Ab Initio Analysis of Point Defects
in Plane-Stressed Si Single Crystal*

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Abstract
The effect of compressive or tensile plane-stress on formation energies and
electronic properties of point defects in Si single crystal was studied by first
principles approach for in-plane strain up to 5.0 %. It was found that the
formation energy of interstitial Si (I) decreased under tensile in-plane strain. On
the other hand, the formation energy of vacancy (V) decreased under compressive
in-plane strain. The most stable states of I and V in intrinsic Si were I^2 at T site
and V^0 respectively, independent of type and value of the in-plane strain.

Key words: Ab Initio Analysis, Plane-Stressed Si, Point Defects, Formation Energy

1. Introduction
The performance of LSI by using silicon (Si) substrates has progressed with device
scaling by reducing channel length. For applications with physical size limitations, novel
materials for carrier-mobility enhancement are under intensive research and development.
Strained Si substrates attract considerable attentions as one of the promising technology for
high performance LSI technology [1]. It is known that the carrier-mobility changes due to
the change of the energy band structure of Si by the application of the lattice strain.
Especially, both the electron and the hole mobility enhance with controlling the type and the
magnitude of the applied strain [2]. Therefore, theoretical and experimental studies have
been performed intensively for strain-applied Si single crystals (strained Si) to clarify their
physical properties [2].

In this technology, strained Si layers grown on SiGe layer/Si substrates are used as
active layers for LSI. Since the lattice constant of SiGe is larger than that of Si, tensile
stress paralleled to the surface arises in the Si layer. If the Si layer is sufficiently thin and
the stress in the normal direction is sufficiently relaxed, the stress state in the Si layer can
be treated as plane-stress [2]. The surface orientation of the strained Si is generally (001).

Self-interstitials (I) and Vacancies (V) in Si crystal have been studied widely due to their
importance in the manufacturing of Si wafers and devices. That is, I and V affect the
precipitation of interstitial oxygen atoms [3] and the diffusion of dopant atoms [4].
Regarding the unstrained Si, present authors reported analyzed results of the stability of
point defects with ab initio calculation [5]. On the other hand, until recently, little
information is available regarding the point defect properties in strained Si.

In this study, we analyzed the stability of point defects in strained Si under
plane-stresses with ab initio calculation.
2. Calculation details

2.1 Calculation cells

Si crystal has a diamond structure including 8 atoms in the conventional cell. In the calculation, 64-atom cubic supercell surrounded with (100), (010), and (001) planes was used. Figure 1 shows a supercell of 64 Si atoms used in this work. The cell size $L = 10.732$ Å, and each edge of the cell lay along the [100], [010], and [001] directions. To simulate the strain effect, the supercell was strained equally along the [100] and [010] directions up to ±5 %, while relaxation in the [001] direction was allowed to minimize the energy of the system. That is, we simulated Si crystals in the plane-stressed loading mode. The strain imposed along the [100] and [010] directions is described as in-plane strain. Three-dimensional periodic boundary conditions were set in each calculation.

![Figure 1](image1)

One vacancy ($V$) was introduced by eliminating one Si atom located at the center of the supercell. On the other hand, for a self-interstitial atom ($I$), ideal interstitial sites in the diamond structure, i.e., tetrahedral (T), hexagonal (H), bond-center (B) sites in Fig. 2(a) and [110] dumbbell (D) site in Fig. 2(b), were considered [5]. For the [110] D site, two Si atoms indicated by arrows are equivalent in the <110> direction, and one atom is $I$ ($I$ is shown as D in this figure). The formation energies $E_f$ of $V$ and $I$ were obtained with the calculated results of the total energies of fully relaxed supercells.

![Figure 2](image2)
2.2 Calculation procedure of the formation energy $E_f$ of point defects

Calculations were based on the density functional theory [6] using the local density approximation and the pseudopotential method. The CASTEP code [7] was used to obtain the ground state of the system by solving the Kohn-Sham equation [8] self-consistently for the given atomic configuration. That is, the calculation was performed for the static system at 0 K. The wave function was expanded with the plane waves, and the ultra-soft pseudopotential method [9] was used to reduce the plane wave numbers. The cutoff energy of the plane waves was chosen as 310 eV. For the exchange-correlation energy in the generalized gradient approximation (GGA), the expression proposed by Perdew et al. [10] was used. The RMM-DIIS method was used to optimize the wave function and the Pulay method was used for charge-mixing [11]. The BFGS Geometry Optimization Method was used to optimize the atomic configurations [12]. The convergence condition of the electronic structure optimization was set at a total energy change of less than $1 \times 10^{-6}$ eV/atom. The convergence conditions of the geometry optimization were set at a total energy change of less than $1 \times 10^{-6}$ eV/atom, atomic displacement of less than $1 \times 10^{-3}$ Å, atomic force of less than 0.03 eV/Å, and stress in the cell of less than 0.05 GPa. Here, 1 eV equals to $1.602 \times 10^{-19}$ J. The $k$ point sampling was performed at special points of the Monkhorst-Pack grid [13] for $2 \times 2 \times 2$.

Point defects in Si crystals form energy levels in the band gap. As the wave function of these energy levels is relatively expanded in Si crystals due to mixing with the other orbits, these energy levels capture or release electrons to or from the Fermi level depending on the position of the Fermi level. As a result, the point defects have a negative or a positive charge state [14]. Here, we define the charge state of the Si crystal including the point defects as “the charge state of the point defects.” The total energy of the fully relaxed supercell including one $V$ with charge $Q$, $E[\text{Si}_6V_1](Q)$, was obtained by solving the Kohn-Sham equation after eliminating the $Q$ electrons from the supercell. Five charge states of $Q = -2, -1, 0, +1, +2$ were considered for $V$ [14]. On the other hand, for a self-interstitial atom ($I$), the total energy of the fully relaxed supercell including one $I$ with charge $Q$, $E[\text{Si}_6I_1](Q)$, was obtained by first principles analysis. Three charge states of $Q = 0, +1, +2$ were considered for $I$ [14]. Finally, the formation energies $E_f$ of $V$ and $I$ were obtained with the calculated results of the total energies. We added a neutralizing background in the calculation for the system of $Q \neq 0$.

3. Results and discussion

3.1 Dependence of the normal strain and of the cell volume on in-plane strain

To simulate the strain effect, the supercell was strained equally along the [100] and [010] directions from $-5\% \sim +5\%$, while relaxation in the [001] direction was allowed to minimize the energy of the system. Figure 3 shows the dependence of the normal strain along the [001] direction and of the cell volume of Si crystal on in-plane strain. A linear relation was observed between the normal and in-plane strain. This result agreed quantitatively with the $ab$ initio calculation by Nicolaysen et al [15]. The cell volume was found to increase for tensile in-plane strain, while it decreased for compressive in-plane strain.
3.2 Calculated band gap of Si crystal

It is known that the excited states cannot be considered in the density functional theory. Based on this limitation, the calculated band gap obtained from Kohn-Sham eigen values becomes about 0.5 - 0.7 times the experimental values [16]. Furthermore, the Kohn-Sham eigen values have no physical meaning except the highest occupied level [16]. The highest occupied level is proved as the ionization energy [16]. Therefore, the ionization energy obtained with $E_v = E[Si_{64}](0) - E[Si_{64}](+1)$ can be considered as the top of the valence band, $E_v$ [17]. Here, $E[Si_{64}](+1)$ is the total energy of the supercell with charge $Q = +1$ obtained by solving the Kohn-Sham equation after eliminating one electron from the supercell. On the other hand, the ionization energy obtained with $E_c = E[Si_{64}](1) - E[Si_{64}](0)$ can be considered as the bottom of the conduction band, $E_c$ [17]. In the present work, we have calculated the band gap $E_g$ with eq.(1) based on above discussion [17].

$$E_g = E_c - E_v = E[Si_{64}](+1) + E[Si_{64}](1) - 2E[Si_{64}](0).$$  \hspace{1cm} (1)

Figure 4 shows the calculated result of the dependence of Si band gap on in-plane strain.

$$E_g = E_c - E_v = E[Si_{64}](+1) + E[Si_{64}](1) - 2E[Si_{64}](0).$$  \hspace{1cm} (1)
The band gap of the unstrained Si was 1.23 eV, which was close to the experimental value of 1.12 eV at a room temperature [18]. This is the unexpected correspondence. Similar calculation of GaAs band gap showed 2.13 eV, which was far larger than the experimental value of 1.42 eV at a room temperature [19]. A decrease in the band gap of the Si crystal was obtained for both tensile and compressive in-plane strain. The reason of this strain dependence was explained as follows [2]. In the band structure of Si crystal, both the top of the valence band and the bottom of the conduction band degenerate in unstrained state. In plane-stressed Si, both the energy degeneracy at the G point (top of the valence band) and near the X point (bottom of the conduction band) were resolved in higher and lower energy levels. Therefore, the band gap of Si decreases with an increase in in-plane strain independent of the strain type. This tendency was confirmed in the experiments [2].

Experimental results showed that the change of the band gap of Si, \( \Delta E_g \), obeys eq.(2) under hydrostatic pressure \( P \) (GPa) [2].

\[
\Delta E_g \text{ (meV)} = -24.7 \times P \text{ (GPa)}.
\]  

(2)

Regarding the in-plane strain, however, the empirical formula like eq.(2) was not reported yet.

### 3.3 Dependence of \( E_f \) of point defects on in-plane strain

The concentration of point defects in Si crystal is about \( 10^{15} / \text{cm}^3 \) at the highest [20]. Therefore, point defects exist apart from each other, and Si atoms exist regularly between the point defects. Besides, dopant atoms exist in Si crystals, and the Fermi level is determined with the type and the concentration of dopant atoms. As described in section 2.2, point defects in Si crystals form energy levels in the band gap. Therefore, for example, empty levels due to \( V \) capture electrons result in the negatively charged \( V \) when Fermi level is close to the bottom of the conduction band in n-type Si.

In the present work, the formation energy \( E_f \) of the charged point defects was calculated with obeying Puska et al [21] as follows. First, for charged \( V \), the total energy of the supercell including one \( V \) with charge \( Q = 0, \pm 1, \pm 2, E[\text{Si}_{63}V_1](Q) \), was obtained as mentioned in the section 2.2. Next, \( E_f \) was obtained with eqs.(1) and (3).

\[
E_f(Q) = E[\text{Si}_{63}V_1](Q) + Q(\mu E_g + E_v) - 63/64 E[\text{Si}_{64}](0).
\]  

(3)

Here, \( E[\text{Si}_{63}V_1](Q) \) is the total energy of the fully relaxed cell containing one \( V \) with charge \( Q \), and \( E[\text{Si}_{64}](0) \) is the total energy of the perfect neutral cell. \( \mu E_g \) is the Fermi level in the band gap relative to the top of the valence band \( E_v \) in the bulk supercell. \( \mu \) is the electron chemical potential, which is zero for the Fermi level at the top of the valence band and equals +1 for the Fermi level at the bottom of the conduction band.

Figure 5 shows the dependence of the formation energy \( E_f \) of \( V^Q \) on in-plane strain. Here, \( V^2, V^{-1}, V^0, V^{-1}, V^2 \) indicate the five charged state of \( V \). Note that the energies of negatively charged \( V \) refer to the Fermi level at the bottom of the conduction band (n-type Si), while the energies of positively charged \( V \) refer to the Fermi level at the top of the valence band (p-type Si). It was found that, generally, \( E_f \) of \( V \) decreased under compressive in-plane strain, while \( E_f \) of \( V \) increased under tensile in-plane strain. These results can be explained qualitatively by the dependence of the cell volume on in-plane strain as shown in Fig. 3. That is, the formation energy \( E_f \) of \( V \) should decrease in smaller cells, while increase in larger cells.
Next, the total energy of the supercell including one $I$ with charge $Q = 0$, +1, +2, $E[Si_{64}I](Q)$, was calculated and $E_f$ of $I$ was obtained with eqs.(1) and (4).

$$E_f(Q) = E[Si_{64}I](Q) + Q(\mu E_g + E_v) - 65/64 E[Si_{64}](0).$$  \hspace{1cm} (4)

Figure 6 shows the dependence of the formation energy of $I^0$ on in-plane strain. It was found that, generally, $E_f$ of $I$ decreased under tensile in-plane strain. This result can be explained qualitatively by the dependence of the cell volume on in-plane strain as shown in Fig. 3. That is, the formation energy $E_f$ of $I$ should decrease in larger cells. The most stable site of $I^0$ is D site between -1 % and +1 %, and $E_f$ of $I$ increases in the order of D, H, T and B sites.
Figure 7 shows the dependence of the formation energy of $I^{+1}$ and $I^{+2}$ on in-plane strain. Here, the energies refer to the Fermi level at the top of the valence band (p-type Si). $E_f$ of $I$ at H site was not shown in this figure with the reason mentioned below. It was found that, generally, $E_f$ of $I$ decreased when the in-plane strain changed from the compression to the tension. In the positively charged state, the energy barrier between the T and H sites in Si disappeared, and the $I$ atom moved to the T site from the H site during geometry optimization. The most stable site of positively charged $I$ is T site, and $E_f$ of $I$ increases in the order of T, D and B sites.

3.4 Dependence of $E_f$ of point defects on Fermi level

Figure 8 shows the formation energy $E_f$ of $V^Q$ with -0.5 %, 0 %, and +0.5 % in-plane strain as a function of Fermi level. In this figure, $V^{-2}$, $V^{-1}$, $V^0$, $V^{+1}$, and $V^{+2}$ indicate the five charge states of the vacancy. The horizontal axis indicates the Fermi level normalized with $E_g$, and the top of the valence band was set to zero.

Figure 7. Dependence of formation energy $E_f$ of $I^{+1}$ and $I^{+2}$ on in-plane strain.

Figure 8. Dependence of formation energy $E_f$ of $V^0$ on Fermi energy.
The formation energy $E_F$ of $I^Q$ with -0.5 %, 0 %, and +0.5 % in-plane strain was calculated as a function of Fermi level. It was found that $I^{+2}$ at T site was most stable for a wide range of the Fermi level in the band gap. Figure 9 shows the formation energy $E_F$ of $I^Q$ with -0.5 %, 0 %, and +0.5 % in-plane strain as a function of Fermi level. In this figure, $I^0$, $I^{+1}$, and $I^{+2}$ indicate the three charge states of the self-interstitial.

![Figure 9](image)

**Figure 9.** Dependence of formation energy $E_F$ of $I^Q$ at T site on Fermi energy.

The present authors reported that the formation energy of charged $V$ and $I$ in unstrained Si in Figs. 8 and 9 agrees well with the theoretical and experimental values [5]. The value of the in-plane strain used in the strained Si technology is about ±0.5 %. Besides, the Fermi level locates at around 0.5 in most cases. Table 1 summarizes the calculated difference of $E_F$ of point defects, $\Delta E_F$, between strained Si with ±0.5 % in-plane strain and unstrained Si at $\mu = 0.5$.

<table>
<thead>
<tr>
<th>In-plane strain</th>
<th>$\Delta E_F$ (eV)</th>
<th>$V^0$</th>
<th>$I^{+2}$ at T site</th>
</tr>
</thead>
<tbody>
<tr>
<td>-0.5 %</td>
<td>-0.045</td>
<td></td>
<td>+0.055</td>
</tr>
<tr>
<td>+0.5 %</td>
<td>+0.032</td>
<td></td>
<td>-0.039</td>
</tr>
</tbody>
</table>

Here, we estimate the thermal equilibrium concentrations of $V$ and $I$ in strained Si with ±0.5 % in-plane strain by using the calculated results in Table 1. The ratio of the number of $V$ to the number of Si atoms, $C_V$, can be written with the formation energy $E_F$ of $V$ and the absolute temperature $T$ as [22],

$$C_V = \exp \left( -\frac{E_F}{kT} \right).$$

(5)

Here, $k$ is the Boltzmann constant. The ratio of the number of $I$ to the number of Si atoms, $C_I$, can be written with a similar formula. By using eq.(5), $C_V$ and $C_I$ at 800 °C, which is the typical temperature of LSI processes, were calculated with Table 1. It was found that (i) the value of $C_V$ and $C_I$ with -0.5 % in-plane strain becomes 1.63 times and 0.55 times as large as that without in-plane strain, respectively, and (ii) the value of $C_V$ and $C_I$ with
+0.5 % in-plane strain becomes 0.71 times and 1.52 times as large as that without in-plane strain, respectively. In Si single crystals, both \( V \) and \( I \) affect the precipitation of interstitial oxygen atoms and the diffusion of dopant atoms. Furthermore, the change of the thermal equilibrium concentrations affects the supersaturated degree of point defects. Based on these viewpoints, the in-plane strain appeared in an actual strained Si technology affects the point defect behavior in Si crystals.

In \textit{ab initio} calculations with three-dimensional periodic boundary conditions, the calculated results include some error due to the interaction between the calculation and image cells. We used a supercell of 64 Si atoms to minimize the error in the present work. However, recent studies [21,23] showed that the error cannot be neglected even if the use of a supercell of 64 Si atoms. The calculation by using the larger cells will be a future study.

4. Conclusions

We studied the effects of compressive and tensile in-plane strain on the stability of vacancies (\( V \)) and self-interstitials (\( I \)) in Si crystals by calculating the formation energy \( E_f \) of point defects in plane-stressed Si with an \textit{ab initio} approach. It was found that the band gap of Si crystal decreased for both tensile and compressive in-plane strain. This calculation well reproduced the reported experimental result.

The calculated results showed that \( E_f \) of \( I \) decreased under tensile in-plane strain. On the other hand, \( E_f \) of \( V \) decreased under compressive in-plane strain. Furthermore, it was estimated that the thermal equilibrium concentrations of point defects with an actual in-plane strain become about 0.5 ~ 1.6 times from those of point defects in unstrained Si crystals.

References

(7) The \textit{CASTEP} code is available from Accelrys Software Inc.


