

Structural and electronic properties of wide band gap silicon carbon nitride materials—a first-principles study

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Abstract

First-principles calculations have been carried to study the structural and electronic properties of the series of α -silicon carbon nitride crystals which have been successfully synthesized and demonstrate interesting mechanical, electronic, optical properties. The bulk modulus values of the SiCN structures have been observed to progressively increase up as more C atoms substituted for Si atoms in the crystal due to strong covalent C–N bonds compared to Si–N bonds. The band structure calculations indicate that the electronic properties of the α -SiCN crystals are closer to α -Si₃N₄ than to α -C₃N₄. In addition, to improve the underestimation of local density approximation, we implement the generalized density functional scheme to correct the band gap values for SiCN crystals. The size of the band gap for α -Si₂CN₄ after gap opening shows a value of 3.82 eV which demonstrates a good approximation with that of the Si-rich SiCN crystals measured by the piezoreflectance spectroscopy, ranging from 3.81 to 4.66 eV.

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1. Introduction

Intense theoretical and experimental interests have been focused on the possibility of new low-compressible materials with bulk moduli and hardness exceeding that of diamond. Covalently bonded β -C₃N₄ crystals have been proposed as superhard materials based on the theoretical prediction by Cohen [1]. The β -C₃N₄ that is isomorphic to β -Si₃N₄ might have a bulk modulus comparable to that of diamond. Motivated by the theoretical results and a great deal of potential applications, a considerable effort has been put forth to synthesize and characterize such materials. However, growth of crystalline C₃N₄ solid with a large enough size has not been achieved so far. Despite the difficulties in synthesizing crystal forms of C₃N₄, exceptional hardness and yield strength have been reported for some CN_x films even with a very limited degree of crystallinity [2,3]. More recently, a new class of ternary silicon carbon

nitride (SiCN) materials with large (several tens of microns) and well-facet crystals have been grown successfully by microwave plasma-enhanced chemical vapor deposition (MW-CVD) by Chen [4,5] and Badzian [6]. These newly discovered SiCN crystals have been found to demonstrate a great potential for application in semiconductor technology as well as a structural material. They show excellent mechanical properties with hardness and bulk modulus of approximately 30 and 322 GPa, respectively. The optical investigation of polycrystalline SiC_xN_y films shows a direct band gap of approximately 3.8 eV and a strong optical emission of approximately 2.8 eV [5]. The ternary SiCN compound constitutes an important wide band gap material with a gap energy within the blue-UV spectral region. It is believed that the chemical bonding and atomic local order can be quite complex in the ternary SiCN system. The atomic structure of SiCN crystals can be described as the pseudo α -Si₃N₄ phase, which shows some deviation from the pure α -Si₃N₄ pattern in the X-ray diffraction experiment. The similarity of atomic structures between SiCN and α -Si₃N₄ is also evident

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from the experiment by the X-ray-absorption spectroscopy [7]. Although many experiments have been carried out to study the properties of SiCN compounds, theoretical work that may provide useful knowledge and interpretation for experimental data is still very limited at this stage. β -Si₂CN₄ and β -SiC₂N₄ crystals have been studied by Wang [8] and Lowther [9]. They show that as more C atoms are substituted for Si in β -Si₃N₄ the bulk modulus is observed to increase up progressively. Musin et al. have carried the calculations to study the properties of cubic SiCN crystals [10]. In this article, a systematical and comparative study has been performed by the first-principles calculations to investigate the structural and electronic properties of α -Si_{3-n}C_nN₄ ($n = 0, 1, 2, 3$) crystals.

2. Computational methods

The calculations were performed using the *ab initio* plane-wave-pseudopotential approach within the framework of density functional theory (DFT) implemented in the CASTEP codes [11,12]. The exchange-correction functional is approximated with the local density approximation (LDA) [13]. The ion–electron interaction is modeled by the non-local, norm conserving pseudopotential [14]. The summation over the Brillouin zone was carried out with a k -point sampling using a Monkhorst and Pack grid [15]. A kinetic-energy cutoff of 280 eV and 25 special k points were used to ensure the convergence in the calculations. In searching the lowest-energy geometries for these crystals, each structure was optimized for a specified cell geometry with relaxation of both lattice parameters and atomic positions.

3. Structural properties

3.1. Optimized structures and bonding

The systems investigated here are based on the starting structure of α -Si₃N₄ which can be represented by a hexagonal unit cell. There are 12 Si and 16 N atoms per unit cell and the space group of α -Si₃N₄ is P31c. The structure of α -C₃N₄ is similar to α -Si₃N₄ with C atoms substituted for all Si atoms. The unit cell of α phase is twice as large as the β phase, and they differ in the stacking sequence of the layer subunits along the z axis. The α structure can be described as stacking planes ABCDABCD..., whereas for the β phase it is the type of ABAB... For the ternary SiCN crystals, composition and bonding analysis experiments strongly suggest the structure of SiCN to be a solid solution of Si₃N₄ and C₃N₄. Carbon atoms are partially substituted only for Si in α -Si₃N₄. Many possible structures exist with low symmetry. Here we consider two configurations that possess relatively higher symmetry, one for α -Si₂CN₄ and the other for α -SiC₂N₄, which represent Si-

rich and C-rich SiCN crystal structures, respectively. The perfect crystalline α -Si_{3-n}C_nN₄ ($n = 0, 1, 2, 3$) structures serve as pure reference systems for studying the properties of real SiCN materials that are inherently imperfect under real experimental conditions.

Our model for α -Si₂CN₄ is the one with four C atoms substituted for Si atoms on four different stacking layers as indicated in Fig. 1. In the model of α -SiC₂N₄, eight Si sites on four different stacking layers in the α -Si₃N₄ structure are then replaced by C atoms. These two structures yield an overall symmetry of Cc symmetry as opposed to P31c as for α -Si₃N₄. The Cc symmetry structure is identical to P31c when the magnitude of its primitive unit cell vectors a and b are the same and the angle between a and b is 120°. Full geometric optimization was performed for allowing the relaxation of atomic positions and lattice parameters in each case. The detailed structural information of these models is summarized in Table 1. It is noted that the primitive unit cell for our α -Si₂CN₄ and α -SiC₂N₄ structures is hexagonal before relaxation with $a=b$ and $\gamma=120^\circ$. The final relaxed structures for α -Si₂CN₄ and α -SiC₂N₄ exhibit a ‘quasi-hexagonal’ configuration with the angle between the unit cell vectors a and b slightly deviating from the ideal value of 120°, which is 119.13° for α -Si₂CN₄ and 120.93° for α -SiC₂N₄, respectively. As one may expect from the fact that C atoms are smaller than Si atoms, it is found that as more C atoms are substituted for Si both lattice constants a and c are reduced and c/a shows a close ratio with a nearly isotropic contraction as shown in Table 1. In order to study the bonding configurations of these structures in more detail, the calculated effective charge Q^* and the overlap population based on the Mulliken scheme [16] for each atom are also listed in Table 1. A larger overlap population corresponds to a shorter bond length between the pair of atoms. It can be seen that α -C₃N₄ has the highest covalent character due to its least charge transfer from that cation C to the anion N, leading to the largest bond order and shortest bond length among all the crystals we study here. All the C–N bonds are found to be close in length ranging from 1.43 to 1.48 Å. The α -Si₃N₄ structure, on the other hand, demonstrates the least bond order with largest charge transfer and longest bond length between Si and N atoms. The Si–N bonds are found to be close in length ranging from 1.71 to 1.74 Å. For the α -SiCN structures, the difference in the charge transfer from cation C or Si to anion N leads to different bonding characteristics compared to pure carbon nitride and silicon nitride systems. In the α -Si₂CN₄ structure, N atoms show less anion-like properties with less effective charge transfer and a shorter Si–N bond length compared to those in α -Si₃N₄, ranging from 1.66 to 1.74 Å. The enhanced covalent bonding characters are also reflected in other structural parameters such as bulk modulus values as

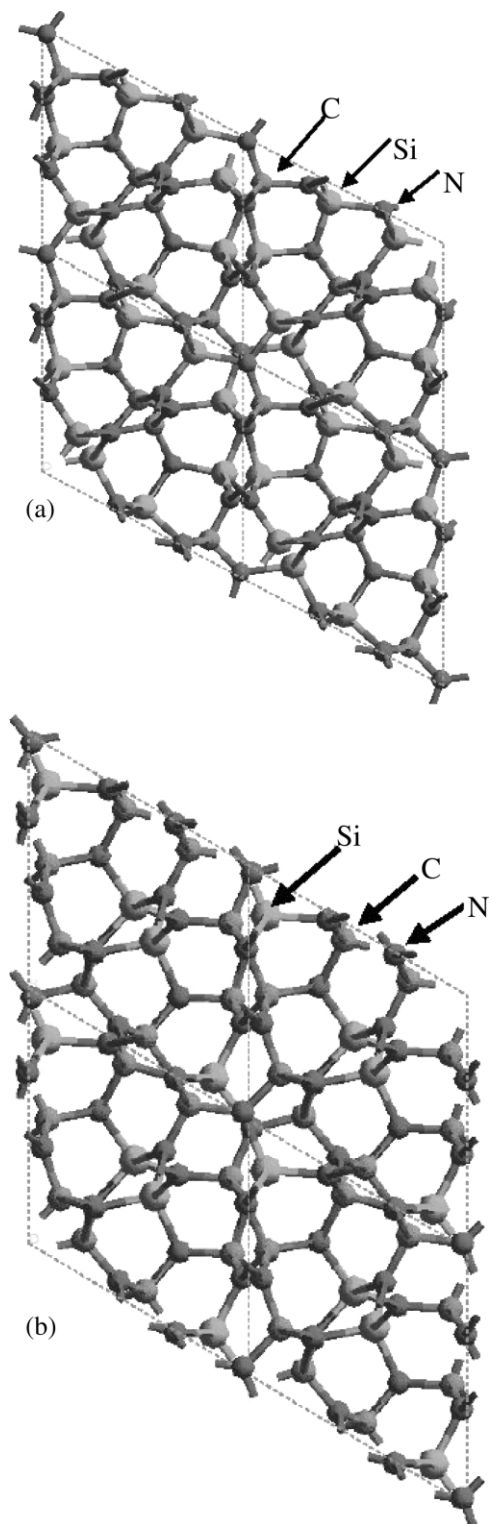


Fig. 1. (a) The model of α phase Si_2CN_4 . (b) For $\alpha\text{-SiC}_2\text{N}_4$, the positions of Si and C sites are interchanged. For $\alpha\text{-Si}_3\text{N}_4$ and $\alpha\text{-C}_3\text{N}_4$, all these sites of Si and C atoms are replaced by Si and C atoms, respectively.

discussed below. The average bond length of C–N bonds in the $\alpha\text{-Si}_2\text{CN}_2$ is longer than that in the $\alpha\text{-C}_3\text{N}_4$ structure, indicating its less covalent characters of $\alpha\text{-Si}_2\text{CN}_2$ compared to $\alpha\text{-C}_3\text{N}_4$. The existence of three N sites with different bonding properties have been found, corresponding to the N atom with zero, one and two C neighboring atoms. The N atoms become less charged with the increased number of C neighboring atoms. For the $\alpha\text{-SiC}_2\text{N}_4$ structure, it shows less covalent character compared to the $\alpha\text{-C}_3\text{N}_4$ structure. The N atoms in the $\alpha\text{-SiC}_2\text{N}_4$ structure show more anion-like properties with larger effective charge transfer and a longer C–N bond length than those of the $\alpha\text{-C}_3\text{N}_4$ structure. It shows more covalent characters compared to the $\alpha\text{-Si}_3\text{N}_4$ and $\alpha\text{-Si}_2\text{CN}_4$ counterparts. Similar to the $\alpha\text{-Si}_2\text{CN}_4$ crystal, the C–N bond length in the $\alpha\text{-SiC}_2\text{N}_4$ structure shows a wider range of variation from 1.42 to 1.60 Å compared to that of Si–N bonding ranging from 1.65 to 1.72 Å. In Fig. 2, the calculated valence charge densities for $\alpha\text{-Si}_2\text{CN}_4$ and $\alpha\text{-SiC}_2\text{N}_4$ crystals on the (0 0 1) plane are presented. It is found that very little charge is located at the Si atom indicating that the Si–N bond is insignificant compared to the strong covalent C–N bond as expected. In addition to the higher charge density in the covalent C–N bond, charge arising from the lone pair of N 2p orbitals is found to distribute along the direction perpendicular to the C–N bond. The non-spherical charge distribution at the N atom for the Si–N bond suggesting a mixture of covalent and ionic behavior. Difference in valency between atoms in different columns of the periodic table and difference in core states between atoms in different rows result in more ionic character of the Si–N bond. From the calculated ionic formula of the four crystals in Table 1, it is found that the covalent feature of the C–N bond as well as the ionic behavior of the Si–N bond are more pronounced as more C atoms are substituted for Si atoms in the $\alpha\text{-SiCN}$ crystals. The population of strong covalent C–N bonds in the $\alpha\text{-SiCN}$ crystal therefore plays the key role to determine the hardness and other mechanical properties of materials.

The Birch–Murnaghan equation of state is used to fit the total energy vs. volume data (E – V) in determining bulk modulus B_0 , and its pressure derivative B' of the bulk modulus ($B' = dB/dP$). For the four crystals, the B values vary from 242 to 407 GPa. As more C atoms are substituted for Si leading to a reduction of both bond length and lattice constant, the bulk modulus increases and reaches a maximum value in the $\alpha\text{-C}_3\text{N}_4$ structure. Our calculated value for $\alpha\text{-Si}_3\text{N}_4$ of 242 GPa is in accordance with the experimental measured value of 248 GPa [17]. These four crystals can generally be considered as hard materials with low compressibility related to strong covalent bonding character. It is worth mentioning that in the real experimental situation the successful synthesis of C-rich $\alpha\text{-SiCN}$ crystal is difficult to achieve due to various forms of C bonding to N

Table 1

Comparison of crystal structural information of α -Si₃N₄, α -Si₂CN₄, α -SiC₂N₄ and α -C₃N₄

	α -Si ₃ N ₄	α -Si ₂ CN ₄	α -SiC ₂ N ₄	α -C ₃ N ₄
<i>Unit cell (Å)</i>				
<i>a</i>	7.716	7.281	6.954	6.487
<i>c</i>	5.581	5.297	5.006	4.719
γ	120°	119.13°	120.93°	120°
<i>Other LDA results (Å)</i>				
<i>a</i>	7.766 ^a			6.467 ^b
<i>c</i>	5.615			4.710
Space group	P31c(159)	Cc(9)	Cc(9)	P31c(159)
<i>Bond distance (Å)</i>				
Si–N (average)	1.722	1.703	1.680	
C–N (average)		1.510	1.489	1.457
<i>Effective charge Q^* in electron</i>				
Si	2.28	2.25	2.13	
C		3.74	3.77	3.75
N	6.29	5.94	5.58	5.19
<i>Bulk modulus</i>				
<i>B</i> (GPa)	242	277	327	407
<i>B'</i>	3.86	3.84	3.95	3.91
Experiment for <i>B</i> (GPa)	248 ^c			
Other LDA for <i>B</i> (GPa)	257 ^d			425 ^b

^a Ref. [18].^b Ref. [31].^c Ref. [17].^d Ref. [32].

(C–N, C=N, C≡N), the same reason accounting for the lack of success with the C₃N₄ crystals. For the Si-rich α -SiCN crystal, due to the majority of the network formed by Si–N, C atoms substituted for Si atoms tend to keep the sp³ bonding configuration when the C content is low. When the carbon content is increased over a certain value, the formations of C–N, C=N and C≡N appear, leading to the difficulty to form the α -SiCN crystals. This result accounts for the fact that the available α -SiCN crystals so far are found to be Si-rich, having the C content below a critical limit [6].

4. Electronic properties

The calculated LDA electronic band structures of α -Si₃N₄, α -Si₂CN₄, α -SiC₂N₄ and α -C₃N₄ crystals are shown in Fig. 3. Due to the different symmetry between α -Si₃N₄, α -C₃N₄ (P31c) and α -Si₂CN₄, α -SiC₂N₄ (Cc), we have chosen larger unit cells for α -Si₃N₄ and α -C₃N₄ crystals with a Cc symmetry to ensure that the four band structures we study are along the same *k* directions for the convenience of comparison. As mentioned above, the Cc symmetry structure is identical to P31c when the magnitude of its primitive unit cell vector *a* and *b* is the same and the angle between *a* and *b* is 120°. This is the case for α -Si₃N₄ and α -C₃N₄ crystals. It is well known that the LDA generally underestimates the value of band gap; therefore, after discussing the LDA results, we will describe approxi-

mate corrections using a generalized density functional theory (GDFT) to obtain corrected estimate of the band gap values for these crystals. In Fig. 3, it appears that four band structures are very similar in their valence band (VB) regions. The top of the VB is located at the point $\bar{A}$ for the four crystals. The very small energy variation along the direction Γ to *B* results in a nearly flat band along these directions. The major differences for these four crystals are the locations of the states near the conduction band (CB) minimum as shown in Fig. 3. The bottoms of the CB for α -Si₃N₄, α -Si₂CN₄, α -SiC₂N₄ are located at the Γ point while the CB minimum for the α -C₃N₄ crystal is located at a point along the *B*–*D* direction, which suggests the electronic properties of α -SiCN crystals be closer to that of α -Si₃N₄ than to that of α -C₃N₄. The dissimilarity of the CB structure of the α -C₃N₄ crystal from that of α -Si₃N₄ crystal is also found in the band structure calculations of β -C₃N₄ and β -Si₃N₄ carried by Liu and Cohen [1]. The sizes of the LDA band gap for the α -Si₃N₄, α -Si₂CN₄, α -SiC₂N₄ and α -C₃N₄ crystals are 4.61, 3.50, 3.34 and 3.69 eV, respectively. All these gaps are found to be indirect. The direct band gaps at the Γ point for these four crystals are 4.62, 3.51, 3.35 and 3.97 eV, respectively. The other self-consistent calculations carried by Xu and Ching [18] also show the similar band gap value of 4.67 eV for α -Si₃N₄. These calculated values are below the experimental results available with no surprise due to the underestimation for the band gap

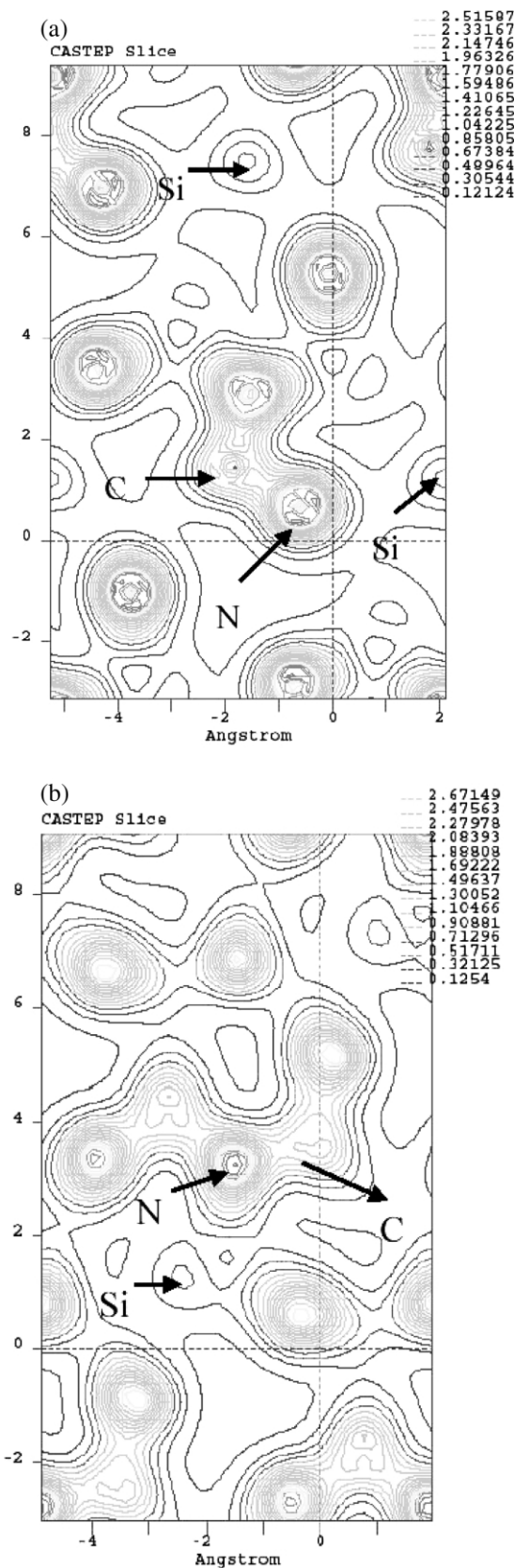


Fig. 2. Charge density of α -Si₂CN₄ (a) and α -SiC₂N₄ (b) plotted perpendicular to the *c* axis.

by LDA. For example, the experimental band gap energy for Si₃N₄ has been reported to be near 5.01 eV [19]. In addition, the piezorefectance (PzR) spectroscopy has also been used to study the band gap energies of SiCN materials with various Si:C:N ratio [5]. It shows that the energy gap values of 3.81 and 4.66 eV are obtained for Si₃₅C₂₆N₃₉ and Si₃₈C₅N₅₇ films, respectively, corresponding to Si-rich SiCN structures. The energy gap value progressively decreases with increasing C content in the film.

Due to the difficulty of LDA/DFT in predicting band gaps quantitatively, we have used a GDFT to obtain an improved estimate of the band gaps for the above crystals. This theory was first proposed by Fritsche [20–24] in the framework of the all-electron calculation scheme and was later simplified by Remediakis and Kaxiras [25] in the framework of planewave pseudopotential methods used in solid with smooth valence charge density and is called GDFT/LDA. It has been tested to be capable of reducing the ‘Kohn-Sham band-gap’ errors, which generally are 50–100% in DFT/LDA, to 10–20% in GDFT/LDA. A slightly modified version, core-corrected GDFT/LDA [26,27], was further developed by one of the authors to make GDFT/LDA applicable to systems with shallow core electrons in its pseudopotential scheme as well as to systems with less smooth valence density. In those cases, a cutoff radius is introduced for each chemical element species to remove the highly localized core density using the GDFT/LDA formalism. This is the method used to improve calculated band gap values in the present work. No unexpectedly, the sizes of the band gap for these four crystals are all increased after the GDFT scheme is implemented and the indirect band gap values after gap opening are 5.05, 3.81, 3.58 and 3.97 eV for α -Si₃N₄, α -Si₂CN₄, α -SiC₂N₄ and α -C₃N₄ crystals, respectively. Table 2 shows the calculated results with and without band gap opening. The calculated value 5.05 eV for α -Si₃N₄ is in good accordance with the experimental measurement of 5.01 eV. The calculated band gap for α -Si₂CN₄ is 3.81 eV which shows a good approximation with that of the Si-rich SiCN crystal deposited by MW-CVD [5,6]. The band gap values progressively decrease with the increasing C content for α -Si₃N₄, α -Si₂CN₄ and α -SiC₂N₄ crystals. Such a reduction of the band gap with an increasing C content does not further apply to the α -C₃N₄ crystal that exhibits a band gap value of 3.97 eV. This may be attributed to the dissimilarity of the band structures between α -C₃N₄ and the other three crystals. From the above results, it indicates indirectly that the electronic properties of the α -SiCN crystals are closer to those of α -Si₃N₄ than to α -C₃N₄.

Fig. 4 shows the density of states (DOS) and the projected partial density of states (PDOS) of these four structures. The total valence bandwidth is found to increase with increasing C content. The VB DOS con-

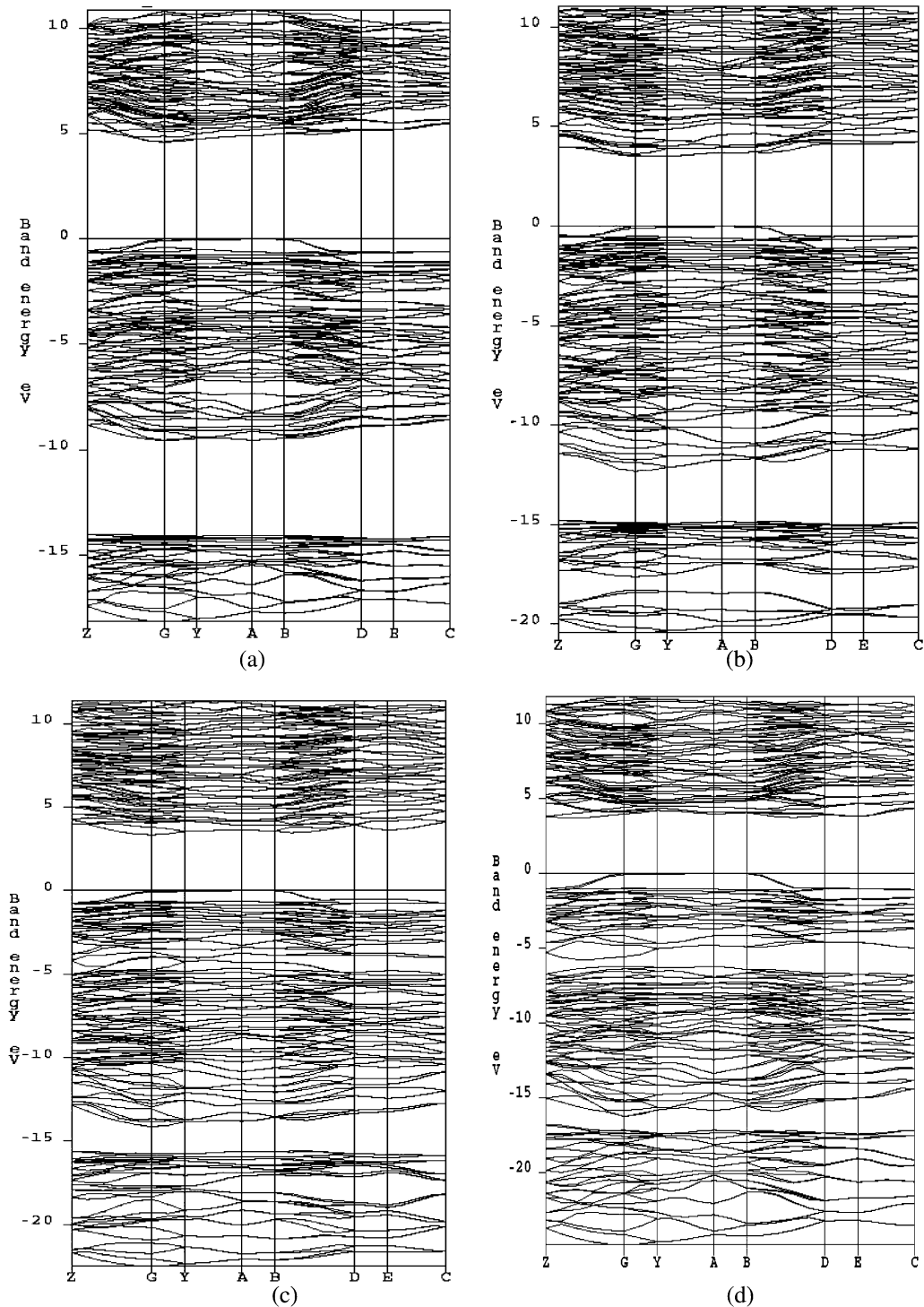


Fig. 3. Calculated band structures for α - Si_3N_4 (a), α - Si_2CN_4 (b), α - SiC_2N_4 (c) and α - C_3N_4 (d), respectively.

sists of the bonding and nonbonding bands that are merged at the upper part of VB approximately -3 to -5 eV, depending on different compositions. The non-bonding bands arise from the lone pairs of N 2p orbitals that are oriented perpendicular to the bonding plane. It has been suggested [28,29] that $\text{pd}\pi$ interaction between

Si and N may stabilize the formation of the 120° Si–N–Si bond angle compared to the smaller bond angles found in other trivalent group-V systems such as As. However, the importance of $\text{pd}\pi$ interaction has been an argued question of long standing. Our present calculation indicates that Si d orbitals do participate in

Table 2

The experimental and theoretical (LDA and GDFT) band gap values for α -Si₃N₄, α -Si₂CN₄, α -SiC₂N₄ and α -C₃N₄ crystals

	α -Si ₃ N ₄	α -Si ₂ CN ₄	α -SiC ₂ N ₄	α -C ₃ N ₄
LDA				
Direct E_g (eV)	4.62	3.51	3.35	3.97
Indirect E_g (eV)	4.61	3.50	3.34	3.69
GDFT				
Direct E_g (eV)	5.07	3.82	3.60	4.24
Indirect E_g (eV)	5.05	3.81	3.58	3.97
Other LDA				
Direct E_g (eV)	4.67 ^a			4.0
Indirect E_g (eV)	4.63 ^a			3.2
Experiment (eV)	~5.0 ^b	3.81–4.66 ^c		

^a Ref. [18].

^b Ref. [19].

^c Ref. [5].

the bonding at the VB states. This does not necessarily mean that Si 3d orbital is crucial in the formation of Si–N bonds since, in the first-principles calculations, the orbital states are generally mixed, and it will be difficult

to quantify the importance of the Si 3d orbital itself. The non-bonding states at the upper part of VB in the SiCN crystals are also found to be responsible for the interesting optical properties that will be discussed elsewhere [30]. For the lower part of VB, stronger mixing exists between the low-lying C and N states compared to Si and N states, indicating the stronger covalent bonding characters of C–N bonding than Si–N bonding. In addition, the split-off of lowest lying part of the VB can be seen in the Si₃N₄ structure while the split-off disappears in the C₃N₄ structure. For the SiCN crystals, the size of the split-off at the lowest lying portion of VB decreases with increasing C content.

5. Conclusion

We have made a comparative study of the structural and electronic properties of a new class of hard materials of α -Si₃N₄, α -Si₂CN₄, α -SiC₂N₄ and α -C₃N₄ by first-principles calculations. From our calculations, it has been found that the covalent features of the C–N bond as well as the ionic behaviors of the Si–N bond are

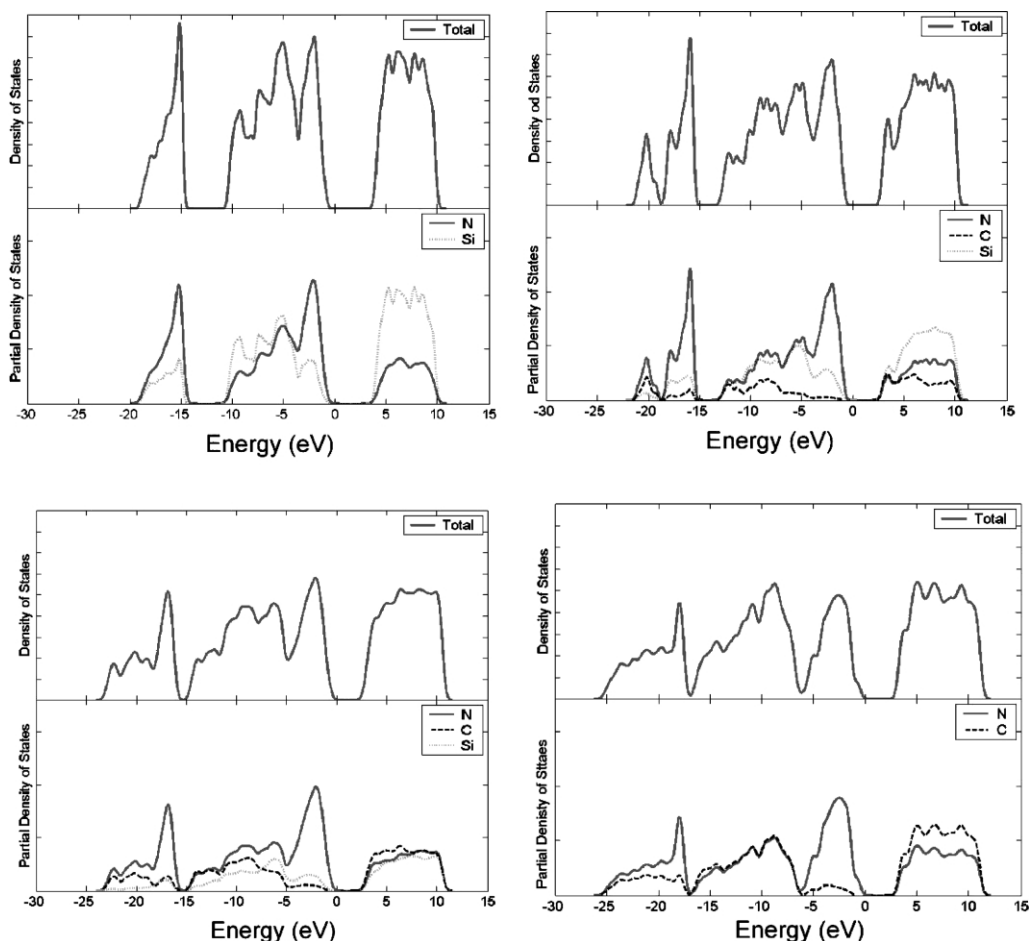


Fig. 4. DOS and PDOS of α -Si₃N₄ (a), α -Si₂CN₄ (b), α -SiC₂N₄ (c) and α -C₃N₄ (d), respectively.

more pronounced as more C atoms are substituted for Si atoms in the α -SiCN crystals. The population of strong covalent C–N bonds in the α -SiCN crystal therefore plays the key role to determine the hardness and other mechanical properties of materials. From the band structure calculations, it is shown that the sizes of the indirect band gap for α -Si₃N₄, α -Si₂CN₄, α -SiC₂N₄ and α -C₃N₄ are 4.62, 3.50, 3.34 and 3.69 eV, respectively, within the LDA, and 5.05, 3.81, 3.58 and 3.97 eV within the GDFT scheme. The direct band gaps at the Γ point for these four crystals after opening by the GDFT scheme are 5.07, 3.82, 3.60 and 4.24 eV, respectively. This result shows a good approximation with the experimental band gap energy of 5.01 eV for α -Si₃N₄ and of 3.81–4.66 eV for Si-rich SiCN crystals by the PzR spectroscopy. The electronic properties of the α -SiCN crystals are found to be closer to α -Si₃N₄ than to α -C₃N₄ from their band structures.

Acknowledgments

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