

Effect of residual oxygen in a vacuum chamber on the deposition of cubic boron nitride thin film

Seung-Keun Oh^{a,b}, Sang Do Kang^a, Youngman Kim^b and Soon Sub Park^{c,*}

^aMPNICS Co., Ltd., 45 Cheomdan venture-ro, Buk-gu, Gwangju, 500-460 Korea

^bDepartment of Materials Science and Engineering, Chonnam National University, Gwangju 500-757 Korea

^cSeonam Regional Division, Korea Institute of Industrial Technology, 6, Cheomdan-gwagiro 208beon-gil, Buk-gu, Gwangju, 500-480 Korea

The structural characterization of cubic boron nitride (c-BN) thin films was performed using a B₄C target in a radio-frequency magnetron sputtering system. The deposition processing conditions, including the substrate bias voltage, substrate temperature, and base pressure were varied. Fourier-transform infrared spectroscopy and X-ray photoelectron spectroscopy were used to analyze the crystal structures and chemical binding energy of the films. For the BN film deposited at room temperature, c-BN was formed in the substrate bias voltage range of –400 V to –600 V. Less c-BN fraction was observed as the deposition temperature increased, and more c-BN fraction was observed as the base pressure increased.

Key words: c-BN, B₄C, Oxygen addition, Base pressure, Magnetron sputtering.

Introduction

Boron nitride exists in four different forms including hexagonal-boron nitride and turbostratic-boron nitride, which are sp² bonded and exhibit relatively low densities, and cubic-boron nitride (c-BN) and wurtzite-boron nitride, which are sp³ bonded and exhibit relatively high densities and stability [1]. Of these materials, c-BN has a diamond-like hardness and is chemically stable with a very high thermal stability, which makes it highly useful as a wear-resistant coating in fields where the use of diamond is restricted [2–4]. Diamond is stable under normal conditions but is thermodynamically unstable, whereas c-BN is thermodynamically stable [5, 6].

The synthesis mechanism for c-BN thin films has not yet been clearly described. However, several mechanisms for synthesizing c-BN have been proposed, and the common idea is that high impact energy is required when synthesizing c-BN. The deposition temperature is also an important factor in c-BN synthesis. When creating c-BN, a critical temperature exists. Below the critical temperature, there is not sufficient energy to make the phase transition from h-BN to c-BN; therefore, c-BN cannot be produced. In addition, a buffer layer of h-BN exists at the interface between the c-BN thin film and the base material, and c-BN nucleation occurs on top of the h-BN (0002) lattice. If sufficient residual stress accumulates as the buffer layer is forming, c-BN is

created, and at high temperatures above the critical temperature for creating c-BN, h-BN and c-BN form at the same time, and the c-BN content is reduced [7, 8]. One major problem when forming a c-BN thin film is that it can be very brittle because of the impurities that are mixed in during formation. It has been reported that the base pressure in the reactor before deposition begins [9] as well as oxygen and hydrogen adulteration [10, 11] significantly affect the c-BN synthesis.

In this study, the effect of the substrate bias and deposition temperature on the formation of c-BN thin films was examined. The amount of oxygen in the c-BN thin film as a function of the base pressure was also evaluated. The c-BN fraction was measured, and the effect of oxygen on c-BN thin-film formation was examined.

Experiment Method

Magnetron sputtering was used to deposit the BN thin films. A Si (100) wafer polished on both sides was used as the substrate. A 99.5% pure, 4-inch B₄C target was used for the sputter target. Before deposition, Ar ion etching was performed for 5 min with a substrate bias of –600 V. Before depositing the BN thin film, Ar gas was used to deposit a B₄C thin film for 15 min to improve the adhesion. Then, the BN thin film was deposited while the Ar and N₂ flux were regulated at 10 and 5 sccm, respectively. While the BN thin film was being deposited, the substrate bias was changed from –100 to –600 V, and the deposition temperature was changed from room temperature to 400 °C (Table 1). To heat the specimen, halogen lamps were

*Corresponding author:
Tel : +82-62-600-6250
Fax: +82-62-600-6259
E-mail: pss4633@kitech.re.kr

Table.1. Deposition conditions for BN film.

	Ion-etching	B ₄ C layer	BN layer
Substrate bias (-V)	600	100	100 ~ 600
Ar:N ₂ flow (sccm)	10 : 0	10 : 0	10 : 5
Deposition temperature (°C)	RT ~ 400	RT ~ 400	RT ~ 400
Deposition time (min)	5	10	15

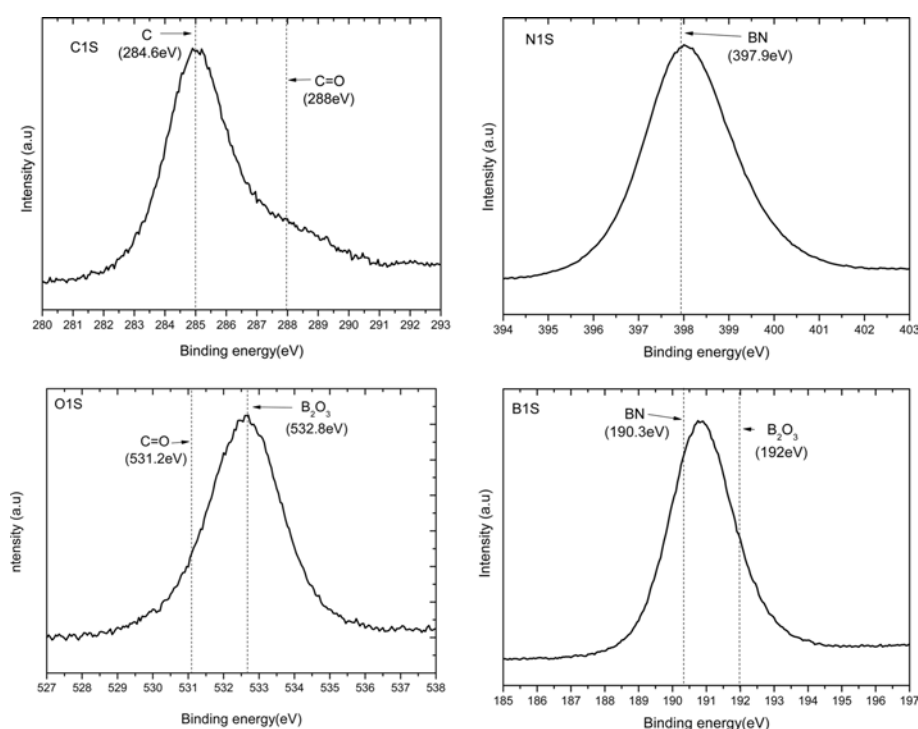
used to heat the entire atmosphere of the chamber. To change the base pressure, the temperature was maintained at 250 °C for 2 hrs while the vacuum was maintained until the temperature was reduced to room temperature, and the base pressure was maintained below 9×10^{-7} Torr. The composition and binding energy of the deposited thin film were analyzed using X-ray photoelectron spectroscopy (XPS), and the bond structure of the BN thin film was analyzed using Fourier-transform infrared spectroscopy (FT-IR).

Results and Discussion

Fig. 1 presents the XPS results of the BN thin film deposited at room temperature with a substrate bias of -400 V. The deposited thin film exhibited BN bonding and contained carbon (12 at.%) and oxygen (6 at.%). It has been reported that a BN thin film deposited using a B₄C target has a 5-10% carbon content [12]. In addition, using a B₄C target is advantageous in that it is possible to deposit a BCN inter-layer along with the B₄C, and the adhesion of the easily peeled c-BN thin film increases via high residual stress. Moreover, a higher deposition speed

is attained than when a non-conducting h-BN target is used. It is believed that oxygen adulteration in the BN thin film is caused by the heating method, which uses halogen lamps to heat the entire chamber. When the BN thin film is adulterated with oxygen, the difference in electronegativity causes B-O bonding to occur rather than B-N bonding, creating B₂O₃. The XPS analysis results indicate that the detected carbon existed as carbon alone, except for part of it that formed C = O bonds.

Fig. 2 presents the FT-IR results for the BN thin film deposited at room temperature, which show the c-BN absorption lines (1080 cm⁻¹) and h-BN absorption lines (780 cm⁻¹, 1308 cm⁻¹) as a function of the substrate bias. In the BN thin film, the sp²-bonding h-BN exhibits an absorption line, which is affected by both B-N in-plane stretching vibration and B-N-B out-of-plane bending vibration at 1308 cm⁻¹ and 780 cm⁻¹, respectively, while the sp³-bonding c-BN has a characteristic absorption line at 1080 cm⁻¹ due to the transverse optical TO mode, making it possible to see the crystallization of the easily absorbed thin film. When the substrate bias was -400 V, the 1080 cm⁻¹ absorption line corresponding to c-BN was more clear, and as the bias increased, the intensity of the absorption line decreased. When the substrate bias was -700 V, the thin film began to peel, and it could not be analyzed. It is believed that the c-BN absorption line varied with the changes in the substrate bias because c-BN formation requires high ion energy, and as the substrate bias increased, the c-BN absorption line intensity decreased because of re-sputtering of the thin film due to overly high ion energy. Kester et al. performed research on the conditions for forming a c-

**Fig. 1** XPS spectra of BN thin film.

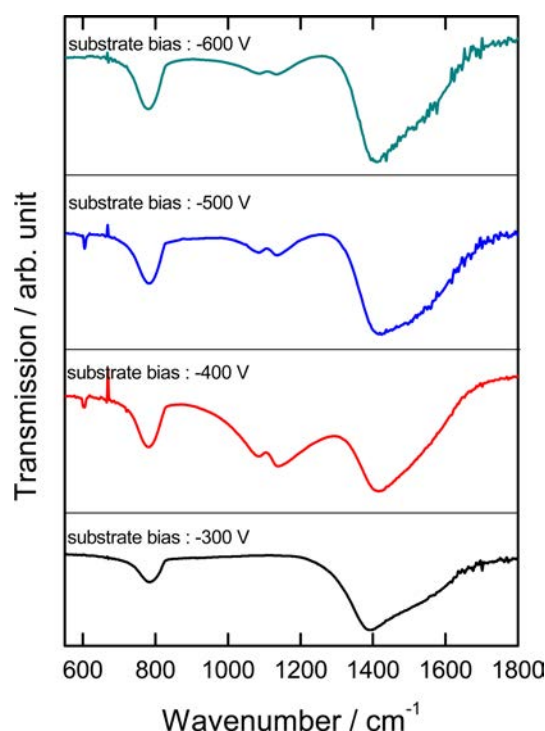


Fig. 2. FTIR spectra of BN films deposited at RT.

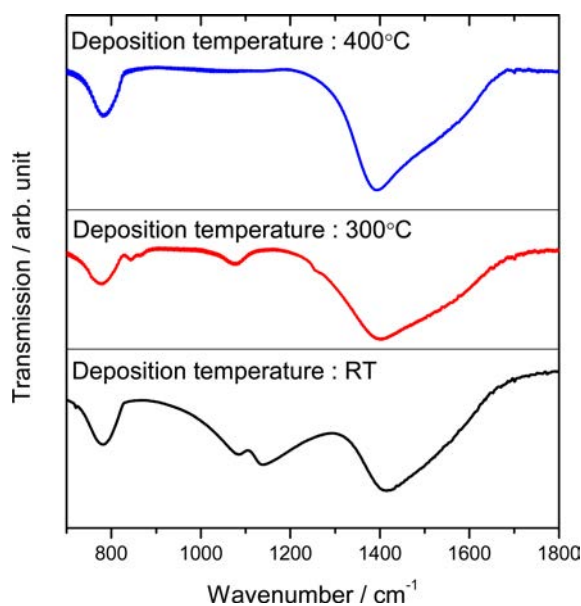
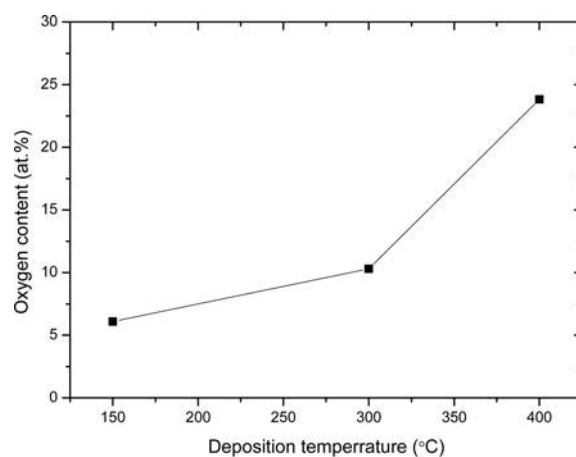


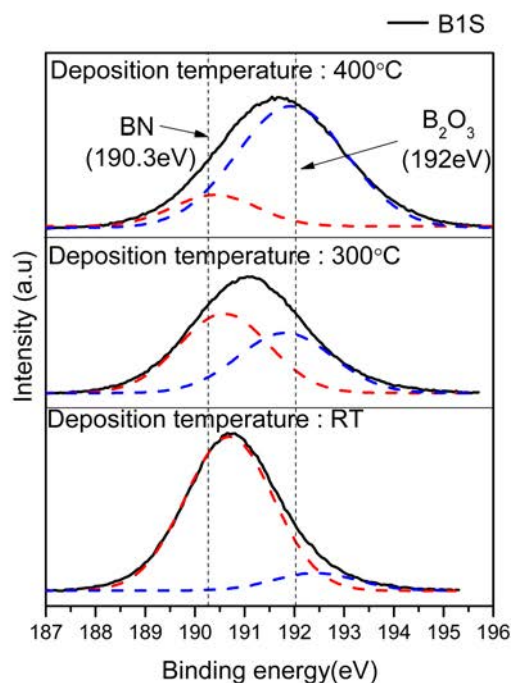
Fig. 3. FTIR spectra of BN films deposited at a substrate bias of -400 V.

BN thin film and reported similar results; it was observed that re-sputtering occurred because of higher than normal ion energy, which reduced the c-BN content [13].

Fig. 3 presents the FT-IR results for the BN thin film as a function of temperature. In the experiments, the substrate bias was maintained at -400 V, and deposition temperatures of room temperature, 300 °C, and 400 °C were used. When the BN thin film was deposited at 300 °C, a c-BN absorption line was observed; however,



(a)



(b)

Fig. 4. XPS data of BN films deposited at a substrate bias of -400 V. (a) Oxygen content as a function of the deposition temperature. (b) Binding energy of boron as a function of the deposition temperature.

its intensity was lower than that of the thin film deposited at room temperature. When the BN thin film was deposited at 400 °C, only a h-BN absorption line was observed. In general, when a BN thin film is deposited at a high temperature, a buffer layer of h-BN is formed at the same time or the h-BN buffer layer is deposited irregularly because of the high temperature, which prevents the accumulation of residual stress in the thin film and reduces the BN content. However, in this experiment, it has been concluded that the inflow of oxygen due to the increased deposition temperature caused a reduction in c-BN formation rather than the

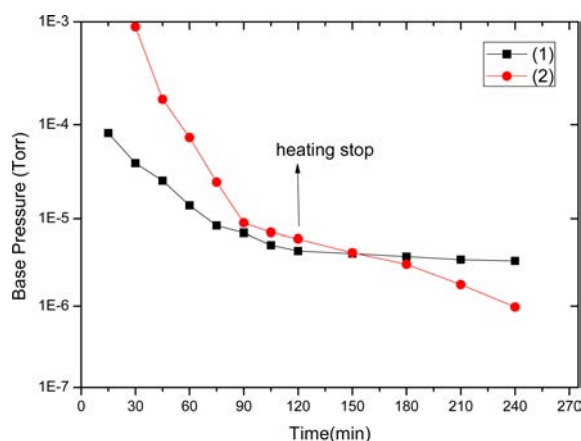


Fig. 5 Variation of chamber pressure as a function evacuation time.

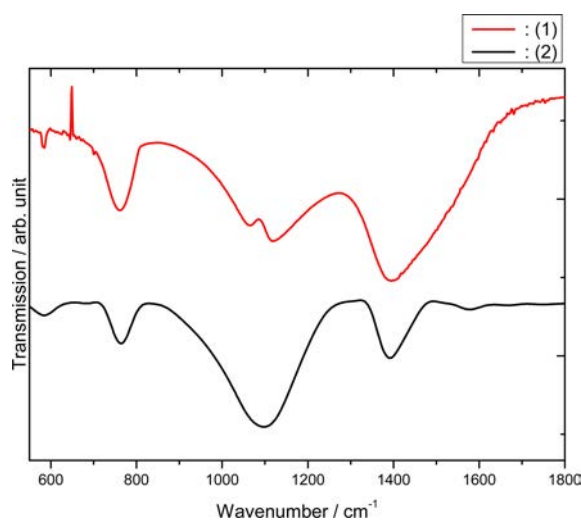


Fig. 6 FTIR spectra of BN films deposited after chamber heating.

effect of the buffer layer.

Fig. 4(a) presents a graph of the oxygen content of the BN thin film as a function of the deposition temperature. As the temperature increased, the oxygen content of the BN thin film increased. It is believed that this result is due to the inflow of oxygen caused by the heating method of the equipment used in the experiment. The method heated the entire atmosphere of the chamber, which caused the amount of inflowing oxygen in the chamber to increase as the temperature increased. Fig. 4(b) presents the boron binding energy peaks of the BN thin film as a function of the deposition temperature. The boron binding energy peaks for the BN thin film deposited at room temperature were comparatively consistent with the BN binding energy (190.3 eV); however, as the deposition temperature increased, the boron binding energy peaks moved closer to the binding energy of B_2O_3 (192 eV). In addition, as the deposition temperature increased, the boron binding energy peaks grew wider, which is closer to the B_2O_3 binding energy. It is believed that as the deposition temperature increased, the oxygen content of the BN

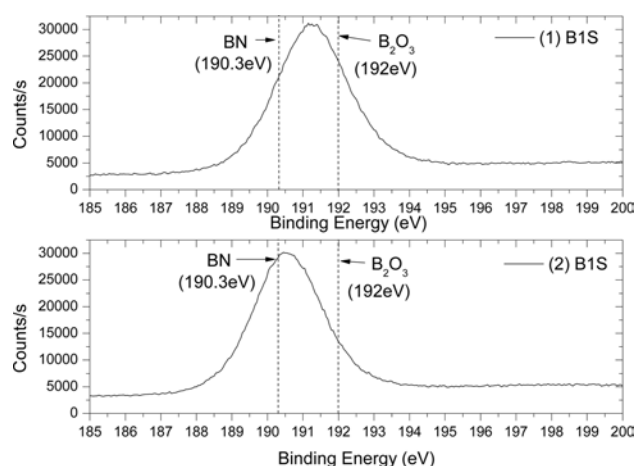


Fig. 7 XPS spectra of BN films deposited after chamber heating.

thin film increased, and thus, more B_2O_3 creation occurred.

If the BN thin film is adulterated with oxygen, B_2O_3 is created because of the difference in electronegativity. The B-O bond, which has a larger difference in electronegativity, takes precedence over the B-N bond. The electronegativity difference of B-O is 1.5, whereas that of B-N is 1.0. To make c-BN nucleation likely, the boron and nitrogen stoichiometric ratio must be maintained at 1 : 1 [10]. However, if a more than normal amount of oxygen is included, it interferes with the boron and nitrogen reaction, which ultimately disrupts the boron and nitrogen composition ratio and interferes with c-BN nucleation. The sp^2 bond characteristics observed in B_2O_3 also disrupt c-BN nucleation and growth because they hamper the sp^3 bond environment required for c-BN nucleation [14].

Fig. 5 presents the data for the pressure as a function of the vacuum conditions. Under condition (1), the vacuum was maintained at room temperature. Under condition (2), the vacuum was maintained for 2 hrs at 250 °C, and then, the specimen was returned to room temperature. With the same vacuum time, as the temperature increased, a lower pressure was observed. It is believed that because of this difference in the pressure, as the deposition temperature increased, the oxygen content in the BN thin film increased.

Fig. 6 presents the FT-IR results for the c-BN thin film as a function of the base pressure. The deposition temperature was maintained at room temperature, and the substrate bias was maintained at -400 V. Specimen (1) had a base pressure of 3×10^{-6} Torr, and Specimen (2) had a base pressure of 9×10^{-7} Torr when deposition began. Because the vacuum in Specimen (1) was maintained at room temperature, a pressure below the base pressure of 3×10^{-6} Torr could not be achieved. The vacuum in Specimen (2), however, was maintained at 250 °C for 2 h and then the specimen was returned to room temperature such that a base pressure of 9×10^{-7} Torr could be achieved. Even though the

deposition temperature and substrate bias were the same, at a high base vacuum level, a clear c-BN absorption line (1080 cm^{-1}) could be observed. This result indicates that pressure has a great effect on c-BN formation. As observed in Fig. 7, the pressure had an effect on the c-BN thin film oxygen content. In Specimen (1), the boron binding energy peak was between the binding energy of B_2O_3 and that of BN; however, in Specimen (2), the boron binding energy peak moved toward the binding energy of BN because of the low oxygen content. Most of the oxygen in the chamber existed as moisture, and this moisture existed through physical and chemical absorption. For physical absorption, it is easy to remove most of the moisture through a vacuum; however, for chemical absorption, a higher than normal temperature is required [15]. It is believed that in this experiment, the process of maintaining a vacuum for 2 hrs at 250°C to achieve the base pressure for Specimen (2) effectively removed the moisture that existed in the chamber and reduced the oxygen content in the c-BN thin film.

Conclusions

In this research, we studied the effect of the substrate bias, deposition temperature, and base pressure on c-BN synthesis. c-BN synthesis only occurred at a higher than normal substrate bias, and as the substrate bias increased, the c-BN content decreased. Because of the specifics of the equipment, the oxygen content of the c-BN thin film increased as the deposition temperature increased, and c-BN synthesis became difficult. When the vacuum was maintained at 250°C to create a high

base vacuum level, the moisture in the chamber was effectively removed, and it became possible to produce a c-BN thin film with a better fraction of c-BN.

References

1. H. Lüthje, K. Bewilogua, S. Daaud, M. Johansson, and L. Hultman, *Thin Solid Films* 257[1] (1995) 40-45.
2. H. Holleck, *J. Vac. Sci. Technol. A* 4[6] (1986) 2661-2669.
3. R.C. DeVries, in: R.E. Clausing (ed.), "Diamond and Diamond Like Films and Coatings" (Plenum Press, New York, 1991) 151.
4. R. Haubner and B. Lux, *Diamond Relat. Mater.* 2[9] (1993) 1277-1294.
5. F.P. Bundy and R.H. Wentorf, *J. Chem. Phys.* 38[5] (1963) 1144-1149.
6. F.P. Bundy and J.S. Kasper, *J. Chem. Phys.* 46[9] (1967) 3437-3446.
7. W. Zhou and Y. Ikuhara, *Mater. T. JIM* 37[5] (1996) 1122-1126.
8. W. Zhou and Y. Ikuhara, *Appl. Phys. Lett.* 66[19] (1995) 2490-2492.
9. E.S. Lee, J.K. Park, W.S. Lee, T.Y. Seong, and Y.J. Baik, *J. Korean Ceram. Soc.* 49[6] (2012) 620-624.
10. M. Lattermann, S. Ulrich, and J. Ye, *Thin Solid Films* 515[3] (2006) 1058-1062.
11. H.S. Kim, J.K. Park, W.S. Lee, and Y.J. Baik, *Thin Solid Films* 519[22] (2011) 7871-7874.
12. A. Schütze, K. Bewilogua, H. Lüthje, S. Kouptsidis, and M. Gaertner, *Surf. Coat. Tech.* 97[1-3] (1997) 33-38.
13. D.J. Kester and R. Messier, *J. Appl. Phys.* 72[2] (1992) 504-513.
14. H.Y. Jang, J.K. Park, W.S. Lee, Y.J. Baik, D.S. Lim, and J.H. Jeong, *J. Kor. Inst. Surf. Eng.* 40[2] (2007) 91-97.
15. J.F. O'Hanlon, in "A User's Guide to Vacuum Technology" (Wiley, U.S.A, 1989) 58.