Charge carrier induced lattice strain and stress effects on As activation in Si

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We studied lattice expansion coefficient due to As using density functional theory with particular attention to separating the impact of electrons and ions. Based on As deactivation mechanism under equilibrium conditions, the effect of stress on As activation is predicted. We find that biaxial stress results in minimal impact on As activation, which is consistent with experimental observations by Sugii et al. [J. Appl. Phys. 96, 261 (2004)] and Bennett et al. [J. Vac. Sci. Tech. B 26, 391 (2008)].

Stress effects are of great interest in modern ULSI technology since they can be employed to improve various material properties. Uniaxial stress has been employed in MOSFET devices since the 90 nm node technology step to improve carrier mobility [1]. Properly applied stress can also suppress dopant diffusion [2, 3, 4], enhance activation [5, 6], and reduce the band gap [7]. Therefore, understanding stress effects becomes essential for further MOSFET scaling.

As deactivation is governed by As\textsubscript{m}V\textsubscript{n} cluster formation, and clusters with \( m = 1 - 4 \) and \( n = 1 \) are considered as the dominant species in deactivation kinetics [8]. Under equilibrium conditions, the concentrations of defect \( X \) (As, V or As\textsubscript{m}V) is determined by the free As and V concentrations and cluster formation energies:

\[
C_X = A \exp \left( -\frac{E_f^X}{kT} \right), \quad \text{where } E_f^X \text{ is the formation enthalpy, and } A \text{ includes the configuration and formation entropy.}
\]

The total chemical As concentration is given by

\[
C_{As}^{total} = C_{As} + \sum_{m=1}^{4} m C_{As_mV}.
\]

Table I lists the formation energies of As\textsubscript{m}V complexes based on the total free energy of 64-atom (or 63-atom, with vacancy) super-cells using the density functional theory (DFT) code VASP \textsuperscript{9} with PW91 GGA potential [10]. All calculations were done at a 250 eV energy cut-off with \( 2^{3} \) Monkhorst-Pack \textbf{k}-point sampling [11]. Each time an As atom is added to a vacancy, the formation energy is lowered by about 1.5 eV, and thus a larger complex is more stable than a smaller one. We calculated the As\textsubscript{m}V concentrations based on the formation energies listed in Table I. Since DFT GGA underestimates the vacancy formation energy by about 1 eV [12], we also applied a correction for the As\textsubscript{m}V formation energies using experimental values [13]. As\textsubscript{4}V has the lowest formation energy and becomes the dominant cluster under equilibrium conditions. Smaller clusters can be formed during epitaxial As-doped Si growth and early stages of annealing, and can dominate before full equilibration is reached [14, 15], but we restrict our analysis to equilibrium conditions.

Fig. 1 shows the isolated As concentration as a function of the total chemical As concentration. The As\textsuperscript{4}V concentration as a function of the total chemical As concentration for \( E_F = E_c \). Solid lines are plotted with correction for vacancy formation energy and broken lines are plotted with DFT formation energies. Smaller clusters don’t appear due to low concentration.
TABLE I: Formation energy of $\text{As}_m\text{V}$ clusters. When the experimental vacancy formation energy is used (4.60 eV [13]), formation energies increase by about 1 eV. The experimental value of the V formation energy was calculated by subtracting the migration barrier (0.26 eV, DFT value) from the activation enthalpy (4.86 eV [13]). In the second row, the first value is based on the DFT result, and the second is based on the experimental V formation energy.

| V AsV As$_2$V As$_3$V As$_4$V | $E'$ (eV) |
|-------------------------------|---------|
| V AsV As$_2$V As$_3$V As$_4$V |         |
| E' (eV)                       |         |
| 3.59                         | 2.15    |
| 0.68                         | -0.66   |
| -2.22                        |         |
| 4.60                         | 3.16    |
| 1.69                         | 0.35    |
| -1.21                        |         |

TABLE II: Induced strain for As and As$_m$V complexes. As produces small lattice expansion and As$_m$V complexes result in lattice contraction.

| As V AsV As$_2$V As$_3$V As$_4$V | $\Delta \varepsilon$ |
|----------------------------------|----------------------|
| As V AsV As$_2$V As$_3$V As$_4$V | 0.018                |
| $\Delta \varepsilon$            | -0.25                |
| -0.21                           | -0.22                |
| -0.11                           | -0.08                |

where $V_0$ is the volume of a lattice, $\Delta \varepsilon_{As_mV}$ ($\Delta \varepsilon_{As}$) is the induced strain due to As$_m$V (As), $C$ is the elastic stiffness tensor of Si, and $\varepsilon$ is applied strain. The induced strain can be determined from the energy vs. strain curve. A detailed explanation can be found in Ref. [17]. The results are summarized in Table III. We repeated calculations using 216 supercell for selected structures and acquired the same induced strains.

As shown in Table III As is calculated to give a small lattice expansion. However, several authors have observed lattice contractions in heavily As-doped Si, which they attributed to free electrons in the conduction band [18, 20, 21]. In contrast to their conclusion, DFT calculations predict a lattice expansion due to free electrons in the conduction band (Table III). In Cargill et al., the total induced strain ($\Delta \varepsilon_{As} = \beta \Delta N_{As}$) is assumed to be given by the sum of the induced strain due to ions ($\Delta \varepsilon_{As^+} = \beta_{size} N_{As}$) and free electrons ($\Delta \varepsilon_e = \beta_e N_{As}$). As shown in Table III the calculated induced strain due to As$^0$ has opposite sign to measured value, but the absolute difference is small and thus its impact on stress effects is minimal. However, the reasoning is very different in each case, which raises a fundamental question about the role of electrons: Do electrons cause expansion or contraction in the lattice? To answer this question, we performed DFT calculations to find equilibrium lattice constants of charged supercells. From the carrier concentration vs. change in lattice constant (Fig. 2), we conclude that electrons expand the lattice while holes cause lattice contraction.

The lattice expansion due to electrons raises another question about the relation between Si-As bond length and the lattice parameter. We looked into the local structure around As in Si matrix to answer this question. As

FIG. 2: Change in lattice constant due to free charge carriers. The lattice undergoes expansion (contraction) as free electrons (holes) are added. Induced strains are obtained by finding equilibrium lattice constant of charged supercell with various dopants. One electron in a 64-atom supercell corresponds to $7.8 \times 10^{20}$ cm$^{-3}$.

FIG. 3: Stress effects on As and As$_m$V cluster concentration under biaxial stress. Note that the two dominant complexes, As and As$_4$V, have minimal stress effects.

TABLE III: Induced strain due to $\text{As}^+$, $\text{As}^0$, and free electrons and holes. The numbers in parenthesis are extracted from Cargill et al. [18]. Note that in spite of longer As-Si bond length in Si$_{63}$As$^+$ supercell (Table IV), the lattice undergoes contraction.

| $\text{As}^+$ | $\text{As}^0$ | e$^-$ | h$^+$ |
|---------------|---------------|-------|-------|
| $\Delta \varepsilon$ | 0.018 (-0.019) | -0.22 (0.07) | 0.22 (-0.09) | -0.26 |
As results in an overall tiny expansion ($\Delta \epsilon = 0.018$). Based on our analysis, it is likely that experimentally observed lattice contractions originate from reasons other than free electrons. We attribute them to high concentrations of vacancies in the form of As$_m$V, and find that a vacancy concentration of about 15% of the As concentration can reproduce the lattice contraction observed by Cargill et al. [18]. This level of vacancy concentration was reported based on ab-initio calculations by Berding et al. [8] and positron annihilation spectroscopy by Borot et al. [23].

Effects of stress on As and As$_m$V concentrations are plotted in Fig. 3 based on Eqs. 2 and 3. The concentrations of the two dominant configurations, As and As$_4$V, undergo changes in opposite directions under biaxial stress, but the magnitude is minimal due to the small induced strain. Finally, the free As concentration as a function of the total As concentration is plotted in Fig. 4. At a given total As concentration, compressive biaxial stress enhances As$_m$V formation, and thus the number of active As decreases. However, stress effects are minimal due to the small induced strains of dominant structures, in accordance with previous experiments [24, 25].

In conclusion, by performing DFT calculations of the local structure around As in the silicon lattice, we found that lattice expansion due to the larger size of an As atom is limited to within 3NN distances. The lattice contraction in highly As-doped Si can be explained by As$_m$V cluster formation rather than free electron as previously suggested [18]. The small induced strain due to both isolated As and the dominant deactivated cluster As$_4$V results in negligible stress effects on the carrier concentration, in accordance with experimental observations [24, 25].

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