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# First-principles study of $Si_{34-x}Ge_x$ clathrates: Direct wide-gap semiconductors in Si-Ge alloys

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Energetics and electronic states of $Si_{34-x}Ge_x$ clathrate alloys have been investigated. The atomistic structures, the equations of state, and the lineup of band structures for these clathrates are calculated using the Vanderbilt ultra-soft pseudopotential method within the local-density-functional formalism. Some of these $Si_{34-x}Ge_x$ clathrate alloys with an ideal $Fd\overline{3}m$ symmetry are found to have direct band gap at the $\pi/a(111)$ $(L)$ point in the Brillouin zone. The entire band gap of the $Si_{34-x}Ge_x$ alloys is predicted to range between 1.2 and 2.0 eV. The total-energy difference between these clathrate alloys and the well-known $sp^3$ Si-Ge alloys is less than 0.08 eV/atom. A method to synthesize these clathrate systems is also discussed. These Si-Ge clathrate alloys may find applications in optoelectronics semiconductor devices based on the Group-IV elements.

## I. INTRODUCTION

Expanded-volume silicons and/or germaniums named clathrates have been drawing considerable interest during the past few years. Though two forms of silicon clathrate, $Si_{46}$ and $Si_{34}$ (often referred to as $Si_{136}$) have been known for many years,[1,2] two phenomena experimentally confirmed in clathrates have triggered intensive theoretical and experimental investigations. One is the discovery of superconductivity in a metal-doped clathrate, $Ba_xNa_ySi_{46}$.[3] Another is the potential of clathrates for thermoelectric applications, where the figure of merit can be made arbitrary large with the ''phonon glass and electron crystal (PGEC)'' mechanism.[4–6]

This interest in Si clathrates may arise from the following viewpoints. One is the similarity to $C_{60}$ compounds and their related carbon fullerene materials.[7] The superconductivity of metal-doped $Si_{46}$ clathrates has been attributed to a cage structure peculiar to the $C_{60}$ compounds.[3,8–10] As for thermoelectrics of clathrates, metal atoms, ''rattlers,'' in the endohedral sites, also play a key role to show the large figure of merit with the PGEC mechanism.[4–6] The other viewpoint is a wider energy band gap of pristine Si clathrates. Theoretical calculations have predicted that the pristine Si clathrates have about a 0.7 eV larger gap than a cubic diamond silicon (*cd*-Si).[8,10–13] This widening of the band gap is almost the same magnitude as compared with a silicon dot and a porous Si. Hence, the pristine Si clathrates are promising candidates for applications in optoelectronic semiconductor devices.

The energetics and the band structures of the pristine Si clathrates, $Si_{46}$ and $Si_{34}$, have been investigated by some groups.[8,10–14] An electronic structure calculation[15] also suggests that a hypothetical Si clathrate, Hex-$Si_{40}$, may be applied to a photoluminescent material. In these studies, the tight-bindinglike formalism[11,13] and the plane-wave one[8,10–12,14,15] within the local-density approximation (LDA) have been employed. Though the energy dispersion relations are somewhat different depending on the calculation formalism used,[8,11] all calculations reported so far have predicted that these pristine Si clathrates are semiconductors with an indirect gap about 0.7 eV wider than that of the *cd*-Si. There are only a few reports for Ge clathrates with regard to their energetics and band structures,[16–18] albeit their experimental studies are as abundant as those for the Si clathrates.[2,4–6]

Since semiconducting alloys and superlattices have a great potential in terms of superior optical and electrical properties, a study of alloys and superlattices composed of Si and Ge is of paramount importance. Recently, Herrmann *et al.*[19] have experimentally shown an evidence of the existence of Si-Ge binary-framework clathrates, though these clathrates are doped with metals in the endohedral sites. In this report, we have investigated the energetics and the band structures of Si-Ge binary-framework clathrates, $Si_{34-x}Ge_x$, with an ideal $Fd\overline{3}m$ symmetry. Some of these clathrates are found to have direct band gap at the $\pi/a(111)$ $(L)$ point in the Brillouin zone. The band gap of $Si_{34-x}Ge_x$ alloys is estimated as a function of Ge mole fraction. The entire band gap for these $Si_{34-x}Ge_x$ alloys is predicted to range between 1.2 and 2.0 eV. A part of these gap energies is located in the visible-light region. The total-energy difference between these clathrate alloys and the well-known $sp^3$ Si-Ge alloys is found to be less than 0.08 eV/atom. We also report the structural and electronic properties of the two most important clathrate materials of germanium, $Ge_{46}$ and $Ge_{34}$, for comparison.

## II. CALCULATION METHOD

Our calculations are based on the *ab initio* pseudopotential theory within the LDA. We adopt the ultrasoft pseudopotential proposed by Vanderbilt.[20] The Perdew-Zunger parametrization[21] of the LDA is employed. We use the *CASTEP* code[22] in order to solve the pseudopotential Schrődinger equation self-consistently. From the convergence tests of total energies, we choose the kinetic energy cutoff of 300 eV of plane-wave basis sets for all the systems examined. As for the Brillouin-zone sampling, we adopt 10 special **k** points for all the clathrate systems studied. In the present scheme, the indirect band gap of the cubic diamond structure is calculated as 0.44 eV from $\Gamma$ to $0.85X$ for Si and 0.35 eV from $\Gamma$ to $L$ for Ge. While the calculated positions in the Brillouin zone for the valence-band maximum and the conduction-band minimum are in good agreement with experimental results,[23] the magnitude of the energy gaps is strongly underestimated. This can be taken as usual when the *ab initio* LDA calculations are employed. The bulk moduli are deduced by applying a fitting procedure of the total energy versus volume to the Murnaghan's equation of state.

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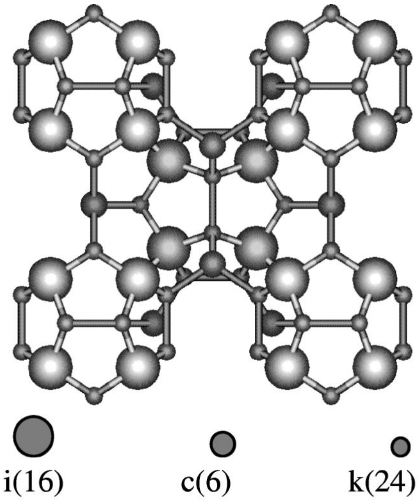
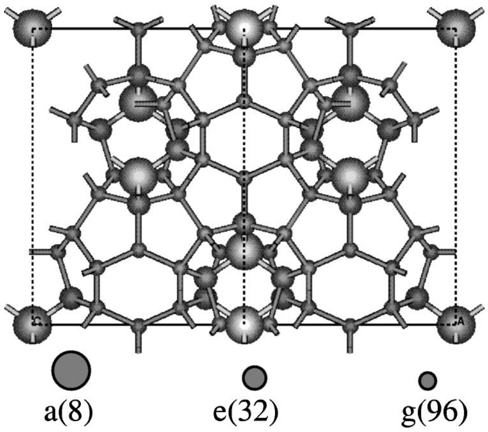


(a) CL(46)



(b) CL(34)

FIG. 1. Schematic diagrams of crystal structure for (a) CL(46) $[Pm\overline{3}n]$ and (b) CL(34) $[Fd\overline{3}m]$. There are three kinds of inequivalent atomic sites in each structure. The notation of atomic positions follows that of the *International Tables for Crystallography*.

## III. RESULTS AND DISCUSSION

### A. Structure and elastic properties

Figure 1 illustrates the two clathrate structures examined in this work. One is a structure containing 46 atoms in a simple-cubic (sc) unit cell and another contains 34 atoms in a fcc unit cell. Hereafter, we denote these clathrate structures by CL(46) and CL(34), respectively. The calculated atomic volumes, cohesive energies, and bulk moduli of Si and Ge with those structures, are listed in Table I. One of the interesting energetics features is that CL(34) is slightly stabler than CL(46) for both Si and Ge. This tendency agrees well with the calculated results using the Tersoff's potential.[16]

TABLE I. Calculated static structural properties of Si and Ge clathrates. The results of cubic diamond systems are also listed for reference. The calculated total energies are shifted so that the energies of $cd$-Si and $cd$-Ge are equal to the experimental negative cohesive energies.

| | Lattice | Atomic volume (Å $^3$/atom) | Cohesive energy (eV/atom) | Bulk modulus (GPa) |
|---|---|---|---|---|
| $cd$-Si | fcc | 19.471 | 4.63[a] | 95 |
| $Si_{46}$ | sc | 22.190 | 4.54 | 83 |
| $Si_{34}$ | fcc | 22.477 | 4.55 | 82 |
| $cd$-Ge | fcc | 21.361 | 3.85[a] | 79 |
| $Ge_{46}$ | sc | 24.174 | 3.80 | 68 |
| $Ge_{34}$ | fcc | 24.454 | 3.81 | 67 |

[a] Reference 23.

The bulk moduli of the clathrate structures are about 15% smaller than that of the diamond structure. The reduction of the bulk modulus for Si clathrates has been pointed out theoretically by Kahn and Lu[24] and Dong *et al.*[25] and experimentally observed by San-Miguel *et al.*[26] A qualitative comprehension of this bulk modulus reduction is as follows: (i) The bulk modulus depends on the number of the chemical bonds subjected to a compressive state in a unit volume. (ii) In an $sp^3$ network like a clathrate structure, in which the spreading of the bond distances is as small as only 1% of the diamond structure, the number of the chemical bonds in a unit volume is proportional to the density of the material. (iii) Thus, a rate of the energy increase due to the compression should be reduced for lower-density materials, which leads to a smaller bulk modulus. This comprehension is reminiscent of the work of Lam *et al.*[27] Starting with the pseudopotential total-energy formalism, they proposed an analytic relation between the bulk modulus of a solid and its equilibrium constant. For the Group-IV compounds, they have reached an expression as

$$B_0=\frac{1}{9\Omega_0}\left(\frac{178}{R_0^2}-\frac{98}{R_0}+\frac{166(R_0-1.14)^2}{R_0^3}\right)14\,700\ \ \text{GPa}, \tag{3.1}$$

where $B_0$, $R_0$, and $\Omega_0$ are the bulk modulus in the unit of GPa, equilibrium Wigner-Seitz radius in a.u., and equilibrium atomic volume in a.u., respectively. Using the atomic volumes in Table I, Eq. (3.1) predicts the bulk moduli of 103, 88, and 89 GPa for $cd$-Si, $Si_{34}$, and $Si_{46}$, respectively. These are in reasonable agreement with the results in Table I. This finding suggests that the theory by Lam *et al.*[27] is efficient for explaining the bulk modulus reduction in Si clathrates. San-Miguel *et al.*,[26] however, have suggested that the relation between the bulk modulus and the density is not so simple in the case of clathrate structures. They have pointed out the probable contributions from other mechanisms such as a charge transfer, which induces more of a decrease of the bulk modulus in clathrates than in the diamond system. In order to clarify the exact cause for the bulk modulus reduction in clathrate structures, it may become an interesting study to theoretically illustrate the trends between the bulk modulus and the density using some expanded-volume silicons proposed by the Arizona State University group.[16,18,28,29]

### B. Electronic structure of pure components

The band structures and the density-of-states for $Si_{46}$, $Si_{34}$, $Ge_{46}$, and $Ge_{34}$ are shown in Fig. 2. For $Si_{46}$, both the valence-band top and the conduction-band bottom are located on the $\Gamma$-$X$ line. The calculated indirect gap (1.11 eV)

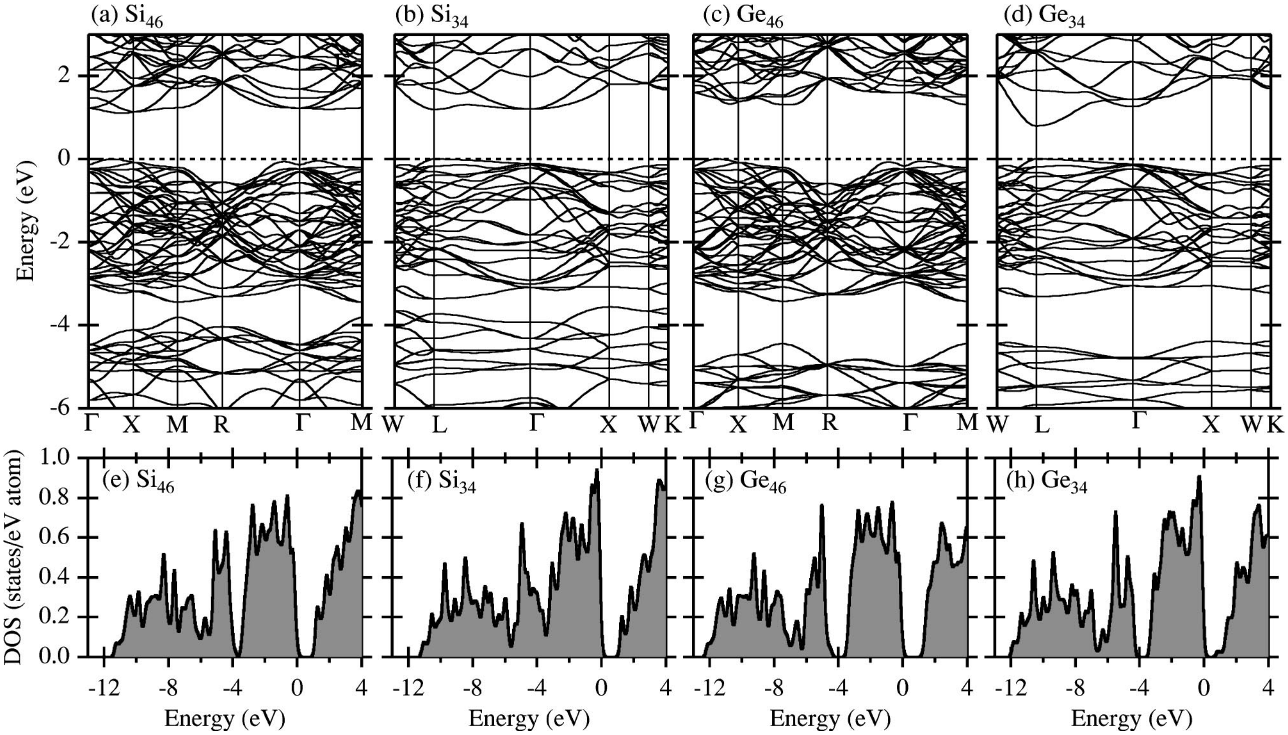


FIG. 2. Band structures [(a)–(d)] and density-of-states [(e)–(h)] for $Si_{46}$, $Si_{34}$, $Ge_{46}$, and $Ge_{34}$. Density-of-states is calculated using 0.1 eV Gaussian broadening of the band structure. Energy is measured from the top of the valence band, which is denoted by a horizontal broken line.

is 0.67 eV larger than that of *cd*-Si. Based on the experimental value of the *cd*-Si (1.17 eV), the indirect gap of $Si_{46}$ is estimated to be about 1.8 eV. These results agree well with the previous report employing the norm-conserving pseudopotential method.[8] For $Si_{34}$, the present LDA calculation shows that $Si_{34}$ has the direct band gap (1.20 eV) at the $\pi/a(111)$ ($L$) point, while the eigenenergy of the conduction-band edge at the $\Gamma$ point is only 10 meV higher than that of the conduction-band minimum at the $L$ point. Because the calculated band-gap value of $Si_{34}$ is 0.76 eV larger than that of *cd*-Si, the experimental gap of $Si_{34}$ is predicted to be about 1.9 eV. Adams *et al.*[11] have reported a slightly different band structure in $Si_{34}$, where the valence-band maximum is located at the $L$ point, while the conduction-band minimum is located at the $\Gamma$ point. It is not clear at present whether the cause of this difference is attributable to the calculation formalism.

In $Ge_{46}$, the valence-band top is located on the $\Gamma$-$X$ line, and the conduction-band bottom is on the $M$-$R$ line. The fundamental-gap value obtained (1.31 eV) is much larger than that for the *cd*-Ge lattice (0.35 eV). The indirect gap of $Ge_{46}$ is expected to be about 1.7 eV from the gap of the *cd*-Ge (0.74 eV) experimentally determined. While the lowest conduction band is relatively flat and the eigenenergies of the conduction-band edge are almost degenerate at $L$ and $\Gamma$ in $Si_{34}$, both the valence-band top and the conduction-band bottom in $Ge_{34}$ are distinctly located on the $L$ point. It should be noted that the difference in energy between the conduction-band minimum at $L$ and the conduction-band edge at $\Gamma$ reaches to 0.46 eV. The gap value obtained here (0.80 eV) suggests that $Ge_{34}$ should have the direct gap of about 1.2 eV. It is also interesting that the difference of the band gap values between CL(46) and CL(34) in Ge clathrates is much larger than that in Si clathrates. The direct band gap at the $L$ point in $Ge_{34}$ has been also reported from the *ab initio* tight-binding approach using a self-consistent method by Sankey *et al.*,[17,18,30] while their band-gap value is slightly larger than ours. In Ge, it is well known that the spin-orbit splitting is relatively large, which is about 0.3 eV in *cd*-Ge.[31,32] In addition, the upper valence dispersion band of the $Ge_{34}$ clathrate is rather flat. Therefore, the pristine $Ge_{34}$ clathrate could be classified into quasidirect band-gap semiconductors within the present scheme.

It has been known that a new gap forms within the valence band in $Si_{46}$.[8] This has been attributed to the existence of five-membered rings in $Si_{46}$, since Si-3$s$ orbitals cannot form complete antibonding states, like a six-membered ring in *cd*-Si.[7,8] The density-of-states (DOS), however, shows that this clear gap within the valence band in $Si_{34}$ becomes narrower, despite the fact that the average ring size (5.064 atoms/ring) in CL(34) is smaller than that (5.094 atoms/ring) in CL(46). This result manifests that the band modifications in clathrate systems cannot be simply attributed to the density of five-membered rings in the systems. Moreover, the DOS's in $Ge_{46}$ and $Ge_{34}$ exhibit clearer gaps than in Si clathrates. Saito and Oshiyama have reported that a hypothetical $C_{46}$ clathrate does not generate this new gap within the valence band.[33] These results indicate that the valence-band structure in clathrates has a strong dependence upon the $s$ and $p$ orbital properties of component elements. The formation of a subband gap within the valence band is well observed in Group III–V compounds, which is owing to the charge transfer.[34–36] The subband gap suggests that an $sp$ mixing is poor in these systems. In clathrate structures, effi-

TABLE II. Components at the three inequivalent sites in the Si-Ge clathrate alloys, $Si_{34-x}Ge_x$, with an ideal $Fd\overline{3}m$ symmetry. The numbers of $N_{\text{Si-Si}}$, $N_{\text{Ge-Ge}}$, and $N_{\text{Si-Ge}}$ are the numbers of Si-Si, Ge-Ge, and Si-Ge bonds per unit cell, respectively. The notation of atomic positions follows that of the International Tables for Crystallography.

| | Sites | | | Number of bonds | | |
|---|---|---|---|---|---|---|
| Composition | $a(8)$ | $e(32)$ | $g(96)$ | $N_{\text{Si-Si}}$ | $N_{\text{Ge-Ge}}$ | $N_{\text{Si-Ge}}$ |
| $Si_{32}Ge_2$ | Ge | Si | Si | 60 | 0 | 8 |
| $Si_{26}Ge_8$ | Si | Ge | Si | 36 | 0 | 32 |
| $Si_{24}Ge_{10}$ | Ge | Ge | Si | 36 | 8 | 24 |
| $Si_{10}Ge_{24}$ | Si | Si | Ge | 8 | 36 | 24 |
| $Si_8Ge_{26}$ | Ge | Si | Ge | 0 | 36 | 32 |
| $Si_2Ge_{32}$ | Si | Ge | Ge | 0 | 60 | 8 |

cient charge transfer is expected because of odd membered rings, as suggested by San-Miguel *et al.*[26] It is not well understood at present about the exact cause for the subband gap narrowing in $Si_{34}$, but the smaller bond-angle distortions in six-membered rings of $Si_{34}$, than those in $Si_{46}$, may be related to this phenomenon. There are strong angular distortions of $\angle \text{Si}[c(6)]\text{-Si}[k(24)]\text{-Si}[k(24)]$ in six-membered rings of $Si_{46}$, whose maximum bond angle is 124.6°. In contrast to $Si_{46}$, the largest bond angle is 119.9° in the $Si_{34}$ structure.

### C. Structural and electronic properties of alloys

Since the band-structure calculations in Si(34) and Ge(34) have shown that these systems are categorized as direct band-gap semiconductors, we have further investigated the energetics and the electronic properties of Si-Ge composite systems with the CL(34) structure. It is well known that the Si-Ge alloys with the ordinary diamond $sp^3$ network form a solid solution in the entire composition range. We assume that Si-Ge alloys with the CL(34) structure are also solid solutions in any mole fractions, that is, they are random crystalline Si-Ge alloys. In the present calculation, an ideal $Fd\overline{3}m$ symmetry structure, which can be constructed by substituting Si (Ge) atoms by Ge (Si) atoms in each equivalent site [see Fig. 1(b)], has been chosen for simplicity. The models adopted are $Si_{32}Ge_2$, $Si_{26}Ge_8$, $Si_{24}Ge_{10}$, $Si_{10}Ge_{24}$, $Si_8Ge_{26}$, and $Si_2Ge_{32}$ clathrates, which are listed in Table II. The bond lengths in these Si-Ge clathrate alloys caculated via geometry optimization are 2.31–2.37 Å for Si-Si, 2.34–2.38 Å for Si-Ge, and 2.37–2.43 Åfor Ge-Ge, respectively. These values are satisfactorily compared with 2.33 Å for *cd*-Si, 2.36 Å for zinc-blende (ZB)-SiGe, 2.40 Å for *cd*-Ge, which are obtained in the same calculation scheme.

Figure 3 shows the calculated atomic volumes, cohesive energies, and bulk moduli for the CL(34) structure alloys as a function of Ge mole fraction. Also shown are those for the well-known $sp^3$ Si-Ge alloys estimated from the results of *cd*-Si, *cd*-Ge, and ZB-SiGe. It is known that the physical properties of ordinary Si-Ge alloys deviate very slightly from the averaged values estimated from the homopolar constituents (*cd*-Si and *cd*-Ge);[37] this means that Vegard's law holds with regard to the variation in lattice constant in these alloys.[38] As shown in Fig. 3, the Si-Ge alloys with the CL(34) structure also exhibit the same relation as the ordinary Si-Ge alloys. The total-energy difference between these clathrate alloys and the well-known Si-Ge alloys is found to be less than 0.08 eV/atom.

A lineup of the band structures for these $Si_{34-x}Ge_x$ alloys is depicted in Fig. 4. The eigenenergies of the conduction-band edge at $L$ and $\Gamma$ and the valence-band edge at $\Gamma$ point are shown in Fig. 5 as a function of Ge mole fraction. In the present calculation, the valence-band maximum in the CL(34) alloys is always located at the $L$ point, irrespective of the Ge mole fraction. The eigenenergies of the conduction-band and the valence-band edges at $\Gamma$ point are not sensitive to the Ge mole fraction. A salient change of the band structure near the fundamental gap is observed in the lower conduction band. As Ge becomes the major component in the alloy, that is, the Ge-Ge bond becomes the majority in the alloy (see Table II), the lowest conduction band begins to change and the degeneracy at $L$ and $\Gamma$ points is noticeably broken. This finding suggests that the Si-Ge alloys in these structures could be also classified into quasidirect band-gap semiconductors. The entire band gap calculated for the $Si_{34-x}Ge_x$ alloys ranges from 0.8 eV ($Ge_{34}$) to 1.3 eV ($Si_{24}Ge_{10}$). With the experimental gaps of *cd*-Si and *cd*-Ge considered, the "true" gap of these clathrate alloys is ex-

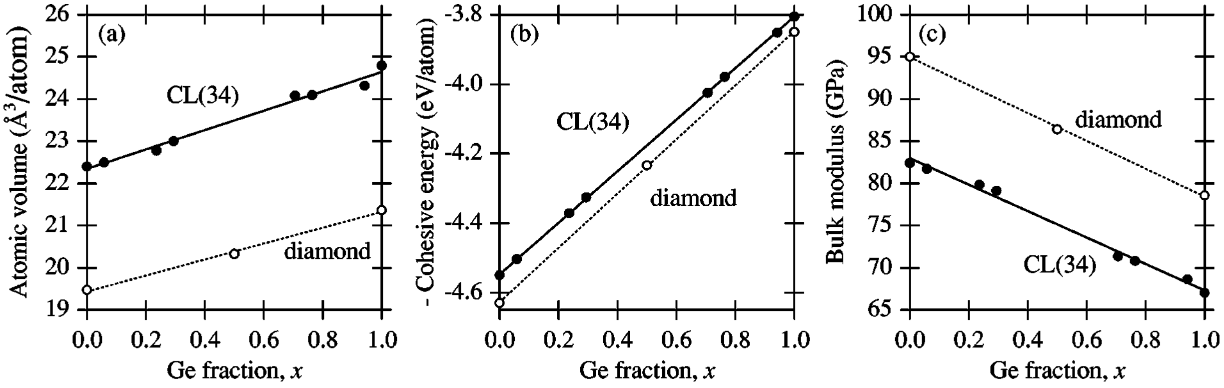
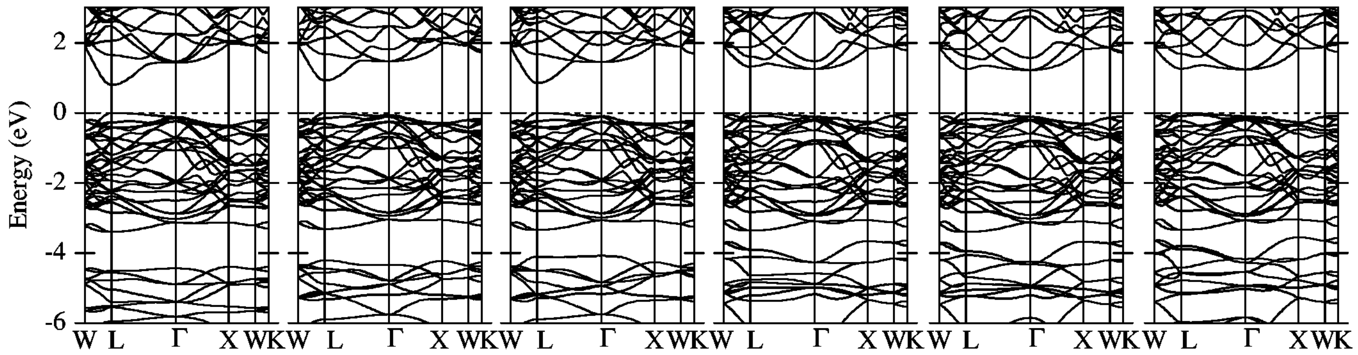


FIG. 3. Calculated (a) atomic volumes, (b) cohesive energies, and (c) bulk moduli as a function of Ge mole fraction in Si-Ge alloys with the CL(34) structure. The Ge mole fraction $x$ is normalized to $Si_{1-x}Ge_x$. Properties of the well-known $sp^3$ Si-Ge alloys (denoted by "diamond") estimated from the results of *cd*-Si, *cd*-Ge, and ZB-SiGe are also shown for comparison. Lines are deduced by a least-squares-fitting of the calculated values.



(a) $Si_2Ge_{32}$ (b) $Si_8Ge_{26}$ (c) $Si_{10}Ge_{24}$ (d) $Si_{24}Ge_{10}$ (e) $Si_{26}Ge_8$ (f) $Si_{32}Ge_2$

FIG. 4. LDA band structures of $Si_{34-x}Ge_x$ [$x=$(a) 32, (b) 26, (c) 24, (d) 10, (e) 8, (f) 2] alloys with an ideal $Fd\overline{3}m$ symmetry.

pected to be within a range of 1.2 eV to 2.0 eV. A part of these gap energies are situated in the visible-light energy range.

### D. A possible method to synthesize pristine clathrates

Negative opinions for synthesizing pristine Si and/or Ge clathrates mainly stem from the facts that these structures have larger atomic volumes than their absolute ground-state structures and there is no simple way to experimentally realize negative pressures. It will be, however, possible to synthesize these clathrates without negative pressures, if we could employ an epitaxial growth technique using a seed crystal. Recently, it has been shown that some metal-doped clathrate compounds could be synthesized in a controllable manner, resulting in a desired crystal structure and a chemical composition. For example, Yamanaka *et al.*[9] have utilized high pressures to succeed in the synthesis of ''bulk'' barium-doped binary silicon clathrate compounds, $Ba_8Si_{46}$, instead of ''powder'' compounds. In addition, a single crystal of $Sr_8Ga_{16}Ge_{30}$ clathrate has been reportedly prepared in the size of $2\times2\times2$ $mm^3$.[39] Using these kinds of metal-doped clathrates as a seed crystal, a bulk of the pristine Si and/or Ge clathrates may be epitaxially grown. In addition, it has been shown theoretically and experimentally that the lattice constant of these clathrate structures is not sensitive to the existence or the kind of metals in the cage structures, because the clathrate frameworks are quite stable.[3,8–10] This property is especially suitable for the epitaxial growth because the lattice constant of the seed crystal is very close to that of growing layers. Hence, the molecular-dynamics study of a crystal growth of clathrate materials is currently under way in our group.

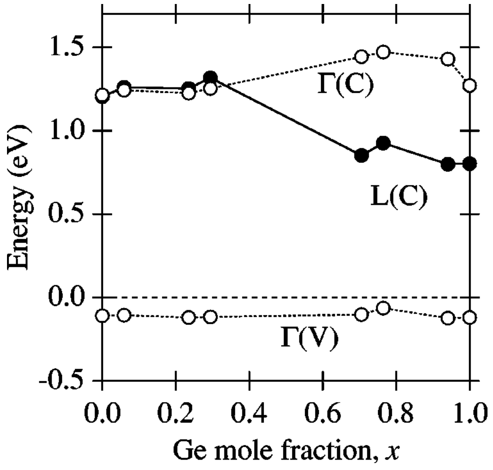


FIG. 5. Eigenenergies of the conduction-band edge at the $L$ point, $L(C)$ and Γ point, Γ(C), and the valence-band edge at the Γ point, Γ(V), as a function of Ge mole fraction in $Si_{34-x}Ge_x$ alloys. All energies are measured from the top of the valence-band. The valence-band tops are located at L point in every Ge mole fraction. The Ge mole fraction $x$ is normalized to $Si_{1-x}Ge_x$. The lines are helpful guides.

## IV. CONCLUSIONS

We have investigated the energetics and electronic states of $Si_{34-x}Ge_x$ clathrate alloys within the framework of density-functional theory. Some of these $Si_{34-x}Ge_x$ clathrate alloys with an ideal $Fd\overline{3}m$ symmetry are found to have direct band gap at the $\pi/a(111)$ $(L)$ point in the Brillouin zone. The entire band gap for the $Si_{34-x}Ge_x$ alloys is predicted to range between 1.2 and 2.0 eV. The total-energy difference between these clathrate alloys and the well-known $sp^3$ Si-Ge alloys is less than 0.08 eV/atom. A possible method to synthesize these clathrate systems is also discussed in which an epitaxial growth technique using a seed crystal is proposed. The present results imply that it is worth while to deepen experimental studies concerning those clathrate materials to find new electronics applications based on the Group–IV elements.

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