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Ternary silicon germanium nitrides: A class of tunable band gap materials

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Ternary silicon germanium nitrides with compositions of both $Si_{1-x}Ge_xN$ and $(Si_{1-x}Ge_x)_3N_4$ are predicted to have a band gap that decreases as the germanium:silicon ratio increases. The band gap is indirect for the silicon-rich compounds but becomes direct as the germanium content increases, due to greater mixing of *s* and *p* states in the conduction band. This effect of band gap tunability has recently been reported for $(Si_{1-x}Ge_x)_3N_4$ in the spinel structure [Boyko *et al.*, Phys. Rev. B **81**, 155207 (2010)]. Our results suggest that this is a more general effect and that ternary group-14 nitrides should form a class of semiconducting materials for which the band gap can be tuned by controlling the composition.

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I. INTRODUCTION

We have recently investigated in detail the crystal structures of a range of binary group-14 nitrides and phosphides,[1–3] including predictions of many structures that are, as yet, unreported experimentally. We established that for many compositions a structure derived from the β-InS structure is low in energy for the 1:1 stoichiometry. In previous work, we have referred to these structures as β-InS-like. For CN, this structure can be considered to be nitrogen-substituted graphite with C-C bonds between the layers.

Several reports suggest that binary group-14 nitrides and phosphides have a range of potential applications; for example, β-Ge_3N_4 (Ref. 4) and graphitic C_3N_4 (Ref. 5) have both been reported to have photocatalytic properties, while amorphous silicon phosphide has been reported to be a semiconductor.[6] Thus, in this work, we turn to the electronic properties of group-14 nitrides and investigate these using *ab initio* calculations.

The binary group-14 nitrides and phosphides are often isostructural and semiconducting, suggesting that it may be possible to create solid solutions from two binary compounds with different band gaps, and this may make accessible band gaps intermediate between those of the two binary compounds. In confirmation of this hypothesis, $(Si_{1-x}Ge_x)_3N_4$ in the spinel structure has recently been reported to have a band gap that can be tuned by changing the Si:Ge ratio.[7] Tunable band gap materials are particularly useful in applications such as light-emitting diodes (LEDs), hybrid solar cells, sensors, and photocatalysts.

In previous work,[2] we found that SiN and GeN have the same lowest-energy structure, referred to as β-InS-like (space group *Pnnm*). In this structure, the group-14 element is four-coordinated with three bonds to nitrogen and one bond to another atom of the group-14 element, while the nitrogen is three-coordinated with all bonds to atoms of the group-14 element (Fig. 1). These structures can be viewed as sheets of $(SiGe)_3N_3$ rings connected by bonds between atoms of the group-14 elements. Calculated band gaps (2.95 eV for SiN and 1.44 eV for GeN) indicate that these materials are semiconductors, consistent with previous experimental reports of the semiconductivity of amorphous silicon nitride with a range of stoichiometries.[8–11] In this paper, we investigate the effect of the Si:Ge ratio on the band gap of ternary $Si_{1-x}Ge_xN$ with the same β-InS-like structure and compare this with the behavior of other ternary silicon germanium nitrides with different structures and nitrogen content.

II. METHOD

The electronic band structures of both $Si_{1-x}Ge_xN$ and β-$(Si_{1-x}Ge_x)_3N_4$ (space group $P63/m$) were calculated with the CRYSTAL code,[13–15] using previously published basis sets[16–18] and the Becke three-parameter Lee-Yang-Parr (B3LYP) hybrid method.[19,20] The unit cells used for $Si_{1-x}Ge_xN$ and β-$(Si_{1-x}Ge_x)_3N_4$ contained eight and 14 atoms, respectively, for all compositions. For $Si_{1-x}Ge_xN$, we considered x values of 0, 0.25, 0.5, 0.75, 1, and also 0.83, which was included by doubling the unit cell in the z direction. For β-$(Si_{1-x}Ge_x)_3N_4$, values of x considered were 0, 0.17, 0.33, 0.5, 0.67, 0.83, and 1. For $Si_{0.5}Ge_{0.5}N$, the effect of different ordering of the group-14 atoms was investigated; for other compositions of $Si_{1-x}Ge_xN$, only one arrangement is possible in the unit cell used. The effect of ordering was not investigated for β-$(Si_{1-x}Ge_x)_3N_4$. Electronic band structures and densities of states (DOSs) were calculated after a full geometry optimization of all lattice parameters and atomic positions with no symmetry constraints.

III. RESULTS AND DISCUSSION

A. $Si_{1-x}Ge_xN$

The density of states of SiN is shown in Fig. 2. In accordance with the crystal orbital scheme presented by Benco[21] for Si_3N_4, different parts of the DOS can be assigned to different interactions. States at energies between ∼−15 eV and ∼−12 eV can be attributed predominantly to bonding interactions between nitrogen 2*p* and silicon 3*s* states, while those at energies between ∼−12 eV and ∼−2 eV can be attributed to bonding interactions between nitrogen 2*p* and silicon 3*p* states as well as bonding interactions between 3*p* states on neighboring silicon atoms. States at energies between ∼−6 eV and ∼−3 eV are mainly due to the nitrogen lone pair. The conduction band states are due to antibonding

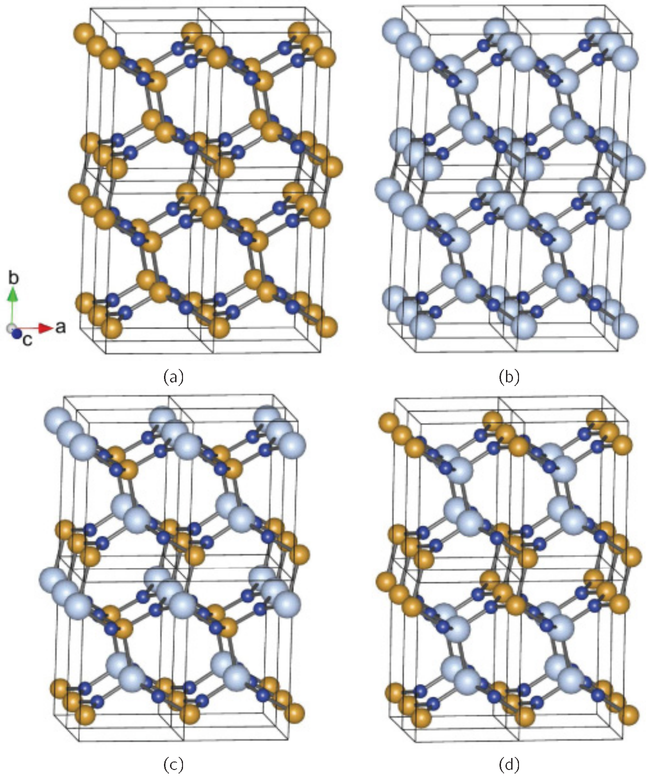


FIG. 1. (Color online) Optimized low-energy structures of (a) SiN, (b) GeN, (c) ternary silicon germanium nitride $Si_{0.5}Ge_{0.5}N$ (there are no Si-Si or Ge-Ge bonds), and (d) ternary silicon germanium nitride $Si_{0.5}Ge_{0.5}N$, with an alternative ordering of the group-14 atoms (there are no Si-Ge bonds). The medium yellow, large light blue, and small dark blue atoms are Si, Ge, and N, respectively, and the black lines show the unit cell boundaries. Images of structures were produced with VESTA (Ref. 12).

interactions between nitrogen $2p$ and silicon $3p$ states, located predominantly on silicon, as well as antibonding interactions between $3p$ states on neighboring silicon atoms.

Since the binary compounds share a common low-energy structure, ternary compounds with composition $Si_{1-x}Ge_xN$ can be easily created [Figs. 1(c) and 1(d)]. We find that, for all x, the formation energy from the two binary compounds:

$$E_{\text{form}} = E(\text{Si}_{1-x}\text{Ge}_x\text{N}) - (1-x)E(\text{SiN}) - xE(\text{GeN}) \tag{1}$$

is close to zero (<0.01 eV/atom). The energy of formation from the pure elements:

$$\begin{aligned} E_{\text{form}} = {} & E(\text{Si}_{1-x}\text{Ge}_x\text{N}) - (1-x)E(\text{Si}) \\ & - xE(\text{Ge}) - \tfrac{1}{2}E(\text{N}_2) \end{aligned} \tag{2}$$

is negative for silicon-rich compounds but increases as the germanium content increases [Fig. 3(a)]. The energy for disproportionation to Si_3N_4 and Ge_3N_4 and pure Si and Ge:

$$\begin{aligned} E_{\text{disp}} = {} & (1-x)E(\text{Si}_3N_4) + xE(\text{Ge}_3N_4) + (1-x)E(\text{Si}) \\ & + xE(\text{Ge}) - 4E(\text{Si}_{1-x}\text{Ge}_x\text{N}) \end{aligned} \tag{3}$$

is negative but small (>−0.2 eV/atom), so the possibility of kinetic stability should not be neglected. Lattice parameters vary linearly with composition [Fig. 3(b)], in accordance with Vegard's law.[22]

The band gap of $Si_{1-x}Ge_xN$ decreases as the germanium content increases [Fig. 3(c)]. This change in the band gap is consistent with a decrease in the overlap between neighboring atomic orbitals as the germanium content increases, such that the conduction band, comprised of the antibonding states, decreases in energy [Fig. 4(a)]. The valence band, composed predominantly of nitrogen $2p$ states, does not change significantly with germanium content.

GeN has a direct band gap at the Γ point. SiN has an indirect band gap with the valence band maximum at the Γ point and, in contrast to GeN, the conduction band minimum at the U $(\frac{1}{2},0,\frac{1}{2})$ point [Figs. 5(a) and 5(b)]. This difference can be related to the conduction band states; in SiN, the bottom of the conduction band consists predominantly of Si $3p_z$ states [Fig. 4(b)], while in GeN the bottom of the conduction band (i.e., the lowest ~0.5 eV) consists predominantly of Ge $4s$ states [Fig. 4(c)].

In the $Si_{0.75}Ge_{0.25}N$ unit cell we used, there are Si-Si and Si-Ge bonds but no Ge-Ge bonds. The conduction band minimum remains at the U point and consists predominantly of mixed p_z and s states on neighboring group-14 atoms, with those involving $3p_z$ states on silicon in Si-Si bonds [labeled Si(A) in Fig. 4(d)] at a slightly lower energy (by ~0.1 eV) than those involving p_z states on silicon or germanium in Si-Ge bonds [labeled Si(B) in Fig. 4(d)]. The conduction band at the Γ point is comprised of s and p mixed states involving orbitals on all group-14 atoms. The energy difference between the conduction band minimum and the conduction band energy at the Γ point is slightly greater than for SiN.

For $Si_{0.5}Ge_{0.5}N$, several different orderings of the group-14 atoms have been investigated. When there are no Si-Si or Ge-Ge bonds [Fig. 1(c)], the partial DOSs for both silicon and germanium qualitatively show the same variation with energy [Fig. 4(e)]. As for $Si_{0.75}Ge_{0.25}N$, the conduction band minimum at the U point is due to mixed silicon and germanium p_z and s states. The conduction band at the Γ point is comprised of s and p mixed states involving orbitals on all group-14 atoms. The energy difference between the

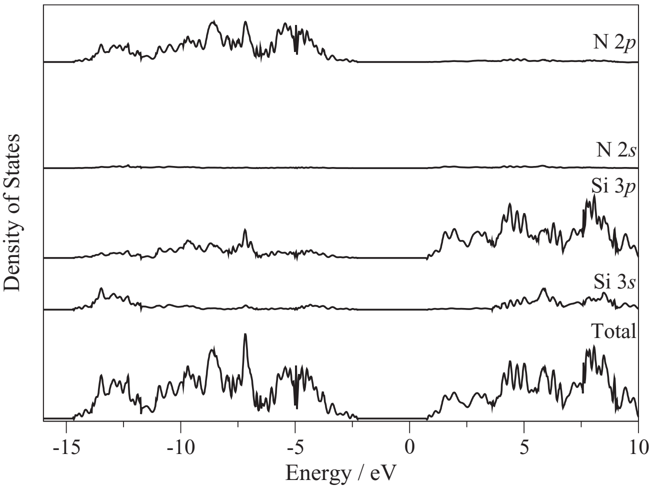


FIG. 2. Total and partial DOSs for SiN.

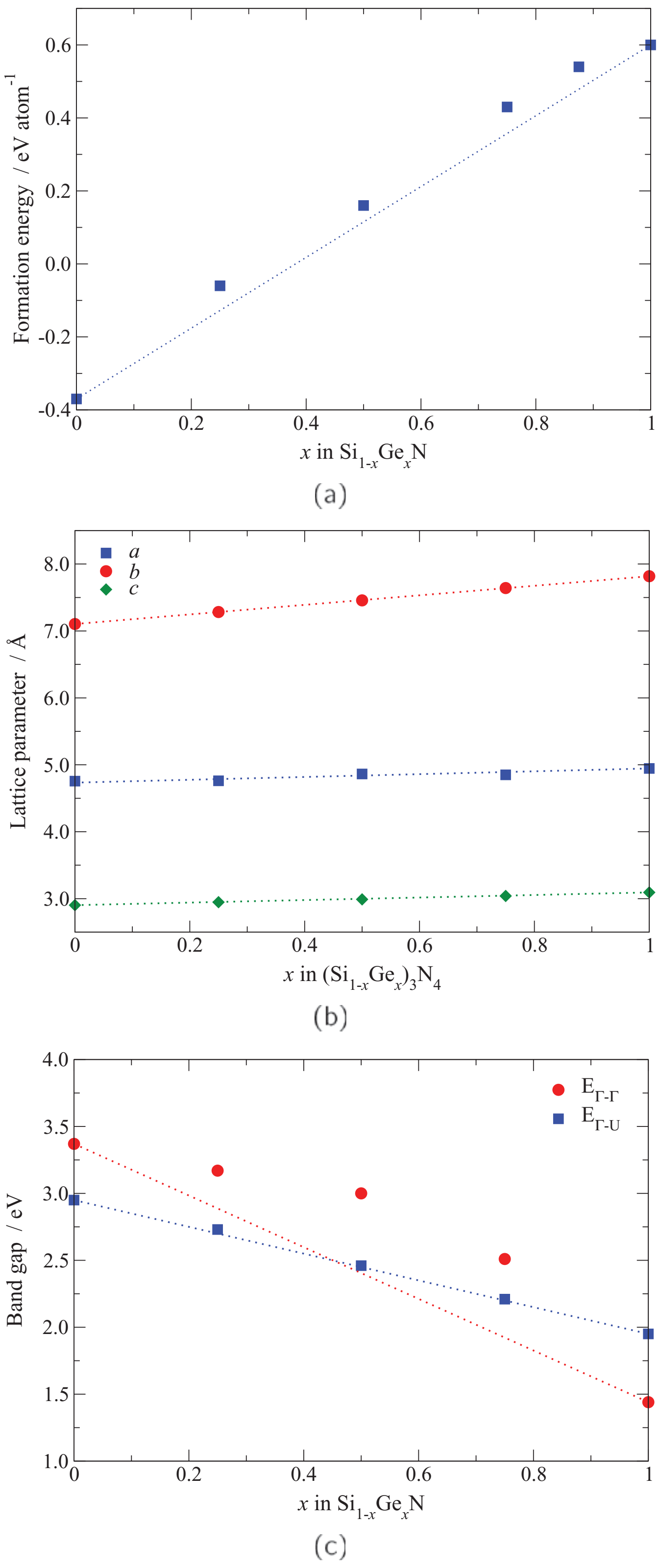


FIG. 3. (Color online) (a) Calculated formation energies from pure Si, Ge, and N_2, (b) lattice parameters, and (c) band gaps (both direct and indirect) of the ternary silicon germanium nitride $Si_{1-x}Ge_xN$ as functions of composition. The values for $Si_{0.5}Ge_{0.5}N$ are for the ordering shown in Fig. 1(c). Dotted lines are linear interpolations between the values for the binary compounds.

conduction band minimum and the conduction band energy at the Γ point is significantly greater than for SiN [Figs. 3(c) and 5(c)].

When all bonds between group-14 atoms are either Si-Si or Ge-Ge [Fig. 1(d)], the conduction band minimum at the U point is due predominantly to mixed Si $3p_z$ and Ge $4s$ states [Fig. 4(f)]. At a higher energy, mixed Ge $4p_z$ and Si $3s$ states appear. This situation gives an even greater energy difference between the conduction band minimum and the conduction band energy at the Γ point, due to the absence of mixed Ge $4p_z$ and Si $3s$ states at the bottom of the conduction band, in contrast to the ordering in which all bonds between group-14 atoms are Si-Ge bonds [Fig. 4(e)]. The conduction band at the Γ point is once again comprised of s and p mixed states involving orbitals on all group-14 atoms, at an energy very similar to that when there are no Si-Si or Ge-Ge bonds. Other possible orderings have also been investigated and these mostly change the energy of the conduction band at the U point; the energy of the conduction band at the Γ point is less dependent on the atomic ordering. The formation energies for these different orderings are not significantly different. For $Si_{0.5}Ge_{0.5}N$, the band gap value in Fig. 3(c) is for the ordering in which all bonds between group-14 atoms are Si-Ge [Fig. 1(c)].

As the germanium content increases further such that the Si:Ge ratio is <1, the energy difference between the conduction band minimum (at the U point) and the conduction band energy at the Γ point decreases [Fig. 3(c)]. In the $Si_{0.75}Ge_{0.25}N$ unit cell we used, there are Ge-Ge and Si-Ge bonds but no Si-Si bonds. The conduction band minimum is at the U point and consists predominantly of mixed p_z states on silicon and germanium in Si-Ge bonds [labeled Ge(A) in Fig. 4(g)] and $4s$ states on germanium in Ge-Ge bonds [labeled Ge(B) in Fig. 4(g)]. However, in this structure, there is significant overlap of $4s$ states on neighboring germanium atoms in Ge-Ge bonds, reducing the energy of the conduction band at the Γ point relative to the conduction band minimum. For $Si_{0.125}Ge_{0.875}N$, the conduction band minimum consists predominantly of Ge $4s$ states and is at the Γ point.

The trend in the indirect band gap ($E_{\Gamma\text{-}U}$) shows almost linear variation with composition [Fig. 3(c)]. In contrast, the direct band gap ($E_{\Gamma\text{-}\Gamma}$) shows significant positive deviation from linearity [also shown in Fig. 3(c)].

In general, the lattice parameters of an isostructural, isovalent semiconductor alloy are expected to vary linearly with composition, in accordance with Vegard's law.[22] The variation of the band gap (either direct or indirect) with composition of a solid solution can be described by

$$E_g(x) = xE_g(AC) + (1-x)E_g(BC) - bx(1-x) \qquad (4)$$

where b is the band gap bowing parameter, which quantifies the deviation from linearity, and $E_g(AC)$ and $E_g(BC)$ are the band gaps of the binary constituents AC and AB, respectively. These parameters will be different for direct and indirect band gaps. Following Bernard and Zunger,[23] the bowing parameter can be decomposed into three parts:

$$b = b_{\text{VD}} + b_{\text{CE}} + b_{\text{SR}}. \qquad (5)$$

The first component, the volume deformation component (b_{VD}), is the sum of the changes in the band gaps of the binary constituents due to compression or dilation when

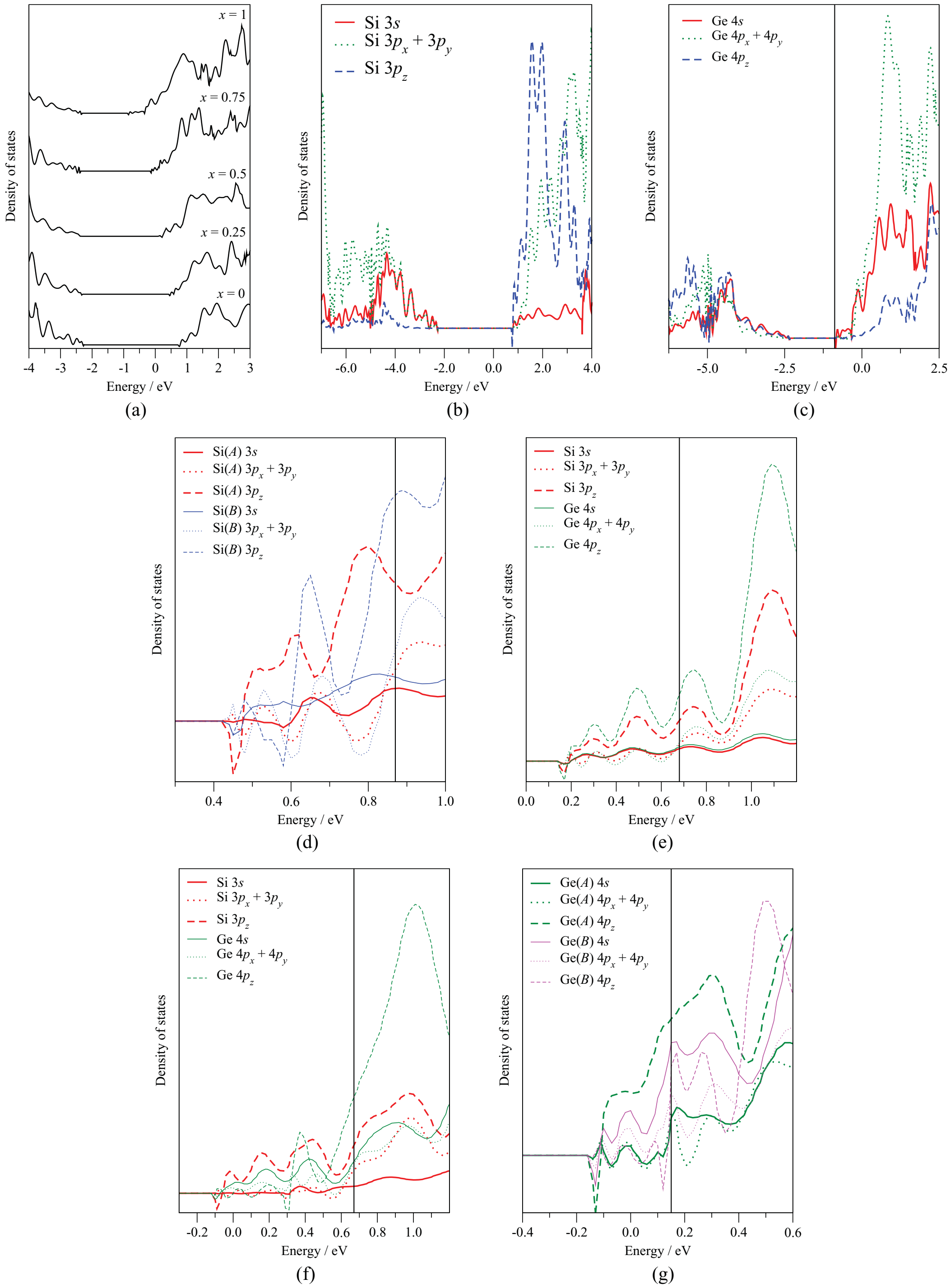
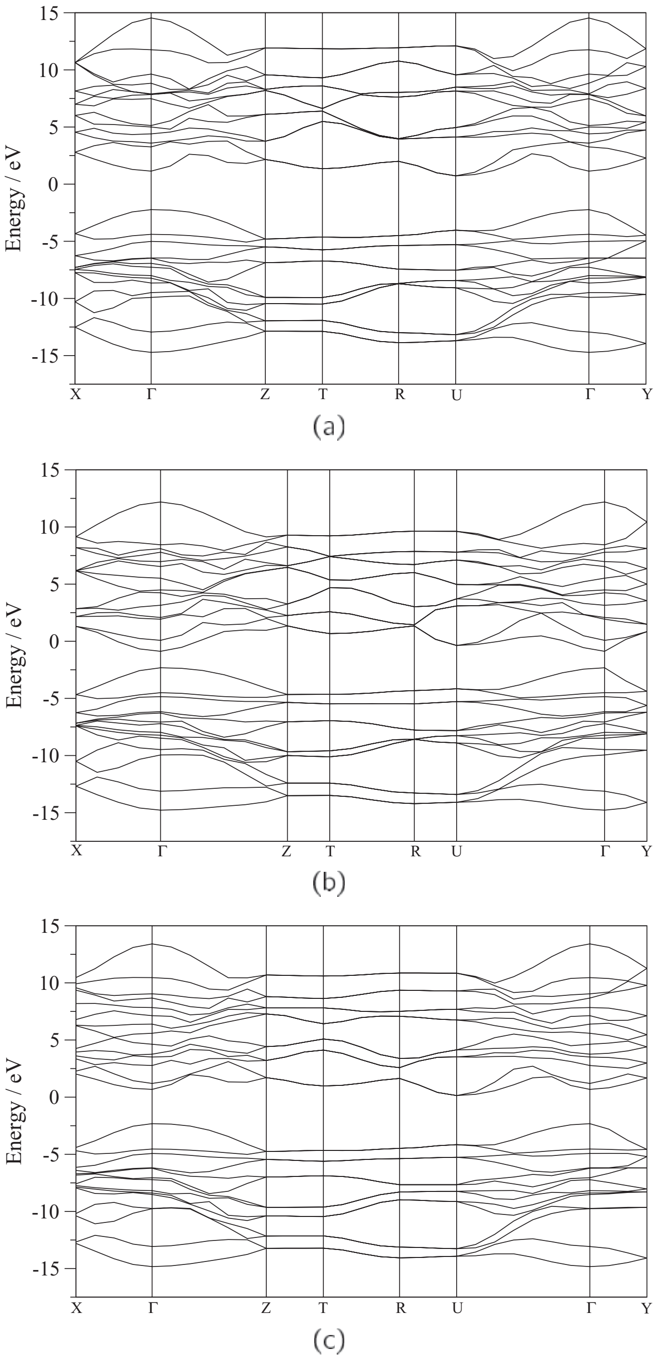


FIG. 4. (Color online) (a) Total DOS for $\mathrm{Si}_{1-x}\mathrm{Ge}_x\mathrm{N}$; (b) silicon partial DOS near the band gap for SiN; (c) germanium partial DOS near the band gap for GeN; (d) silicon partial DOS at the conduction band edge for $\mathrm{Si}_{0.75}\mathrm{Ge}_{0.25}\mathrm{N}$ (results are shown for two silicon atoms in different environments—atom *A* has three bonds to nitrogen and one to another silicon atom, atom *B* has three bonds to nitrogen and one to a germanium atom); (e) silicon and germanium partial DOSs at the conduction band edge for $\mathrm{Si}_{0.5}\mathrm{Ge}_{0.5}\mathrm{N}$ with the ordering of the group-14 elements as shown in Fig. 1(c) (there are no Si-Si or Ge-Ge bonds); (f) silicon and germanium partial DOSs at the conduction band edge for $\mathrm{Si}_{0.5}\mathrm{Ge}_{0.5}\mathrm{N}$ with the ordering of the group-14 elements as shown in Fig. 1(d) (there are no Si-Ge bonds); (g) germanium partial DOS at the conduction band edge for $\mathrm{Si}_{0.25}\mathrm{Ge}_{0.75}\mathrm{N}$ (results are shown for two germanium atoms in different environments—atom *A* has three bonds to nitrogen and one to a silicon atom, atom *B* has three bonds to nitrogen and one to another germanium atom). The solid black lines on the partial DOSs indicate the energy of the conduction band at the Γ point.

the volume is changed to that of the ternary compound (assuming linear variation of the lattice parameters with composition). The charge exchange component (b_{CE}) is obtained by combining the two deformed binary constitutents to form the ternary compound with no change in the bond lengths. The final component (b_{SR}) is the change in the



(a)

(b)

(c)

FIG. 5. Band structures of (a) SiN, (b) GeN, and (c) $Si_{0.5}Ge_{0.5}N$ with the ordering of the group-14 elements as shown in Fig. 1(c) (there are no Si-Si or Ge-Ge bonds).

band gap that occurs upon structural relaxation of the ternary compound.

To understand the difference in the deviation from linearity for the direct and indirect band gaps of $Si_{1-x}Ge_xN$, we have calculated the different components of the bowing parameter for $Si_{0.5}Ge_{0.5}N$. Volume compression of GeN causes a large increase in $E_{\Gamma\text{-}\Gamma}$ (by ~1.0 eV), consistent with a considerable enhancement of overlap between neighboring atomic orbitals, significantly increasing the energy of the antibonding (i.e., conduction band) states. In contrast, volume compression of GeN has relatively little effect on the indirect band gap ($E_{\Gamma\text{-}U}$, increase of ~0.2 eV). Volume expansion of SiN causes only a small decrease in both $E_{\Gamma\text{-}\Gamma}$ and $E_{\Gamma\text{-}U}$ (by ~0.2 eV). Therefore, the value of b_{VD} is negative for the direct band gap and neglible for the indirect band gap (Table I).

TABLE I. Values of the band gap bowing parameter and its components for the $Si_{0.5}Ge_{0.5}N$ structures shown in Figs. 1(c) and 1(d).

	No Si-Si or Ge-Ge bonds		No Si-Ge bonds	
	$E_{\Gamma\text{-}\Gamma}$	$E_{\Gamma\text{-}U}$	$E_{\Gamma\text{-}\Gamma}$	$E_{\Gamma\text{-}U}$
b_{VD} (eV)	−0.40	−0.01	−0.40	−0.01
b_{CE} (eV)	0.03	−0.01	0.02	0.22
b_{SR} (eV)	−0.23	0.01	−0.15	0.09
b (eV)	−0.60	−0.01	−0.53	0.30

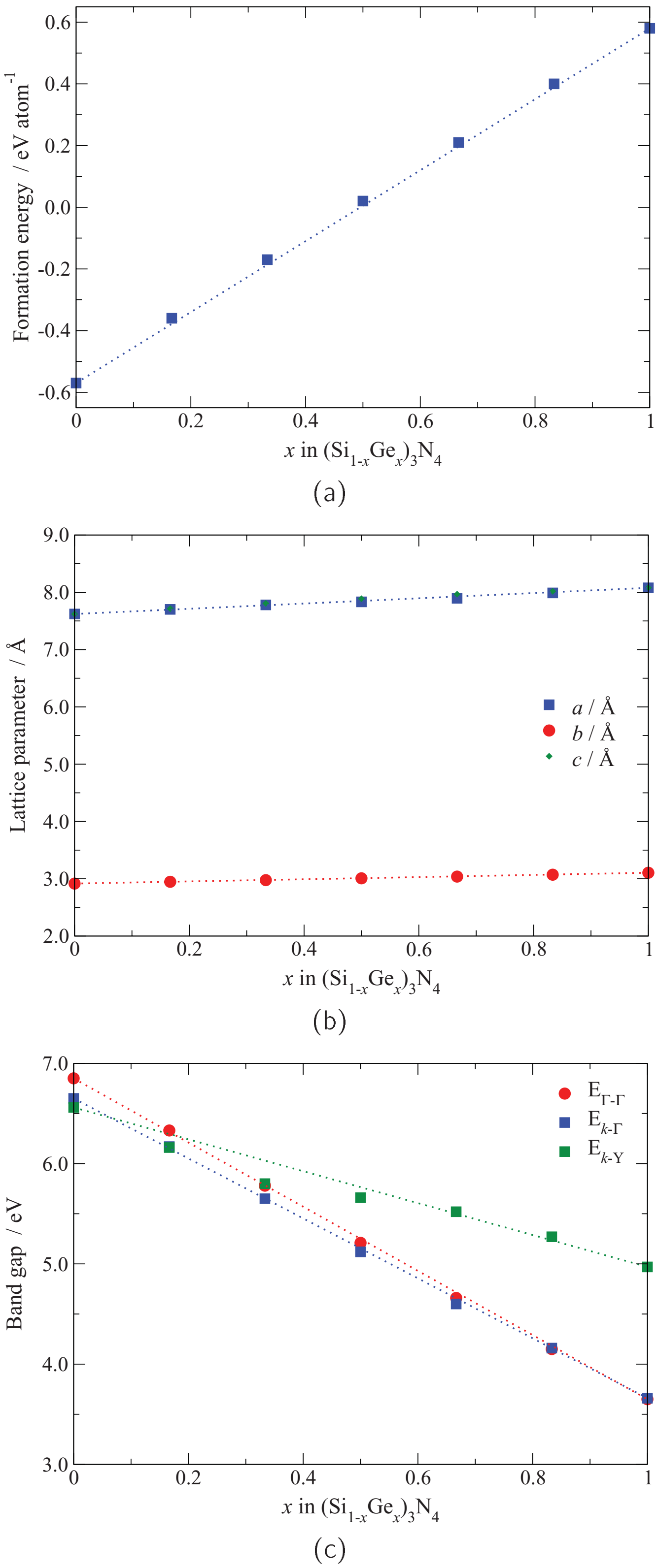
The value of b_{CE} is negligible for the direct band gaps (Table I), regardless of the ordering of the group-14 elements, consistent with the charge on the nitrogen in the ternary compound being intermediate between those for the compressed GeN and expanded SiN. For the indirect band gap, b_{CE} is affected by the ordering of the group-14 atoms. When all bonds between group-14 atoms are Si-Ge, the value of b_{CE} is again negligible. When all bonds between group-14 atoms are Si-Si or Ge-Ge bonds, the indirect band gap is ~0.2 eV smaller than the average of the band gaps of the compressed GeN and dilated SiN, giving a positive value for b_{CE}.

Structural relaxation of the ternary compound results in an increase in $E_{\Gamma\text{-}\Gamma}$ by ~0.2 eV (and hence a negative value of b_{SR}, Table I) due to a decrease in the valence band energy with very little change in the conduction band energy. In contrast to the Γ point, structural relaxation also causes a decrease in the conduction band energy at the U point, resulting in little overall change in the indirect band gap and hence a small value of b_{SR}. Ordering of the group-14 atoms makes a small difference to the value of b_{SR} (Table I).

Combining the three components of the bowing parameter gives a negative value for b for the direct band gap (Table I), due to negative values of b_{VD} and b_{SR}. b has a negligible value for the indirect band gap when all bonds between group-14 atoms are Si-Ge, since all three contributions are very small, and a positive value for the indirect band gap when all bonds between group-14 atoms are Si-Si or Ge-Ge, due predominantly to the positive value of b_{CE}. These values for the bowing parameters are consistent with the observations noted earlier regarding the magnitude of the difference between $E_{\Gamma-\Gamma}$ and $E_{\Gamma-U}$ for different atomic orderings. Ordering affects $E_{\Gamma\text{-}U}$ more than $E_{\Gamma-\Gamma}$ because the energy of the conduction band at the U point and hence the values of b_{CE} and b_{SR} for $E_{\Gamma\text{-}U}$ depend strongly on the atomic ordering.

B. β-$(Si_{1-x}Ge_x)_3N_4$

Similar trends are seen for β-$(Si_{1-x}Ge_x)_3N_4$. The energy of formation from the pure elements increases as the germanium content increases and is negative for silicon-rich compounds [Fig. 6(a)]. The energies of formation for the ternary compounds from the two binary compounds are very low (<0.02 eV/atom). As for $Si_{1-x}Ge_xN$, the lattice parameters increase linearly with composition [Fig. 6(b)].



(a)

(b)

(c)

FIG. 6. (Color online) (a) Calculated formation energies from pure Si, Ge, and N_2, (b) lattice parameters, and (c) band gaps (both direct and indirect) of the ternary silicon germanium nitride β-$(Si_{1-x}Ge_x)_3N_4$ as functions of composition; $k = (0,0,\frac{1}{4})$. Dotted lines are linear interpolations between the values for the binary compounds.

The band gap of ternary β-$(Si_{1-x}Ge_x)_3N_4$ decreases as the germanium content increases [Fig. 6(c)]. As for $Si_{1-x}Ge_xN$, the silicon-rich compounds have an indirect band gap, while the germanium-rich compounds have a direct band gap at the Γ point.

C. γ-$(Si_{1-x}Ge_x)_3N_4$

In the spinel $(Si_{1-x}Ge_x)_3N_4$, when $x \leqslant \frac{1}{3}$ germanium preferentially occupies the tetrahedral sites. Only once all the tetrahedral sites are occupied does germanium start filling the octahedral sites.[24,25] Boyko *et al.*[7] studied the band gap of this ternary spinel phase nitride experimentally and found that the band gap slightly increases with increasing germanium content up to $x = \frac{1}{3}$ when the germanium occupies the tetrahedral sites. For $x \geqslant \frac{1}{3}$, when germanium occupies octahedral sites, the band gap decreases with increasing germanium content. This effect was confirmed by a computational study of the material, using density functional theory with the generalized gradient approximation.[7] The results presented here are for structures in which the group-14 elements occupy only tetrahedral sites and the band gap always decreases with increasing germanium content.

Due to this difference in the trends for different structures, we have investigated the variation in band gap of γ-$(Si_{1-x}Ge_x)_3N_4$ with composition. As for β-Si_3N_4, we used a supercell containing 14 atoms and considered x values of 0, 0.17, 0.33, 0.5, 0.67, 0.83, and 1. Our results are broadly consistent with those of Boyko *et al.* For small values of x with germanium occupying tetrahedral sites, we found a slight decrease in the band gap with germanium content (Fig. 7). Neither the conduction nor the valence band energies

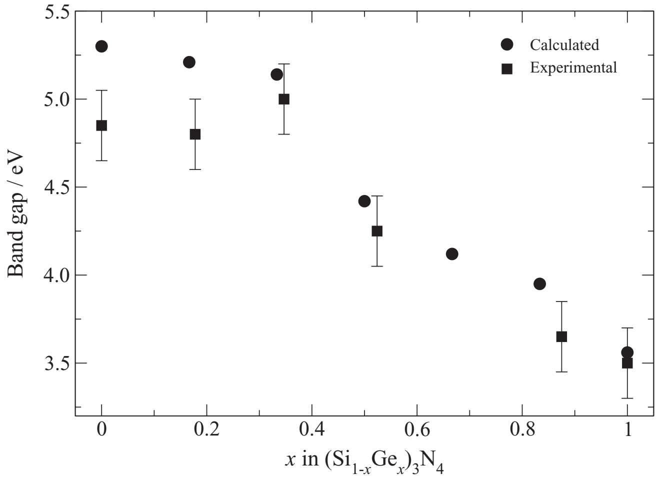


FIG. 7. Band gap of ternary silicon germanium nitride γ-$(Si_{1-x}Ge_x)_3N_4$ as a function of composition. Calculated values are from this study, using the B3LYP hybrid method, and experimental values are taken from Boyko *et al.* (Ref. 7). Note that the band gap values calculated by Boyko *et al.* were significantly lower than the experimental values due to the known underestimation of band gaps by the generalized gradient approximation. The B3LYP method, in contrast, gives band gap values close to the experimental values, although slightly overestimated for silicon-rich compounds.

change significantly. This decrease in the band gap becomes much greater for $x > \frac{1}{3}$ when germanium occupies octahedral sites, with the energy of the conduction band decreasing significantly with increasing germanium content. For $x = 0.17$ with germanium in an octahedral rather than tetrahedral site, there is a large decrease in the band gap; there is also a significantly larger increase in the unit cell volume in this case, suggesting that germanium occupation of octahedral sites more significantly affects the degree of overlap of neighboring atomic orbitals and hence the conduction band energy compared with germanium occupation of tetrahedral sites.

IV. CONCLUSIONS

Ternary silicon germanium nitrides, with compositions $Si_{1-x}Ge_xN$ and $(Si_{1-x}Ge_x)_3N_4$, have a band gap that depends on composition, thus allowing the band gap to be tuned by adjusting the Si:Ge ratio. The band gap of silicon germanium nitrides increases with nitrogen content, an effect that has been observed experimentally for amorphous silicon nitride;[9–11] therefore, for visible light applications such as LEDs and photocatalysts, $Si_{1-x}Ge_xN$ may be more suitable than $(Si_{1-x}Ge_x)_3N_4$.

The tunability of band gaps of ternary silicon germanium nitride has been reported in previous work.[7] However, these results were specific for the spinel structure with a 3:4 stoichiometry. Our results suggest that this is a more general effect expected also for different stoichiometries and structures and for a range of group-14 nitrides and phosphides. There is already limited experimental evidence that this is so; for example, variation in the band gap of $ZnSi_{1-x}Ge_xN_2$ with composition has been demonstrated.[26] It is likely that, by appropriate choice of composition and structure, a very wide range of band gaps should be accessible in such materials.

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