A new crystalline phase of four-fold coordinated silicon and germanium

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\textbf{Abstract.} We have performed first-principles calculations for body-centered tetragonal (bct) Si and Ge consisting solely of four-fold coordinated elements. The structural optimization has been carried out based on the local density approximation (LDA) in the density functional theory (DFT). For total-energy minimized structures, quasi-particle spectra have been calculated using $GW$ approximation. We find that the bct Si and Ge are new stable crystalline phases reachable under tensile stress with moderate magnitude. We also find that the bct Ge is a semimetal with the carrier density of $2 \times 10^{19} \text{ cm}^{-3}$, whereas the bct Si is a semiconductor with the indirect band gap of 0.5 eV. The calculated density of states of the bct Si and Ge show characteristic features which are discriminated from those of the diamond structures. Effective masses of conduction-band electrons and valence-band holes are found to be relatively light compared with those of the diamond Si and Ge. The origins of reduction or closure of band gaps are discussed.
1. Introduction

Group IVB elements such as C, Si and Ge are relatively abundant on the earth and indispensable in our lives. A characteristic of condensed materials consisting of those elements is hybridization of s and p valence orbitals: electrons occupying the lower-energy s orbital of an isolated atom are partly promoted to the p orbitals and thereby stabilize a particular structure called a diamond structure where each atom is four-folded coordinated with sp\(^3\) hybridized orbitals. The materials usually show the energy-band gap (0.6–5.5 eV in their crystalline forms) between occupied bonding and unoccupied antibonding states.

Carbon exhibits more variety in structure: the sp\(^2\) hybridization produces the layered graphite, and mixture between sp\(^2\) and sp\(^3\) causes fascinating nanocarbon materials such as fullerenes [1]–[4], tubes [5, 6] and other exotic structures [7]. The most stable form is graphite. Diamond and other stable forms are higher in total energy by 0.1–0.5 eV per atom. Si and Ge, on the other hand, show no such structural variation in ambient circumstances. Under high pressure, however, Si and Ge show a variety of structures ([8]–[10] and references therein), where the band gap occasionally disappears due to the increase of the coordination numbers.

Recently, two of the present authors and their co-workers [11] have performed constant-pressure molecular-dynamics simulations with a tight-binding model for a variety of carbon materials. They have found that carbon nanotubes under 20 GPa transform to a new carbon crystalline phase. This new phase consists solely of four-fold coordinated C atoms and its unit cell is body-centered tetragonal (bct) with four C atoms. It is expected that Si and Ge also have this bct structure as a stable phase since the constituting atoms are all four-fold coordinated, as in the diamond structure.

In this paper, we report first-principles calculations that clarify the structural stability and quasiparticle spectrum of the bct Si and Ge. We find that the bct phase of Si and Ge is stable with the total energy being higher than the most stable diamond phase by only 0.1 eV per atom. The bct phase is found to be larger in volume than the diamond phase, and therefore is expected to be reachable under tensile stress. We also find that the band gap of the bct phase becomes substantially narrow and the bct Ge is even a four-fold coordinated semimetal.

2. Theoretical method

In figure 1, we show the bct phase discussed below. The structure can be seen as (2,2) nanotubes interconnected by the formation of four-membered rings (figure 1(b)). As a result,
Figure 1. Schematic view of the bct phase: (a) three-dimensional view, (b) top view, (c) side view, and (d) Brillouin zone. Dashed lines denote the rectangle unit cells. $\theta_i$ ($i = 1, 2$ and $3$) and $d_j$ ($j = 1$ and $2$) represent the corresponding bond angles and bond lengths, respectively.

Each constituent atom is four-fold coordinated to its neighboring atoms. The space group of the bct phase is $I4/mmm$ and all the atoms are equivalent to each other. Yet there are two distinctive bond lengths and three bond angles, as shown in figure 1.

Structural optimization has been performed by the local density approximation (LDA) [12, 13] in the density functional theory (DFT) [14]. Normconserving pseudopotentials are used to simulate nuclei and core electrons [15]. Kohn–Sham orbitals and thus electron density are expanded in terms of the plane-wave basis set with the cut-off energy of 25 Ry. Brillouin-zone integration is performed with 512 $k$-point sampling. Convergence of the results with respect to those calculational parameters has been examined and the numerical error in the total energy difference among different phases is 0.04 eV or smaller.

Quasiparticle spectra (energy-band structures) have been calculated in $GW$ approximation (GWA) where the self-energy operator is given by the product of the one-particle

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6 Normconserving pseudopotentials are generated with the core radii of 1.11, 1.27 and 1.27 Å for Si s, p and d states, and 1.11, 1.11 and 1.11 Å for Ge s, p and d states, respectively.

7 Computations have been performed using the Tokyo Ab initio Program Package (TAPP) being developed by a consortium initiated at the University of Tokyo.
Green function \((G)\) and the screened Coulomb interaction \((W)\) [17, 18]. The GWA scheme we have used is implemented in the all-electron full potential linear muffin-tin orbital (FP-LMTO) method [19]. We use 37 MT orbitals per Si atom and 39 MT orbitals per Ge atom to express valence wavefunctions in MT spheres. Scalar relativistic effects and renormalization factor are included. GWA calculations have been performed for the structures optimized by the pseudopotential-DFT scheme described above. Polarization functions, screened interactions and then self-energies are calculated by using Kohn–Sham eigenvalues and orbitals in LDA (one-shot \(GW\)). In this one-shot GWA, we have confirmed that the calculated band gaps of diamond Si and Ge are 1.03 and 0.77 eV, respectively, which are close to the corresponding experimental values, 1.17 and 0.7 eV. Discrepancy among this one-shot GWA, (semi) self-consistent GWA and experiments is well discussed [20], and the obtained band gaps in this paper are expected to be close to the real values.

3. Results and discussion

3.1. Energetics and structure

Figure 2 shows calculated total energies of the bct Si and bct Ge. The bct phase is larger in volume than the diamond phase by 7.2 and 6.5% for Si and Ge, respectively. We have found that the bct phase is a stable phase: the total energy difference from the diamond phase is 0.12 and 0.11 eV per atom for Si and Ge, respectively. This small energy difference infers the existence of the bct phase at ambient conditions.

Figure 2 also shows common tangents of the total-energy curves for the bct and the diamond phases. It is found that the structural transition from the diamond phase to the bct phase takes place under negative pressure. The transition pressures are \(-112\) and \(-92\) kbar for Si and Ge, respectively. The extensions of bond lengths in the diamond structure at these transition pressures are evaluated to be 3.77 and 3.97%, respectively, for Si and Ge, using the values of bulk moduli (990 kbar for Si and 772 kbar for Ge).

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Table 1. Structural parameters of bct Si and Ge optimized in LDA. Lattice constants $a$ and $c$, bond lengths $d_1$ and $d_2$, and bond angles $\theta_1$, $\theta_2$ and $\theta_3$ are depicted in figure 1.

|       | Lattice (Å) | Bond length (Å) | Angle (°) |
|-------|-------------|-----------------|-----------|
| Si    | $a = 6.59$  | $d_1 = 2.36$    | $\theta_1 = 113.8$ |
|       | $c = 3.81$  | $d_2 = 2.32$    | $\theta_2 = 110.4$ |
| Ge    | $a = 6.87$  | $d_1 = 2.45$    | $\theta_1 = 114.0$ |
|       | $c = 3.94$  | $d_2 = 2.41$    | $\theta_2 = 109.7$ |

Applying negative pressure is less feasible than normal positive pressure although the required magnitude to form the bct structure deduced from figure 2 is moderate. In order to form the bct structure, however, we suggest the following possibility. Tensile stress is induced in heterostructures formed in current miniaturization of semiconductor technology [21]: epitaxially grown Si on the Ge substrate or epitaxially grown Ge on the Ge–Sn buffer layer is under tensile stress, corresponding to several percent strains. It is noteworthy that the $\langle 100 \rangle$ face of the bct structure matches well with the $\langle 111 \rangle$ face of the diamond structure, where both faces exhibit hexagonal atomic arrangements. The buckling pattern in the hexagon is the only difference between the two phases. The tensile stress is expected to favor the bct phase which is more porous than the diamond phase. We thus suggest that the hetero-epitaxial growth on the (111) surface of the diamond structure is a possibility to forge the bct structure.

The calculated bond lengths and bond angles in the total-energy minimized bct phase are shown in table 1. From the symmetry, there are two distinctive bond lengths in the bct phase. One is the bond constituting the atomic square in figure 1 and the other is the bond connecting adjacent squares. The former is slightly longer (less than 1%) whereas the latter is shorter by 1–2%, compared with the bond length in the diamond phase. As for the bond angles, there are three distinctive values. One is obviously 90° which constitutes the atomic square. The remaining two angles are slightly larger (but less than 4%) than the ideal sp$^3$ angle of 109.5°. Hence, the structural characteristic of the bct phase is its four-fold coordination of each atom and at the same time the existence of the substantially distorted angle of 90°. This makes the total energy higher than the diamond phase by 0.1 eV per atom and, as will be discussed below, modifies the electronic structure significantly.

3.2. Electronic structure

The calculated energy bands obtained by the present GWA are shown in figure 3. Table 2 summarizes calculated band gaps and effective masses. We have found that the bct Si is a semiconductor with the indirect band gap of 0.47 eV. The valence band top is located at Z point [$k_Z = (1, 0, 0)(2\pi/a)$] and the conduction band bottom is on the $\Lambda$ line connecting $\Gamma$ and another Z point. This obtained band gap for bct Si is 45% of the band gap of diamond-structure Si in the present GWA calculations. The direct gap which is located at Z point is 0.7 eV, being again much smaller than the direct gap at $\Gamma$ point in diamond Si. We thus conclude that the bct Si is a semiconductor with a substantially narrow band gap compared with diamond Si.

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Figure 3. Energy bands of (a) bct Si and (b) bct Ge calculated in LDA (solid lines) and in GWA (dots).

Table 2. Band gaps and effective masses of bct Si and Ge calculated in GWA. Corresponding values calculated in LDA are also shown for comparison. Indirect and direct band gaps ($E_i$ and $E_d$), effective masses of conduction bands ($m^c_i$ and $m^c_t$) and valence bands ($m^v_i$ and $m^v_t$) along the direction parallel ($l$) and perpendicular ($t$) to the [100]-direction are shown. $m^v_t$ shows variation in [100]- and [110]-directions both for heavy and light holes. Effective masses are in units of free-electron mass.

|                | Band gap (eV) | Effective mass |
|----------------|---------------|----------------|
|                | $E_i$         | $E_d$          | $m^c_i$ | $m^c_t$ | $m^v_i$ | $m^v_t$ | Direction |
| bct Si (GWA)   | 0.47          | 0.74           | 0.21    | 0.40    | 0.40    | 0.14    | [100]     |
|                |               |                |         |         |         |         |           |
| bct Si (LDA)   | 0.10          | 0.25           | 0.47    | 0.34    | 0.38    | 0.14    | [100]     |
|                |               |                |         |         |         |         |           |
| bct Ge (GWA)   | −0.12         | 0.51           | 0.30    | 0.14    |         |         | [110]     |
|                |               |                |         |         |         |         |           |
| bct Ge (LDA)   | −0.39         | 0.11           | 0.31    | 0.12    | 0.59    | 0.16    | 0.01      | [110]     |

The bct Ge shows striking features. The valence band top is located at Z point as in bct Si, and the conduction band bottom is at P point [$k_p = (1, 1, a/c)(\pi/a)$]. We have found that the energy of the conduction band bottom is below the valence band top by 0.12 eV in GWA, indicative of the semimetallic character of bct Ge. In the view that the present GWA provides band gaps in quantitative agreement with the experimental values for diamond-structure Si and Ge, we here argue that the bct Ge is a semimetal consisting solely of four-folded Ge atoms. It is extremely unusual that covalency which reflects on the four-folded coordination induces metallic properties. The calculated number of carriers is $2 \times 10^{19}$ cm$^{-3}$ which is comparable with typical semimetals, Bi and graphite.

In diamond Si and Ge, the valence band top and bottom are located at $\Gamma$ point where s and p orbitals are decoupled in a simple tight binding picture and the bottom is of s and the top is of p characters. In the bct Si and Ge, the valence band top consists of three states with splitting of 0.1−0.2 eV at Z point, whereas the valence band bottom is at $\Gamma$ point. Analyses of
Kohn–Sham orbitals clarify that the valence band top at Z point has mainly p characters and the bottom at Γ is of s character. The d-orbital character is also incorporated in electron states in the bct structure. As is shown in table 1, the bond angles in (001)-plane (xy-plane) is 90° and thus sp²d hybridization where dₓ²−y² character as well as s and p becomes important. As a result, the valence band width becomes larger by 0.2–0.4 eV (figure 4) compared with the diamond structure since d character is more incorporated in upper parts of the valence bands. This assists in the closure of the fundamental band gap.

Corrections in the present GWA to the LDA band gaps are relatively small compared with the corrections in diamond Si and Ge. This may be related to the characters of the conduction bands where d characters are more incorporated in bct Si and Ge: incorporation of d characters increase the degree of freedom, making Kohn–Sham orbitals extended in the interstitial region and thereby reducing the corrections.

We have also examined the effects of spin–orbit splitting in bct Ge. Our FP-LMTO calculation shows that the splitting is about 0.1 eV. This also assists in band gap closing and corroborates the metallic nature of bct Ge.

Figure 4 shows density of states (DOS) of bct Si and Ge calculated by LDA with corrections obtained in GWA. It is well known that the DOS of the diamond Si and Ge shows three prominent peaks in the valence band region. In contrast with that, the bct Si and Ge shows five main peaks. We expect that photoemission experiments are capable of distinguishing the bct and the diamond structures clearly.

It is known that amorphous Si and Ge show peculiar photoemission spectra which differ from those of diamond-structured Si and Ge in several aspects [22]. Actually the valence-band densities of states of several polymorphs of Si and Ge have been computed by the empirical scheme [22] and compared with the data. In this context, the present bct structure is also a candidate to explain photoemission spectra of the amorphous structure. Another possibility is that the nanometre-scale bct structure could be realized in bulk amorphous materials since the density of the amorphous structure is occasionally lower than the diamond structure.

As can be seen from table 2, the electron mass is less anisotropic compared with diamond Si and Ge. The averaged values are lighter in the bct structure. The hole mass is significantly anisotropic in the bct structure reflecting the k-point position of the valence band top. The effective mass of light holes is substantially light compared with the diamond structure. These features as well as the metallic nature of the bct Ge infer possible device applications of the bct materials.
4. Conclusions

From the first-principles total-energy study it is predicted that the four-fold coordinated anisotropic bct phase is a new stable phase of Si and Ge. From the $GW$ quasiparticle analysis, we find that bct Si is a semiconductor substantially different in character from diamond Si and that bct Ge is metallic, in sharp contrast with semiconducting diamond Ge.

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