PHYSICAL REVIEW B VOLUME 55, NUMBER 16 15 APRIL 1997-II

Proposed synthesis path for heterodiamond BC_2N

Y. Tateyama, T. Ogitsu, K. Kusakabe, and S. Tsuneyuki
Institute for Solid State Physics, University of Tokyo, Roppongi, Minato-ku, Tokyo 106, Japan

S. Itoh
Advanced Research Laboratory, Toshiba Corporation, 1 Komukai Toshiba-cho, Saiwai-ku, Kawsaki 210, Japan

(Received 3 December 1996)

A probable heterodiamond BC_2N structure that can be obtained from compression of graphitic BC_2N at low temperature is proposed using first-principles calculations. The structure consists of a rhombohedral atomic arrangement and has a large bulk modulus comparable to that of diamond as well as a wide band gap. We also found that the structure can be synthesized from a superlattice with alternate stacking of graphite and hexagonal BN monolayers. Transformations from such layered superlattices open a possibility for control of the properties in synthesized materials. [S0163-1829(97)52216-8]

Heterodiamond BCN compounds have recently attracted significant interest due to their possible application to mechanical and electronic devices.[1–4] Since such compounds have a diamondlike structure in which some of the carbon atoms are substituted with boron and nitrogen atoms, they are expected to have useful properties similar to diamond and cubic boron nitride (c-BN), such as extreme hardness, wide band gaps, and high melting points. Moreover, their electronic and structural properties can be manipulated by changing the atomic composition and arrangement, causing variation of carrier filling and crystal symmetry, respectively. Also, these structures may be synthesized through compression of layered structures, similar to a transformation from graphite to diamond, because the first-row elements B, C, and N can form stable sp^2 as well as sp^3 bonds.

Among such heterodiamond BCN compounds, BC_2N has been most frequently synthesized. In the experiments by Nakano *et al.*,[2] static compression of graphitic BC_2N (gr-BC_2N) at high temperature ($>2150\,°C$) yielded cubic BCN substance; however, there was predominant phase separation into diamond and c-BN. Other experimental results were reported by Kakudate *et al.*,[3] who used shock wave compression of gr-BC_2N to obtain a single phase of heterodiamond BC_2N in which the three kinds of atoms are mixed atomically.

Graphitic BC_2N, used as the starting material in the transformations has been comparatively well examined both experimentally[5–8] and theoretically.[9–12] Established methods of preparation utilize chemical vapor deposition of acetonitrile and boron trichloride at low temperature.[5,6] This enables the synthesis of atomically mixed structures.[7] Although the atomic arrangement of gr-BC_2N has not yet been identified in experiments, the most probable monolayer arrangement has been determined by first-principles calculations in which an eight-atom unit cell was used.[9,10] As for heterodiamond BC_2N, on the other hand, there are only the above-mentioned experiments and calculations indicating a trend toward phase separation.[13,14] The synthesis conditions and atomic arrangement of the heterodiamond structure have not yet been determined.

In this paper, we present investigations of several possible transformation paths into heterodiamond BC_2N from layered structures, and report on the probable structure of single-phase heterodiamond BC_2N that will exist metastably at ambient pressure. We also suggest methods to synthesize it under high pressure in the laboratory. Additionally, we present the mechanical and electronic properties of this structure.

Throughout this paper, the constant pressure first-principles molecular dynamics (CP-FPMD) method[15,16] is used to efficiently optimize the structures under pressure. Calculations of electronic states are based on the density-functional formalism utilizing the local-density approximation (LDA)[17] and norm-conserving soft pseudopotentials.[18] A plane wave basis set is used to expand the electronic wave functions, and a correction to the energy functional[19] is introduced to retain a constant energy cutoff for the basis irrespective of change in the unit-cell volume. Uniform k points sampling is employed for the integration over the first Brillouin zone because the systems we treat here may change their crystal symmetries during simulation. The electronic wave functions are sufficiently converged using a preconditioned conjugate-gradient method before the atomic positions and the shape of the unit cell are updated. Optimization of the structural parameters is performed until the forces on the atoms are less than $0.05\ \text{eV/Å}$ and all stress components are less than $0.003\ \text{eV/Å}^3$. For the estimation of the activation barriers in structural transformations, we use the *force-inversion technique* (FIT)[16] based on the CP-FPMD.

In the investigation here, we consider only transformation paths satisfying the following constraints because we aim at the synthesis of a single phase of heterodiamond BC_2N under feasible conditions: (1) The initial layered material is gr-BC_2N with a monolayer structure suggested by previous calculations.[9,10] (2) Transformations are martensitic due to the compression of the layered structure at a temperature low enough to prevent phase separation. These conditions can be realized in experiments.

Under the above conditions, four different transformation paths, as shown in Fig. 1(a)–1(d), can be considered.[20] They are classified by the stacking of layers in the initial gr-BC_2N phase as well as the interlayer bonding formed dur-

© 1997 The American Physical Society

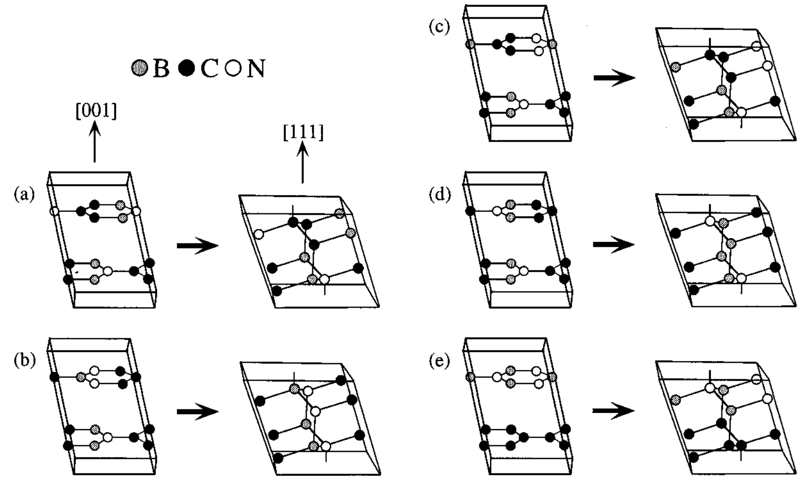

FIG. 1. Schematic representation of the transformation paths from layered BC_2N into heterodiamond BC_2N investigated in this work: (a) gr-BC_2N(I) → α-BC_2N: (b) gr-BC_2N(I) → β-BC_2N: (c) gr-BC_2N(II) → γ-BC_2N: (d) gr-BC_2N(II) → δ-BC_2N: (e) sl-BN/C_2 → β-BC_2N. The framework expresses the monoclinic unit cell with eight atoms used in this work. Orientations in the conventional unit cells are also displayed. Detail of each structure is described in the text.

ing the transformation. The structure of gr-BC_2N is distinguished by the relative orientations of intralayer bonding in adjacent layers. For instance, the orientation of C-B (C-N) bonds in each layer is common to all layers [gr-BC_2N(I)], as shown in Figs. 1(a) and 1(b). Also possible is an alternating orientation between adjacent layers [gr-BC_2N(II)], as shown in Figs. 1(c) and 1(d). By allowing sliding of the layers during transformation, the two different gr-BC_2N structures can each transform into two different heterodiamond structures. In this paper we label the four resulting structures as α, β, γ, and δ-BC_2N. The α-BC_2N [Fig. 1(a)] and β-BC_2N [Fig. 1(b)] structures can be transformed from gr-BC_2N (I). The former is obtained when C-N and C-B bonds between the layers are formed, and the latter when C-C and B-N interlayer bonds are formed. Conversely, gr-BC_2N (II) can transform into γ-BC_2N with C-N and C-B interlayer bondings [Fig. 1(c)], or δ-BC_2N with C-C and B-B (N-N) bonds [Fig. 1(d)].

The total energies of the above heterodiamond structures at ambient pressure, as well as the ratios of the number of contained chemical bonds, are listed in Table I. The energies are obtained from structure optimizations using the monoclinic unit cells with eight atoms displayed in Fig. 1. Calculations of the electronic states are performed by sampling 54 k points and using 75 Ry for the cutoff energy. The difference in total energies is converged to below 0.04 eV. The results (Table I) indicate that the more stable structures have no B-B or N-N bonds, and more C-C and B-N bonds, which have greater bonding energy. Thus the bond counting rule that holds in layered structures of BC_2N[9,10] also holds true for heterodiamond structures. Within energetics, gr-BC_2N (I) will preferentially transform into β-BC_2N, while gr-BC_2N (II) will transform into γ-BC_2N. Among the four possible transformation structures, β-BC_2N is the most energetically favorable. Interestingly, this system does not satisfy the Grimm-Sommerfeld (GS) rule stating that only atomic arrangements ensuring local charge neutrality are allowed for cubic ternary semiconductors. Indeed, even α-BC_2N is more stable than the chalcopyrite structure that satisfies the GS rule.[14]

TABLE I. Calculated total energies E (eV/atom) of α-BC_2N, β-BC_2N, γ-BC_2N and δ-BC_2N at zero pressure. The ratios of the number of chemical bonds (B-N : C-C : C-N : C-B : B-B : N-N) contained in the structures are also shown.

	α-BC_2N	β-BC_2N	γ-BC_2N	δ-BC_2N
E (eV/atom)	−164.391	−164.638	−164.457	−164.210
Ratio	1:1:1:1:0:0	3:3:1:1:0:0	1:1:1:1:0:0	4:6:2:2:1:1

Based on these results, we will limit our discussion to the synthesis of β-BC_2N and γ-BC_2N. As for β-BC_2N, in particular, there is another martensitic transformation path from a layered structure that consists of alternate stacking of graphite and hexagonal BN monolayers, as shown in Fig. 1(e). We name this layered structure superlattice BN/C_2 (sl-BN/C_2) and include it in our discussion.

In order to investigate structural stabilities of the gr-BC_2N, β-BC_2B, γ-BC_2N, and sl-BN/C_2 under pressure, the enthalpy ($H=E+P_{ext}V$) as a function of pressure is calculated using the same conditions as the above total-energy calculations. The enthalpies are given relative to the total energy of β-BC_2N at 0 GPa, $\Delta H=H-H_{\beta}(P_{ext}=0)$, and are shown in Fig. 2. The enthalpies of gr-BC_2N (I) and (II) are displayed by a single line in Fig. 2 because they differ by less than 4 meV. Within the conditions of our calculations, the total energies of layered structures tend to be lower than those in previous calculations[21] by 0.06 eV; however, this does not affect the later discussion qualitatively because it is small enough not to change the order of stability among these structures.

We can see from Fig. 2 that γ-BC_2N becomes more stable than gr-BC_2N above 11 GPa and that β-BC_2N is already more stable at zero pressure. This implies that the transformation from gr-BC_2N to γ-BC_2N can occur at about 11 GPa, while it is possible to transform into β-BC_2N even at nearly ambient pressure. Regarding transformation from sl-BN/C_2, Fig. 2 indicates that sl-BN/C_2 is more stable than

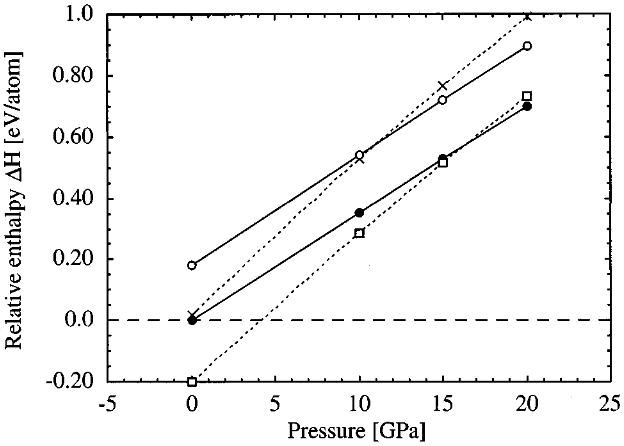

FIG. 2. The pressure dependence of the enthalpies relative to the total energy of β-BC_2N at 0 GPa, $\Delta H = H - H_\beta(P_{ext}=0)$, of gr-$BC_2N$ (crosses), β-BC_2N (filled circles), γ-BC_2N (open circles), and sl-BN/C_2 (squares).

β-BC_2N at zero pressure but transformation can occur with a compression of about 16 GPa. From these results, we can conclude that high-pressure synthesis of β-BC_2N from layered structures has these two possible transformation paths, both of which are experimentally feasible. In particular, sl-BN/C_2, which is free from orientational disorder as well as intralayer defect, is more promising as a starting material for a well-crystallized heterodiamond phase.

To examine the structural stability of the β-BC_2N structure at ambient pressure, we have calculated activation barriers for both transformation paths at 0 GPa using the FIT described above. The calculated barrier for gr-BC_2N is 0.25 eV and that for sl-BN/C_2 is 0.11 eV. These results indicate that the heights of both barriers are high enough to obtain β-BC_2N as a metastable phase at ambient pressure by rapid quenching of the high-pressure phases of the transformations.

We will now discuss the physical properties of β-BC_2N. We have calculated the structural parameters and bulk modulus to know if β-BC_2N could be a superhard material. In the calculations, we initially employ a cubic unit cell and optimize the structure to examine changes in the crystal symmetry and to accurately estimate the isotropic bulk modulus. Since the cubic unit cell necessarily contains at least 64 atoms to express β-BC_2N, we reduce the number of sampling k points (only the Γ point) as well as the cutoff energy (48 Ry). The results are listed in Table II; results for diamond and c-BN calculated under the same conditions are also shown for comparison. The structural parameters and bulk moduli of diamond and c-BN are well reproduced, indicating that these conditions are sufficient for the present discussion.

During the optimization of β-BC_2N, the angle parameters of the unit cell, α, β and γ were allowed to change from 90°, resulting in a structure with rhombohedral symmetry (space group R3m). This symmetry reduction occurs because β-BC_2N violates local-charge neutrality. The zero pressure bulk modulus of β-BC_2N is found to be 438 GPa. Although this value is slightly smaller than that of diamond (464 GPa), it is much larger than that of c-BN (366 GPa). This suggests that β-BC_2N may be a superhard material, and thus useful to mechanical device applications.

We have also calculated the band structures of the materials. The calculated band gaps are shown in Table II. The band gaps of diamond (4.11 eV) and c-BN (4.20 eV) obtained in this work are consistent with those of previous LDA calculations.[21] As for β-BC_2N, we have found that it has an indirect gap of 3.97 eV. Considering that LDA calculations generally underestimate a band gap by 65% (for c-BN)—75% (for diamond), this result would correspond to a real band gap of 5.3–6.1 eV, which is in the ultraviolet region. The band structure of β-BC_2N can be almost taken as the folded one of diamond or c-BN. From the viewpoint of material design, it would be interesting to compress layered superlattices with various stacking of graphite and hexagonal BN monolayers, aiming to create a wide-gap semiconductor with novel optoelectronic properties.

In conclusion, β-BC_2N is the most stable among the possible heterodiamond structures obtained from graphitic BC_2N without atomic diffusion. This result implies that the bond counting rule will hold true for the heterodiamond BC_2N structures. The β-BC_2N structure can be synthesized by compression of graphitic BC_2N ($P_c \sim 0$ GPa) as well as superlattice BN/C_2 ($P_c \sim 16$ GPa) at low temperature, and will exist as a metastable phase at ambient pressure. Although the structure synthesized from graphitic BC_2N de-

TABLE II. Optimized structural parameters, bulk moduli, and band gaps at zero pressure of diamond, cubic BN, and β-BC_2N obtained in this work with results in previous LDA calculations and experiments. The bulk moduli are determined by fitting the total energy as a function of volume to Murnaghan's equation of state (Ref. 22).

	a (Å)			B_0 (GPa)			E_g (eV)		
	This work	Other works		This work	Other works		This work	Other works	
		Calc.[a]	Expt.[b]		Calc.[a]	Expt.[b]		Calc.[a]	Expt.[b]
Diamond	3.561	3.530	3.567	464±8	460	443	4.11	4.25	5.47
c-BN	3.572	3.576	3.615	366±14	397	369 ~	4.20	4.4	6.4
β-BC_2N	3.577			438±14			3.97		
	α=89.38 (deg)								
	β, γ=90.62 (deg)								

[a] Ref. 21.

[b] Ref. 23.

pends on the atomic arrangement and stacking sequence of the initial sample, one could expect superlattice BN/C_2 to transform into β-BC_2N more predictively. The bulk modulus of β-BC_2N is very large with a value slightly smaller than that of diamond. Moreover, β-BC_2N has a wide band gap. Transformations from layered superlattices, as discussed here, open a possibility to control the properties of synthesized heterodiamond BCN compounds.

We thank Dr. T. M. Briere for her help on the manuscript. The computation in this work has been done using FACOM VPP500 at the Supercomputer Center, Institute for Solid State Physics, University of Tokyo. This work was supported by Grant-in-Aids from the Ministry of Education, Science and Culture, Japan.

---

[1] A. R. Badzian,Mater. Res. Bull. **16**, 1385 (1981).

[2] S. Nakano, M. Akaishi, T. Sasaki, and S. Yamaoka, Chem. Mater. **6**, 2246 (1994).

[3] Y. Kakudate, M. Yoshida, S. Usuba, H. Yokoi, S. Fujiwara, M. Kawaguchi, K. Sako, and T. Sawai, Trans. Mat. Res. Soc. Jpn. **14B**, 1447 (1994).

[4] E. Knittle, R. B. Kaner, R. Jeanloz, and M. L. Cohen, Phys. Rev. B **51**, 12 149 (1995).

[5] J. Kouvetakis, T. Sasaki, C. Shen, R. Hagiwara, M. Lerner, K. M. Krishnan, and N. Bartlett, Synth. Met. **34**, 1 (1989).

[6] T. Sasaki, M. Akaishi, S. Yamaoka, Y. Fujiki, and T. Oikawa, Chem. Mater. **5**, 695 (1993).

[7] M. O. Watanabe, S. Itoh, K. Mizushima, and T. Sasaki, Appl. Phys. Lett. **68**, 2962 (1996).

[8] M. O. Watanabe, S. Itoh, K. Mizushima, and T. Sasaki, J. Appl. Phys. **78**, 2880 (1995); Phys. Rev. Lett. **77**, 187 (1996).

[9] A. Y. Liu, R. M. Wentzcovitch, and M. L. Cohen, Phys. Rev. B **39**, 1760 (1989).

[10] H. Nozaki and S. Itoh, J. Phys. Chem. Solids **57**, 41 (1996).

[11] Y. Miyamoto, M. L. Cohen, and S. G. Louie, Phys. Rev. B **52**, 14 971 (1995).

[12] H. Nozaki and S. Itoh, Phys. Rev. B **53**, 14 161 (1996).

[13] W. R. L. Lambrecht and B. Segall, Phys. Rev. B **40**, 9909 (1989).

[14] Y. Tateyama, T. Ogitsu, K. Kusakabe, and S. Tsuneyuki, Proceedings of the U.S.–Japan Seminar on High Pressure and Temperature Research, Hawaii (1997, in press).

[15] R. M. Wentzcovitch, J. L. Martins, and G. D. Price, Phys. Rev. Lett. **70**, 3947 (1993).

[16] Y. Tateyama, T. Ogitsu, K. Kusakabe, and S. Tsuneyuki, Phys. Rev. B **54**, 14 994 (1996).

[17] E. P. Wigner, Trans. Faraday Soc. **34**, 678 (1938).

[18] N. Troullier and J. L. Martins, Phys. Rev. B **43**, 1993 (1991).

[19] M. Bernasconi, G. L. Chiarotti, P. Focher, S. Scandolo, E. Tosatti, and M. Parrinello, J. Phys. Chem. Solids **56**, 501 (1995).

[20] In addition to the transformation paths into cubic diamond (CD)-like structures examined here, there are also four possible paths into hexagonal diamond (HD)-like structures under the conditions. In this work, however, we exclude such paths from our consideration because the HD-like structures are expected to be less stable than the CD-like ones, in analogy with the cases in carbon and boron nitride.

[21] J. Furthmüller, J. Hafner, and G. Kresse, Phys. Rev. B **50**, 15 606 (1994).

[22] F. D. Murnaghan, Proc. Natl. Acad. Sci. USA **30**, 244 (1944).

[23] Phys. Rev. B **50** (Ref. 21), and reference therein.