Effect of isotropic pressure on structural and electronic properties of silicon system with $Fd-3m$ space group

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Abstract. We study on the effect of isotropic pressure on structural and electronic properties of silicon system with $Fd-3m$ space group which are calculated using generalized gradient approximation method with Perdew-Burke-Erzenhof-type exchange-correlation functional energy (PBE-GGA method). As the results, the calculated lattice parameter is $5.475\ \text{Å}$ at room pressure and decreased to $5.287\ \text{Å}$ at the pressure of $11.3\ \text{GPa}$, at which the space group is transformed to $I4_1/amd$. The fit bulk modulus and derivative pressure from the relation between lattice parameter and pressure are $89\ \text{GPa}$ and $3.5$, respectively. Besides, the calculated indirect bandgap is $0.645\ \text{eV}$ ($1.170\ \text{eV}$ after correction) at room pressure and linearly decreased to $0.482\ \text{eV}$ ($1.007\ \text{eV}$ after correction) at $11.3\ \text{GPa}$, when the space group is transformed to $I4_1/amd$. The calculated pressure coefficient ($\alpha = dE_g/dP$) of silicon system is $-14.4\ \text{meV/GPa}$ using the linear relation. On the other hand, the valence and conduction bandwidths are increased by the increase of pressure, mainly promoted by Si $3p$ states. Overall, the result shows that the reasonable pressure-dependence of structural and electronic properties of silicon can be obtained by using PBE-GGA method. This study can be used as a guide for silicon-based photonic applications.

1. Introduction

Silicon (Si) is a semiconductor that has been used for many applications, such as field-effect transistors [1], light-emitting diodes [2], biosensors [3-5], and solar cells [6-8]. Recently, $n$-type Si has been used as the visible light-sensitive photocatalyst, which is combined with tungsten oxide (WO$_3$) to form ohmic-contact between both materials. The ohmic contact is the mediator to transfer electrons or holes between valence band (VB) of $n$-type Si conduction band (CB) of WO$_3$ [9]. In experiments, Si has been used as the substrate for various systems due to several advantages, i.e., the possible use in bulk form for optical or electronic circuits and low cost for high purity [10]. Besides, Si is suitable as the substrate to obtain high-optical-sensitivity thin films due to the high refractive index [11, 12]. Therefore, we used Si as the substrate in investigating electronic and optical properties of ZnO-based films [13, 14].

The electronic properties of Si system in various platforms can be modified by varying techniques, such as bandgap ($E_g$) tuning of Si nanowires by various diameter [15] and $E_g$ tuning by doping or co-doping in Si nanoclusters [16] and nanocrystals films [17] using boron (B) and phosphor (P). Both electronic and structural properties of Si clusters are even able to be modified by various doping with transition metals [18]. Recently, the direct-type $E_g$ of pure Si system can even be found for various
metastable allotropes with the values of $E_g$ of 0.39–1.25 eV, which is in contrast to that of the stable system with cubic crystal structure [19].

Regarding the pure system, indirect $E_g$ of 1.12 eV at room pressure (RP) and temperature (RT) has been observed in Si system with the diamond-type crystal structure [20]. The observed cubic lattice parameter ($a$) is 5.431 Å at RT and RP [21]. However, $E_g$ of pure Si system can be tuned by varying temperature ($T$) [20] or pressure ($P$) [22]. Concerning the variation $P$, the space group of Si system can be changed by tuning $P$. At RP to the onset value of $P = 11.3$ GPa, pure Si system has the diamond-type cubic crystal structure with $Fd-3m$ space group. Beyond the onset $P$, the crystal structure of Si system is transformed into the tetragonal structure with $I4_1/amd$ space group [22]. As cubic Si system, the pressure-dependence of $E_g$ has been experimentally investigated [23, 24] and theoretically [25]. Local-density approximation (LDA) has been used to calculate the pressure-dependence of structural and electronic properties for several diamond-type crystal structure semiconductors, including Si [26-28]. However, pressure-dependence of structural and electronic properties of Si system, calculated by using generalized gradient approximation (GGA) method, is still not clear yet.

In this paper, the structural and electronic properties of pure Si system in the diamond-type crystal structure are calculated using GGA method, as the novelty of this work, for obtaining fully-optimized $a$, band structures, total density of states (TDOS), and projected DOS (PDOS). Therefore, bulk modulus ($B$), derivative pressure ($B'$), and pressure coefficient ($\alpha$) are obtained from those results and comprehensively discussed.

2. Methods

Density-functional calculation [29, 30] using Quantum-ESPRESSO code [31] was conducted to obtain structural and electronic properties of Si system in the diamond-type crystal structure. Broyden mixing algorithm, which employs quasi-Newton methods, was used to perform self-consistent field (SCF) calculation [32].

![Figure 1. Schematic crystal structure of silicon system in diamond-type structure visualized using XCrysDEN [33].](image)

**Table 1.** High-symmetry points in Brillouin zone for $Fd-3m$ space group

| Point | Coordinate in Brillouin zone $(u, v, w)$ |
|-------|----------------------------------------|
| $W$   | (1/2, 1/4, 3/4)                        |
| $\Gamma$ | (0, 0, 0)               |
| $X$   | (1/2, 0, 1/2)                        |
| $W$   | (1/2, 1/4, 3/4)                        |
| $L$   | (1/2, 1/2, 1/2)                        |
| $\Gamma$ | (0, 0, 0)               |
Here, GGA alongside Perdew-Burke-Erzenhof (PBE)-type exchange-correlation (XC) energy [34] (PBE-GGA method) and Rappe-Rabe-Kaxiras-Joannopoulos (RRKJ)-type pseudopotentials [35-37] were used. The employed GGA method has been used for different systems in our previous reports [38-41]. Band structures and density of states (DOS) are calculated based on the results from SCF calculation. Initial cubic \(a\) of Si system is based on the previous experimental parameter for room \(P\) [21] and fully optimized by variable-cell optimization calculation. Crystal structure of Si system is shown in figure 1, which represents bulk Si system. A \(k\)-point mesh of \(10 \times 10 \times 10\) centered at \(\Gamma\) and kinetic cutoff energy of 1361 eV were also employed. In the band structure calculation, high-symmetry points for \(Fd-3m\) space group were used as shown in table 1. For studying the effect of high pressure on the structural and electronic properties, full structural optimization was performed using different values of \(P\), i.e., 0.0 GPa, 2.5 GPa, 5.0 GPa, 7.5 GPa, 10.0 GPa, and 11.3 GPa, at which the space group of Si starts to be \(I\bar{4}_3/\text{amd}\) [22]. Here, lattice \(a\), \(E_g\), and bandwidth (\(\Delta\)) for VB (\(\Delta_{\text{vb}}\)) and CB (\(\Delta_{\text{cb}}\)) are discussed comprehensively.

3. Results and Discussions

3.1. Structural properties

Figure 2 and table 2 show pressure-dependence of \(a\) in Si system. In general, the value of \(a\) is almost linearly decreased by the increase of \(P\). Interestingly, the calculated value of \(a\) at \(P = 11.3\) GPa is close to that of the previous reports, i.e., 5.268 Å [22]. On the other hand, real-space atomic coordinates are not changed relative to the crystal unit cell. Therefore, nearest-neighbor distance in the system is also decreased, promoting the increase of total energy per Si, as shown in table 2. The nearest-neighbor distance is obtained by \(\sqrt{3}a/4\), in a way reminiscent of the relative position of \((1/4, 1/4, 1/4)\), as shown in figure 1. In the employed bulk Si system, work (\(W\)) applied to the system is negative due to the decrease in unit cell volume (\(V\)), obtained from \(a\). It means that \(W\) is applied to the system. The negative \(W\) thermodynamically promotes the increase of total energy per Si. Here, \(B\) and \(B'\) are fit by using the formula obtained from Murnaghan equation of state (EOS) [42, 43]

\[
a(P) = a(0) \left(1 + \frac{B'}{B} \frac{P}{P_0}\right)^{1/3}.
\]

where \(a(P)\) is lattice parameter as function of \(P\) and \(a(P)\) is lattice parameter at \(P = 0\) Pa. It is found that fit \(B\) and \(B'\) are 89 GPa and 3.5, respectively, which are in fair agreement with that of previously reported results (\(B = 97.82\) GPa and \(B' = 4.4\) [42, 44]. Zhu et al. [45] have found the calculated \(B\) and \(B'\) of 90.3 GPa and 4.26, respectively, by using LDA method with the interpolation method by Wigner for XC potential [46, 47]. On the other hand, the calculated \(B\) and \(B'\) of 103.6 GPa and 3.51, respectively, have been found by using the generalized random-phase-approximation (RPA) calculation for the XC potential of uniform electron gas [45, 48]. The employed PBE-GGA method thus provides reasonable structural properties of Si system.

3.2. Electronic properties

The electronic properties of Si system are discussed for valence and conduction states near Fermi level (\(E_g\)). Figure 3 presents TDOS and PDOS of Si system for the different value of \(P\). It is shown that VB mainly is originated from Si 3\(p\) followed by Si 3\(s\) states, for all \(P\) values. However, Si 3\(s\) are more dominant in lower energy levels, indicating that Si 3\(s\) is more stable rather than Si 3\(p\) states. Also, CB mainly comes from Si 3\(p\), followed by Si 3\(s\) states. This result indicates unoccupied Si 3\(d\) orbital. The presence of Si 3\(p\) states in CB indicates that Si 3\(p\) orbital partly occupied. Among six possible sites occupied by electrons in Si 3\(p\) orbital, two sites that are occupied and four sites that are unoccupied. Moreover, PDOS shows the increase of \(\Delta_{\text{vb}}\) and \(\Delta_{\text{cb}}\) by the increase of \(P\).
Table 2. Pressure-dependence of lattice parameter ($a$), unit cell volume ($V$), nearest-neighbor distance ($d_{\text{Si-Si}}$), and total energy per Si ($E_{\text{tot}}$)

| $P$ (GPa) | $a$ (Å) | $V$ (Å$^3$) | $d_{\text{Si-Si}}$ (Å) | $E_{\text{tot}}$ (eV) |
|-----------|---------|-------------|----------------|-----------------|
| 0.0       | 5.475   | 164.137     | 2.371           | −107.090        |
| 2.5       | 5.426   | 159.739     | 2.349           | −107.085        |
| 5.0       | 5.382   | 155.871     | 2.330           | −107.074        |
| 7.5       | 5.342   | 152.428     | 2.313           | −107.057        |
| 10.0      | 5.305   | 149.315     | 2.297           | −107.036        |
| 11.3      | 5.287   | 147.812     | 2.289           | −107.024        |

Figure 2. Lattice parameter and total energy of Si system as functions of pressure.

Figure 3. Total and projected density of states of Si system for (a) room pressure, (b) 2.5 GPa, (c) 5.0 GPa, (d) 7.5 GPa, (e) 10.0 GPa, and (f) 11.3 GPa. Solid and dashed lines denote Si 3$s$ and 3$p$ states, while grey color denotes total density of states.
The increase of $\Delta_{\text{VB}}$ mainly are promoted by Si 3$p$ at VB maximum (VBM) and Si 3$s$ states at VB minimum around 12 eV. On the other hand, the increase of $\Delta_{\text{CB}}$ mainly is promoted by Si 3$p$ at CB minimum (CBM) and CB maximum.

Figure 4 shows band structures of Si system for the different value of $P$. Figure 5 shows the band structures with a shorter energy range near $E_F$ to observe $E_g$ transition. By the increase of $P$, the increases of $E_g$, $\Delta_{\text{VB}}$, and $\Delta_{\text{CB}}$ are obtained, as shown in figure 6 and summarized in table 3. However, the value of $E_g$ for $P = 0.0$ GPa is lower than that of the experimental $E_g$ of 1.17 eV [20]. The lower $E_g$ is caused by the error of GGA in describing $E_g$ of the exact Kohn-Sham electronic structure [49]. Thus, we correct the calculated $E_g$ by a value of 0.525 eV to predict the experimental value for all the values of $P$. The type of $E_g$ transition is indirect, which is same with that of the previous reports [50, 51].

Table 3. Pressure-dependence of bandgap ($E_g$), valence, and conduction bandwidths ($\Delta_{\text{VB}}, \Delta_{\text{CB}}$)

| $P$ (GPa) | $E_g$ (eV) | $E_g$ corrected (eV) | Transition | $\Delta_{\text{VB}}$ (eV) | $\Delta_{\text{CB}}$ (eV) |
|-----------|------------|---------------------|------------|-----------------|-----------------|
| 0.0       | 0.645      | 1.170               | $\Gamma \rightarrow 0.8\Delta$ | 11.736          | 9.264           |
| 2.5       | 0.604      | 1.129               | $\Gamma \rightarrow 0.8\Delta$ | 11.919          | 9.543           |
| 5.0       | 0.566      | 1.091               | $\Gamma \rightarrow 0.8\Delta$ | 12.088          | 9.783           |
| 7.5       | 0.531      | 1.056               | $\Gamma \rightarrow 0.8\Delta$ | 12.245          | 9.981           |
| 10.0      | 0.498      | 1.023               | $\Gamma \rightarrow 0.8\Delta$ | 12.392          | 10.141          |
| 11.3      | 0.482      | 1.007               | $\Gamma \rightarrow 0.8\Delta$ | 12.465          | 10.210          |

Figure 4. Band structures of Si system for (a) room pressure, (b) 2.5 GPa, (c) 5.0 GPa, (d) 7.5 GPa, (e) 10.0 GPa, and (f) 11.3 GPa in a energy range of $-13$ eV to $11$ eV.
Figure 5. Band structures of Si system for (a) room pressure, (b) 2.5 GPa, (c) 5.0 GPa, (d) 7.5 GPa, (e) 10.0 GPa, and (f) 11.3 GPa in a energy range of $-1.2$ eV to 1.2 eV.

Figure 6. Bandgaps, valence and conduction bandwidths of Si system as functions of pressure.
In general, $P$ and $T$ dependences of $E_g$ of semiconductors can be expressed by

$$E_g(P,T) = E_g^{(0)} + aP - \frac{\kappa T^2}{T+c},$$

(2)

where $E_g^{(0)}$ is bandgap at $T = 0$ and $P = 0$, $c$ and $\kappa$ are the temperature coefficients, and $a = dE_g/dP$ is the pressure coefficient [52]. At zero-$T$ limit in the framework of ground-state density-functional theory (DFT) [53], one can obtain a linear equation of $E_g(P)$

$$E_g(P) = E_g^{(0)} + aP,$$

(3)

In this study, we obtain a linear equation of

$$E_g(P) = 1.1662 - 0.0144P,$$

(4)

from figure 6. The fit value of $E_g^{(0)}$ is 1.1662 eV from equation (4), which is close to the calculated $E_g^{(0)}$ after correction (1.17 eV). The obtained value of $a$ is $-0.0144$ eV/GPa or $-14.4$ meV/GPa, which is close to that of previous results, i.e., $-14.1$ meV/GPa [25, 42] and $-13$ meV/GPa [54]. Overall, PBE-GGA method also provides reasonable pressure-dependence of electronic properties in Si system.

4. Conclusions

We have studied the isotropic-pressure-dependence of structural and electronic properties of Si system with the diamond-type crystal structure ($Fd-3m$ space group), calculated using PBE-GGA method. Regarding the structural properties, the calculated value of $a$ is decreased from 5.475 Å to 5.287 Å from for $P = 0$ to 11.3 GPa, at which the space group is transformed to $I4_{1}/amd$. From the relation between $a$ and $P$, we obtain fit $B$ and $B'$ of 89 GPa and 3.5, respectively. Regarding the electronic properties, the calculated $E_g$ is linearly decreased from 0.645 eV to 0.482 eV (1.170 eV to 1.007 eV) by the same increase of $P$ with $a = dE_g/dP$ of $-14.4$ meV/GPa, which is close to that of the previous reports. On the other hand, the increase of $\Delta_{\text{VB}}$ and $\Delta_{\text{CB}}$, which mainly is promoted by Si 3$p$ states, is obtained by the increase of $P$. The result shows that PBE-GGA method can be used to obtain the reasonable pressure-dependence of structural and electronic properties of Si. This study can also be a guide for photonic applications based on Si.

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