

Influence of raw gases on B–C–N films prepared by electron beam excited plasma CVD

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Abstract

B–C–N films were deposited with electron beam excited plasma–chemical vapor deposition focusing on the structural stability where their compositions lie in the vicinity of BN. Film composition was controlled by varying process gas flow rates and was $x=1.08$ – 1.18 and $y=0.01$ – 0.34 for B_xC_yN . The dependence of Fourier transform infrared transmission spectra and hardness on composition show that the structure is very sensitive to film carbon content: a cubic phase is found only in a carbon-poor region and disappears abruptly when carbon content is increased. Results of X-ray diffraction and X-ray photoelectron spectroscopy measurement suggest that films involving a cubic phase of carbon-poor B–C–N compound were obtained. The disadvantage in forming a cubic B–C–N phase in a low carbon region is understood in terms of bonding energy and local charge neutrality, while the entropy of mixing should enable very low carbon solubility.

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1. Introduction

Materials in the B–C–N system show strong promise for mechanical, optical and electronic applications. For mechanical applications, although diamond is known as the hardest substance, oxidation at high temperatures and poor abrasive resistance for iron-based alloys restrict industrial use. Although cubic boron nitride (cBN) is next hardest after diamond, it is more chemically stable than diamond. Cubic B–C–N phases are expected to yield superhard materials and to have high corrosion resistance at high temperatures, making of interest and technological importance to obtain cubic B–C–N phases and to control their major properties by varying their compositions.

Cubic B–C–N phases have been synthesized only by high pressure/temperature treatment [1–3]. For industrial applications, it is important to form hard B–C–N films on other materials as mechanical hard coatings.

Therefore many attempts to produce the B–C–N films by using various chemical vapor deposition (CVD) or physical vapor deposition (PVD) methods has been reported [4–10]. Previously [11,12], we reported the synthesis of B–C–N films by electron beam excited plasma (EBEP)–CVD, characterization of the structure, and tribological properties of films under dry-lubrication, where we found that film hardness increased monotonically with increasing boron content and reached 30 GPa, although sp^2 -bonded and sp^3 -bonded structures coexisted. We studied film properties focusing on composition in the cubic-phase B–C–N (BC_2N) obtained by high pressure/temperature treatment [1–3]. Film composition tended to approach that of B_4C in high boron concentrations of the process gas.

Here, we have attempted to synthesize films whose atomic ratio of B and N is unity, because they should be stable in charge balance among atoms or ions composing films. We controlled film composition by varying process gas flow. Results are plotted in a composition triangle for the ternary B–C–N system and those obtained in previous studies in Fig. 1.

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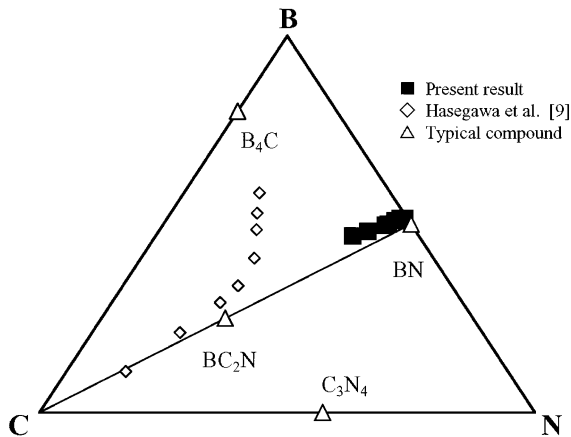


Fig. 1. Ternary boron, carbon and nitrogen composition triangle of films.

2. Experimental procedure

EBEP-CVD was used to synthesize B–C–N film as reported elsewhere [11]. The substrate was a polished p-type single crystal silicon wafer (1 0 0) pre-etched in situ by Ar plasma. A boron layer was prepared on substrates to reduce the internal stress of the films with a plasma of 10% B_2H_6 in He prior to B–C–N film deposition. A mixture of 10% B_2H_6 in He, CH_4 , N_2 and Ar was used as raw gas whose total pressure was 1.33 Pa. CH_4 flow rate was changed from 0 to 3 sccm, while those of other gases were kept constant so the atomic ratio of B and N in the film becomes nearly 1:1 and flow rates of 10% B_2H_6 in He, N_2 and Ar were 80, 10 and 10 sccm. Substrate temperature was maintained at 950 K. The acceleration voltage of the electron beam was 80 V and the bias voltage to the substrate was –225 V in all experiments.

X-ray photoelectron spectroscopy (XPS) was used to determine atomic composition and chemical bonding state. Hydrogen atom content was estimated by elastic recoil detection analysis (ERDA). Chemical bonding states were also studied by Fourier transform infrared (FT-IR) transmission spectroscopy. Film crystal structures were studied by X-ray diffraction (XRD) using a diffractometer with parallel beam optics for measuring thin film. Film hardness was evaluated using a nano-indentation tester in which fused silica was used as a control material.

3. Results and discussion

B–C–N films approximately 200 nm thick were obtained by deposition for 20 min. Films do not peel off, even if left in the atmosphere for a long time, due to the boron layer between the film and substrate. Although the hydrogen atom ratio in the raw gas is

approximately 30%, hydrogen content in films measured by ERDA was 4–6 at.%.

The composition of B–C–N films was determined by XPS and its dependence on the composition of raw gas is shown in Fig. 2, where B , C and N are the fractions of boron, carbon and nitrogen atoms, and suffixes f and g denotes those for the film and process gas. C_f increases in proportion to C_g . Both B_f and N_f decrease monotonically with increasing C_g so ratio B_f/N_f is almost unity, despite a slight increase in the ratio. We obtained films, whose composition is expressed as $B_xC_yN_z$, are $x=1.08$ – 1.18 and $y=0.01$ – 0.34 . As shown in Fig. 1, compositions lie in the vicinity of BN.

Given the charge balance among atoms or ions composing films, it should be advantageous in forming stable compounds that B_f/N_f be nearly equal to unity. FT-IR transmission spectra (Fig. 3) of films synthesized varying C_g indicate that this does not favor formation of a dense phase consisting of an sp^3 -bonded structure. Absorptions corresponding to in-plane stretching of an sp^2 -bonded B=N bond (1400 cm^{-1}) and out-of-plane bending of an sp^2 -bonded B–N–B bond (780 cm^{-1}) show the existence of hexagonal boron nitride (hBN) and/or graphitic B–C–N in all specimens. The peak corresponding to a reststrahlen band (1080 cm^{-1}) [4] of cBN and/or cubic phases of B–C–N [2] becomes very weak abruptly with increasing carbon content ($C_f \geq 0.097$). In $C_f=0.045$, the peak at 1080 cm^{-1} appears to spread to a higher wavenumber, showing that the spectrum may include the peak of absorption caused by icosahedral vibrations in the B_4C structure (1100 cm^{-1}) [5,6]. It may be difficult to form the sp^3 -bonded structure in the vicinity of BN composition for the following reason: when carbon atoms are absent, boron

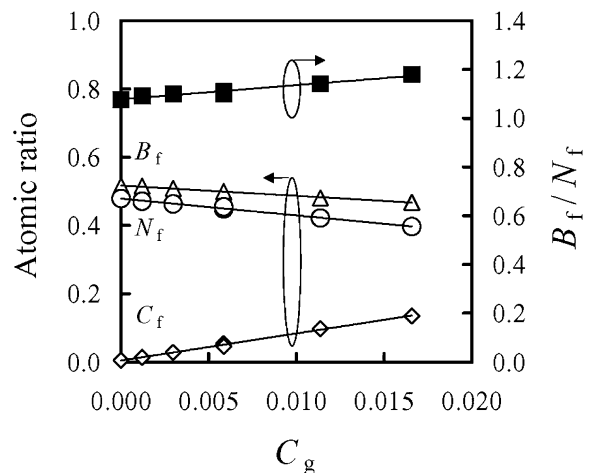


Fig. 2. Atomic ratio of B–C–N films and B_f/N_f as a function of C_g . The 10% B_2H_6 in He, N_2 and Ar flow rates are fixed at 80, 10 and 10 sccm. B , C and N are the fractions of boron, carbon and nitrogen atoms, and suffixes f and g denotes those in film and process gas.

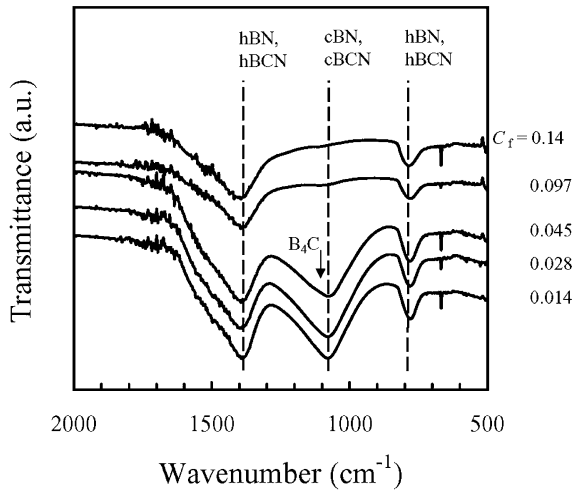


Fig. 3. FT-IR transmission spectra of B-C-N films synthesized by varying carbon content in the process gas.

and nitrogen atoms should be alternated as much possible to avoid the formation of B-B or N-N bonds. When a boron or a nitrogen atom is replaced by a carbon atom, the carbon atom is then surrounded with the same type of atoms if the carbon content is low. This situation should be disadvantageous due to bonding energy and local charge neutrality, which become more serious for the sp³-bonded structure than for the sp²-bonded structure because of the increase of the coordination number. The very low solubility of carbon may be enabled possible by the entropy of mixing in free energy even if film is formed in thermodynamic nonequilibrium.

Measured film hardness was approximately 25 GPa in C_f ≤ 0.045 (Fig. 4). When C_f increases above 0.045, hardness decreases sharply to approximately 10 GPa, reflecting the structural dependence of film on C_f obtained by FT-IR transmission measurement.

Film with a sp³-bonded structure (C_f ≤ 0.045) was studied in detail with XRD and XPS. XRD patterns taken at a fixed low angle (0.3°) of incidence for the X-ray beam are shown in Fig. 5. Three broad diffraction peaks, 2θ = 43.1, 73.6 and 89°, are observed for all specimens except for very broad peaks approximately 26–27°, attributed to the 0 0 2 diffraction peak of hBN or similar hexagonal layered compounds [1]. These three peaks are indexed as 1 1 1, 2 2 0 and 3 1 1 for the cubic lattice, and *d*-values are very close to cBN or cubic phases of B-C-N [1,2]. It is not, however, possible to distinguish their lattice constants from each other because of the very broad peak widths. It is possible that the peak at 43.1° involves a component of the 1 0 0 peak for the hexagonal phase [1]. If the hexagonal phase is strongly oriented so its basal plane is perpendicular to the surface of the substrate, the intensity of the 1 0 0

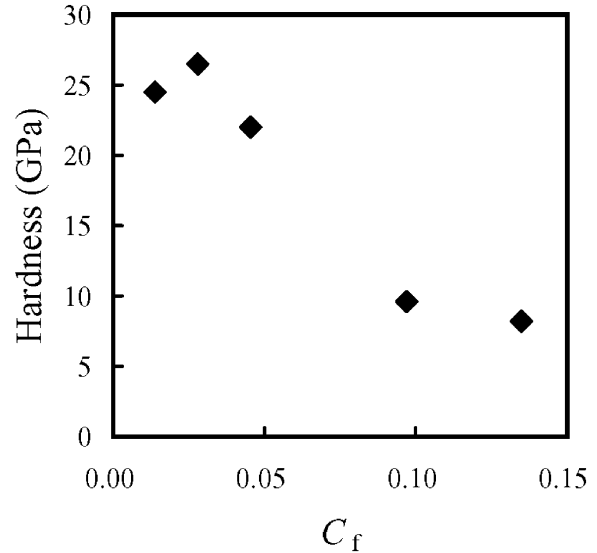


Fig. 4. Dependence of hardness on carbon content in film, C_f.

peak becomes strong, which may bring about ambiguity in precise determination of peak positions.

Fig. 6(a-c) shows XPS spectra for B 1s, C 1s and N 1s core level states. Because the position of B 1s and N 1s for cBN or hBN is 190.5 and 398.1 eV [13–15], no significant influence of carbon content on either spectrum was observed due to the small amount of carbon. With increasing C_f, a spectrum of C 1s grows monotonically without changing shape. Peak positions of C 1s spectra coincide with that of B₄C (282.9 eV) [14,15] and spectra show that films involve a small amount of compositions corresponding to graphite (C=C, 284.5 eV), diamond (C-C, 285.3 eV), or BC_{3,4} (284.3 eV) [13,15]. It then follows that most carbon atoms are not

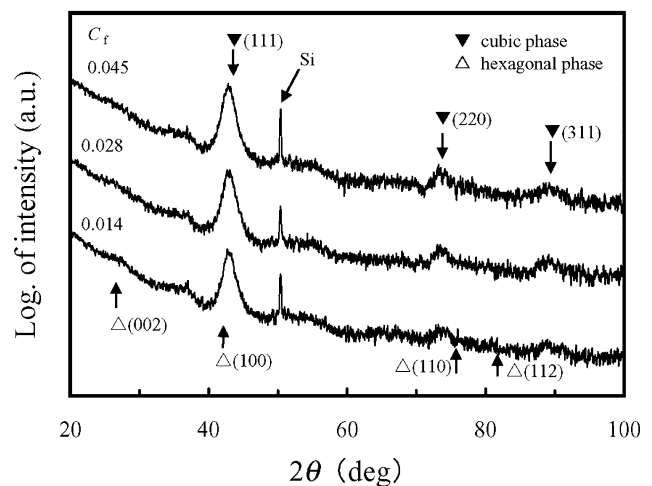


Fig. 5. XRD (Cu Kα) patterns of B-C-N films synthesized by varying carbon content in process gas.

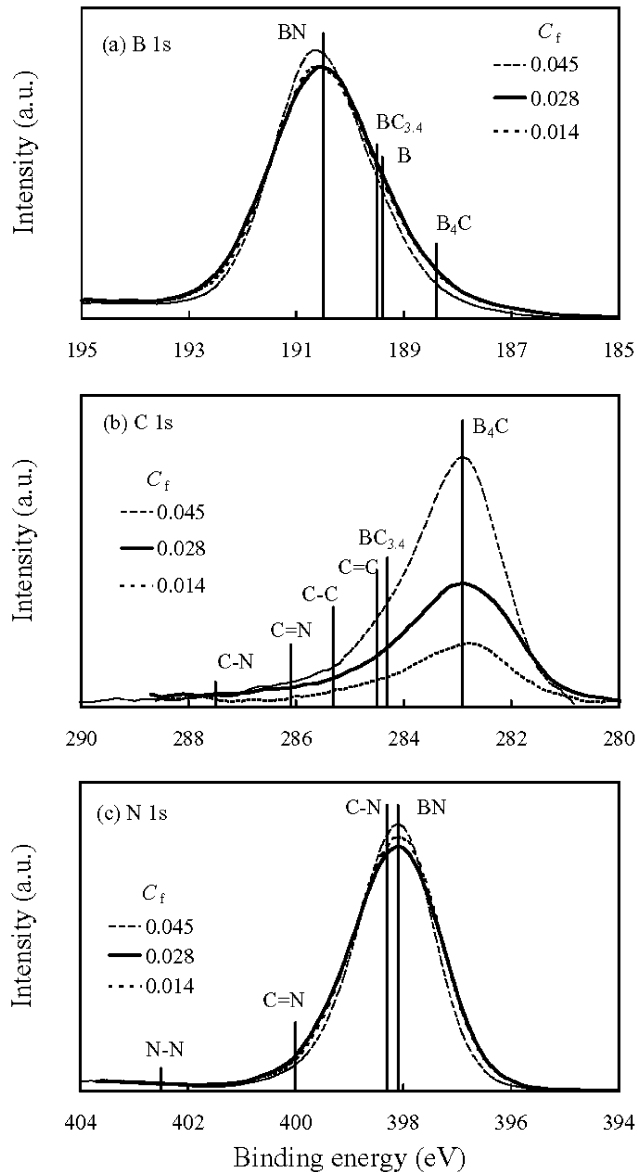


Fig. 6. XPS spectra for (a) B 1s; (b) C 1s and (c) N 1s of B–C–N films synthesized by varying carbon content in process gas.

deposited as pure carbon phases such as graphite or diamond but are put into the sp^3 -bonded structure to form a local structure similar to B_4C . This structure should not be the B_4C crystal itself, because the atomic ratio B_f/N_f keeps almost unity when carbon atoms are introduced into films. Given the result of XRD and FT-IR, it appears most probable that we obtained films involving a cubic phase of carbon-poor B–C–N compound.

4. Conclusions

B–C–N films were deposited with EBEP–CVD focusing on structural stability when their compositions lie in the vicinity of BN. Film composition was controlled by varying process gas flow rates. Dependence of FT-IR transmission spectra and hardness on composition show that the structure is very sensitive to film carbon content; the dense cubic phase found only in a carbon-poor region ($C_f \leq 0.045$) disappears abruptly with increasing carbon content. XRD and XPS results suggest that films involved a cubic phase of a carbon-poor B–C–N compound. The disadvantage of forming a cubic B–C–N phase in a low-carbon region is understood in terms of bonding energy and local charge neutrality, while the entropy of mixing should enable the very low solubility of carbon.

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References

- [1] Y. Kakudate, M. Yoshida, S. Usuba, H. Yokoi, S. Fujiwara, *Trans. Mater. Res. Soc. Jpn.*, Part B 14 (1994) 1447.
- [2] E. Knittle, R.B. Kaner, R. Jeanloz, M.L. Cohen, *Phys. Rev. B* 51 (1995) 12149.
- [3] V.L. Solozhenko, D. Andrault, G. Fiquet, M. Mezouar, D.C. Rubie, *Appl. Phys. Lett.* 78 (2001) 1385.
- [4] S. Ulrich, H. Ehrhardt, T. Theel, et al., *Diamond Relat. Mater.* 7 (1998) 839.
- [5] Y. Wada, Y.K. Yap, M. Yoshimura, Y. Mori, T. Sasaki, *Diamond Relat. Mater.* 9 (2000) 620.
- [6] A. Lousa, J. Esteve, S. Muhl, E. Martinez, *Diamond Relat. Mater.* 9 (2000) 502.
- [7] M.C. Polo, E. Martinez, J. Esteve, J.L. Andújar, *Diamond Relat. Mater.* 8 (1999) 423.
- [8] E.H.A. Dekempeneer, J. Meneve, S. Kuypers, J. Smeets, *Thin Solid Films* 281 (1996) 331.
- [9] D. Kurapov, D. Neuschütz, R. Cremer, T. Pederson, M. Wuttib, D. Pietrich, G. Marx, J.M. Schneider, *Vacuum* 68 (2003) 335.
- [10] L. Linss, I. Hermann, N. Schwarzer, U. Kreissig, F. Richter, *Surf. Coat. Technol.* 163 (2003) 220.
- [11] T. Hasegawa, K. Yamamoto, Y. Kakudate, *Diamond Relat. Mater.* 11 (2002) 1290.
- [12] T. Hasegawa, K. Yamamoto, Y. Kakudate, M. Ban, *Surf. Coat. Technol.*, in press.
- [13] K. Yamamoto, Y. Koga, S. Fujiwara, *Jpn. J. Appl. Phys.* 40 (2001) L123.
- [14] M.O. Watanabe, S. Itoh, K. Mizushima, *Appl. Phys. Lett.* 68 (1996) 2962.
- [15] J.F. Moulder, W.F. Stickle, P.E. Sobol, K.D. Bomben, *Handbook of X-Ray Photoelectron Spectroscopy* published by Physical Electronics, Inc. (PHI 1999).