energies of small clusters of As vacancy complexes, as shown in Table 1 [25]. When the isolated impurities As and V are considered as reference, the formation energy of a cluster is given by

$$E_{formation} = E_{As_n V_m} - n(E_{As} - E_{Si}) - E_{Si} \frac{N - m}{N}, \qquad (2)$$

where E_{Si} has N atoms, E_V has (N-1) atoms, and $E_{As_n V_m}$ has (N-m) atoms in the supercell. The binding energies are given by

$$E_{binding} = \frac{E_{formation} \left(As_n V_m\right) - E_{formation} \left(V_m\right)}{n}.$$
 (3)

The formation energies of vacancy and di-vacancy are slightly increased under 0.79% biaxial tensile strain. Although a biaxial tensile strain ("in-plane" direction) is given, the stress would be released by the compressive strain ("out-of plane" direction), which shows a small change in formation energy of vacancy and di-vacancy. There are small differences in the formation energies of As-vacancy and As-divacancy complexes between unstrained and 0.79% strained Si. Thus, it appears that a biaxial tensile strain will have a very little effect on the stability of these complexes.

IV. ARSENIC DIFFUSION BEHAVIOR IN STRAINED SILICON

Density functional theory calculations were used to examine the interaction of interstitials and various As-vacancy complexes [26]. Harrison *et. al.* have shown that silicon interstitials can easily annihilate existing As-vacancy complexes in silicon with little kinetic barrier to interstitial recombination with the vacancies, As_mV (m=1-4) and As_mV_2 (m=2-3) [27]. The energy gain from the interstitial-vacancy recombination turns out to be significant, implying that As would remain more favorably as As_m (or As_mI_n) complexes, rather than as As_mV_n in the presence of a large amount of excess interstitials [26,27].

ΓABLE Ι.	FORMA	TION EN	JERGY	AND	BINDING	3 ENER	GES (IN	IeV) OF
AS _n V _m COMPI	LEXES. TH	E VALUI	ES ARE	CAL	CULATE	DFOR	ELECTR	ICALLY
		NEUTR	AL CO	MPLE	XES.			

	Unst	rained Si	Strained Si	Strained Si (0.79 % strain)		
	$E_{\textit{formation}}$	E _{binding} per As atom	$E_{\textit{formation}}$	E _{binding} per As atom		
As_2	0.07	0.03	0.09	0.04		
As_3	0.18	0.06	0.20	0.07		
As_4	-0.49	-0.12	-0.44	-0.11		
V	3.67		3.71			
AsV	2.27	1.39	2.33	1.37		
As_2V	0.62	1.52	0.71	1.50		
As_3V	-0.64	1.44	-0.52	1.41		
As_4V	-2.30	1.49	-2.15	1.46		
V_2	5.48		5.53			
As_2V_2	2.32	1.58	2.32	1.60		
As_3V_2	1.07	1.47	1.23	1.43		

Moreover, the formation of a highly mobile As-silicon interstitial pair that can exist in positive, neutral, negative charge state can be explained by experimentally observed As TED mediated by interstitials [6-8]. This suggests the importance that interstitials may play in As TED.

The lowest energy As-Si_i structures were identified in the negative, neutral, and positive charge state [26]. In the negatively charged As-Si_i⁵ structure, the As atom bridges two approximate lattice Si atoms, as depicted in Fig. 1(a). For As-Si_i⁰ and As-Si_i⁺, the lowest energy structure is comprised of As and Si_i atom that are aligned in the [110] direction while sharing a lattice site [Figs 2(a) and 3(a)]. These findings suggest that under intrinsic conditions the diffusion of neutral As-Si_i pairs dominate, while under n-type extrinsic conditions the neutral and negatively charge pairs will both contribute to arsenic diffusion. These results clearly support that the interstitials can contribute significantly to As transient enhanced diffusion, particularly in regions where interstitials exist in excess

We investigated the stability and diffusion of arsenicinterstitial pair under 0.79 % biaxial tensile strain. We assessed the relative stability of these neutral and charged As-Si_i pairs by computing defect ionization levels (μ_i). At a given Fermi level (ϵ_F), the relative formation energy of a charged defect in charge state q=±1 to a neutral is given by

$$E_f^q - E_f^0 = q(\mathcal{E}_F - \mu_i), \tag{4}$$

where ε_F is given relative to the valence band maximum (E_V). Thus, the defect levels can be approximated by

$$E_D^q + q(E_V^q + \mu_i) = E_D^0, (5)$$

where E_D^q and E_D^0 are the total energies of the defects in q and neutral charge states, and E_V^q is the position of the valence band maximum in supercell E_D^q . In calculating a charged defect, a homogeneous background charge is included to maintain the overall charge neutrality in the periodic supercell. To account for the Coulomb energy between the charged defect and background charge, a monopole correction is made to the total energy of the charged system. Assuming a pointlike +1 charge defect in the 216-atom supercell, the monopole correction is estimated to be approximately 0.11 eV [28]. This correction may overestimate the required adjustment if the charge on the defect is significantly delocalized [29].



Figure 1. The negatively charged As-Si_i pair diffusion pathway in unstrained and strained structure.



Figure 2. The As-Si_i pair diffusion pathway for mechanism "A" in unstrained and strained Si.



Figure 3. The As-Si_i pair diffusion pathway for mechanism "B" in unstrained and strained Si.

Note that these relative formation energy is determined using computed Si band gap of 0.63 eV and 0.50 eV in unstrained and strained Si, respectively From the calculations, we determined the positions of As-Si⁰_i acceptor and donor levels at $E_V+0.22$ eV and $E_V+0.11$ eV, respectively for the computed Si band gap of 0.63 eV in unstrained Si. For 0.79% biaxial strain Si, we determined the positions of As-Si⁰_i acceptor and donor levels at $E_V+0.14$ eV and $E_V+0.16$ eV, respectively, for the computed Si band gap of 0.50 eV.

We adopt the same As diffusion mechanism as in [26] to study As diffusion in strained Si as shown Fig. 1, Fig. 2 and Fig. 3. The formation energies, migration barriers, activation energies are shown in the Table 2. When the biaxial strain is induced on the As-Si_i pair in a 216-atom supercell by the [110], [101], and [001] direction, there is no directional dependence on the formation energy of As-Si_i pair. The formation energy of As-Si_i⁰ in strained Si is calculated to be 2.96 eV (= E[AsSi₂₁₆]-E(AsSi₂₁₅]-E[Si₂₁₆]/216), where E[AsSi₂₁₆], and E(AsSi₂₁₅], E[Si₂₁₆] are the total energies of As-Si_i⁰, substitutional As₀, and crystalline Si). This leads to formation energies of 2.87 eV and 3.07 eV in strained Si, respectively for As-Si_i⁻ and As-Si_i⁺ in intrinsic regions. Under intrinsic condition, the binding energies of As-Si_i⁰ As-Si_i⁻, and As-Si_i⁺ are approximated to be 0.72 eV, 0.81 eV, and 0.61 eV, respectively, relative to the dissociation products of substitutional As⁰ and (110)-split Si_i⁰.

Under intrinsic conditions, the neutral and positively charged As-Si_i pair are about 0.1 eV more favorable in strained Si than they are in unstrained Si. For the negatively charged As-Si_i pair, there is almost no difference on the stability in unstrained and strained Si under intrinsic conditions. However, the formation energy of negatively charged As-Si_i pair in strained Si is slightly higher than that in unstrained Si under extrinsic conditions, even though the formation energies of neutral and positively charged As-Si_i pairs in strained Si are lower than they are in unstrained Si. The diffusion barrier is obtained by [110], [101], [001] directions of biaxial tensile strain. The diffusion anisotropy of the migration barrier (ex. [110] \rightarrow [101]) is insignificant.

Based on the activation energies of $As-Si_i$ pair diffusion in Table II, we can evaluate the strain effect on the diffusivity of $As-Si_i$ pair. While the activation energies of neutral and positively charged $As-Si_i$ pair in strained Si are lower in both intrinsic and extrinsic regions, as compared to their activation energies in unstrained Si, the activation energies of the negatively charged $As-Si_i$ in unstrained and strained Si are very comparable.

CONDUCTION BAND EDGE.

Unstrained Si								
	E _f (int)	E _f (ext)	E_m	E _a (int)	E _a (ext)			
As-Si _i	2.88	2.57	0.51	3.39	3.08			
$As-Si_i^0$	3.09	3.09	0.15	3.24	3.24			
$As-Si_i^+$	3.18	3.72	0.12	3.30	3.84			
Strained Si (0.79 % strain)								
	E _f (int)	E _f (ext)	E_m	E _a (int)	E _a (ext)			
As-Si _i	2.87	2.62	0.41	3.28	3.03			
As-Si ⁰	2.96	2.96	0.14	3.10	3.10			
$As-Si_i^+$	3.07	3.32	0.10	3.17	3.42			

For biaxial tensile strain, As will diffuse similarly in unstrained and strained Si under TED conditions as the negatively charged As-Si_i pair will dominate in the case of heavily As-doped Si. [12,13].

V. CONCLUSION

We have studied As-vacancy and interstitial-mediated As diffusion in strained Si by using the density functional theory calculation. First, the biaxial tensile strain was found not to significantly affect As deactivation. Second, the tensile strain increases the stability of As-Si_i pairs. Finally, an interstitial-mediated As diffusion in heavily As-doped Si will not significantly affected by induced biaxial tensile strain.

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