Effects of substrate bias voltages on hardness of BCN films prepared by RF magnetron sputtering

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BCN films are prepared using RF magnetron sputtering with a combined target of semicircle B_4C and graphite, and the microstructure and mechanical properties (hardness and young modulus) are examined as a function of substrate bias voltages in bipolar pulse mode. Positively and negatively pulsed voltages (V_p and V_n) are varied in the range of +10 to +50 V and -100 V to -200V, respectively. The films are composed of B, C, N and O and the composition are different according to the sample position faced to each target side of B_4C (BC-side) and graphite (G-side). It is found that the composition of both BC-side and G-side films does not clearly depend on V_p and V_n except for O which is decreased in concentration with increasing V_n. B-O bonds are also confirmed to be decreased as V_n increases. The films may be amorphous structure including h-BN bonds at low V_p but the crystallization of h-BN and B_4C is observed at high V_p. The hardness and young modulus tends to be increased with increasing V_n. The effectiveness of V_p and V_n is different between BC-side and G-side films.
Key words: BCN films, bipolar pulse, RF magnetron sputtering, nanoindenter, h-BN

1. INTRODUCTION

Ternary B-C-N compound has attracted much interest recently because of the possibility to have excellent properties, such as high hardness and chemical inertness, similar to diamond, diamond-like carbon (DLC) and cubic BN. Many researches on the preparation of BCN films have been done by chemical vapor deposition [1], laser ablation [2] and sputtering [3] methods. The cubic phase of BC_2N is expected to form if the atoms are bonded on equal terms in tetrahedral bonding sites. However, it is not realized to date, indicating difficulty to control the bonding state and the microstructure of BCN films.

On the other hand, it is pointed out that substrate bias voltage (ion bombardment effect) is important to form cubic BN phase [4]. By analogy with this, it is considered that the substrate bias voltage is also one of the important factors for the formation of BCN films. In a previous study, it is reported that the hardness of BCN films which included h-BN phase was increased when bipolar pulsed voltages as well as DC was applied to the substrate during deposition by RF sputtering [5-7]. The results suggested that ion bombardment must be effective for the enhancement of mechanical properties also in the case of BCN films. Thus, the control of the microstructure may be achieved by adjusting the parameters, such as ion energy and ion flux. However, ion energy is not always equal to the substrate bias voltage in our RF sputtering, since the working pressure of 2 Pa was needed at least to keep plasma discharge so that the mean free path of ions was roughly estimated to less than 0.4 mm, which was shorter than the ion sheath of about 2 mm estimated at substrate bias voltage of

-100 V. Therefore, higher vacuum is necessary in sputtering to control ion energy reliably by substrate bias voltage.

To obtain high vacuum sputtering, the equipment was reformed to magnetron-type so that BCN films can be prepared at a pressure as low as 0.3 Pa. In addition, from the fact that bipolar pulse mode also had much effect on the mechanical properties of BCN films [7], it is suggested that electron irradiation due to positively pulsed voltage plays an important role, possibly to reduce the charge-up effect on the surface of the films during deposition. In this study, BCN films are prepared at 0.3 Pa as a function of positively and negatively pulsed voltages (V_p and V_n) by RF magnetron sputtering and the microstructure and mechanical properties of the films are examined to make clear the effects of substrate bias voltages.

2. EXPERIMENTAL

Figure 1 shows illustration of RF magnetron sputter equipment. A couple of semicircle B_4C and graphite targets were set on RF magnetron electrode. A couple of Si(100) substrates were set on substrate holder faced to respective B_4C and graphite targets which were referred to BC-side and G-side films, respectively. A different location of the substrates resulted in a different composition of the films, as mentioned in section 3. A couple of permanent magnets were set on the upper sides of the chamber to make unbalanced magnetic field. Bipolar pulse voltage was applied to the substrate holder through the high-voltage feed-through. Typical conditions for sputtering and substrate bias voltages are listed in Tables I and II, respectively. The chamber was

evacuated to about 0.7 mPa by a turbo molecular pump and a mixture gas (99.999% purity) of Ar (10%) and N_2 was inlet to the chamber. Working pressure was kept 0.3 Pa. RF input power was kept 200 W at a frequency of 13.56MHz and deposition time was 30 min for all samples. The V_p and V_n were varied from +10 to +50 V and from -100V to -200V, respectively. Regrettably, the substrate temperature was not measured, although the substrate should be heated by ion and electron bombardment. To measure the substrate temperature, further modification of the equipment is necessary. Pulse frequency was 1 kHz and duty cycle was 0.5 ms for respective V_p and V_n. The thicknesses of the films are decreased with decreasing V_n, and these are varied from 650 – 390 nm for BC-side films and from 580 – 300 nm for G-side films, respectively.

Surface observation and compositional analysis were performed with FE-SEM/EDX system (XL-S30, Philips) at an accelerating voltage of 20 kV. The microstructure of the films was examined by FT-IR (GX1P, Perkin Elmer) and thin film XRD (RAD-2X, Rigaku) measurements. Hardness and young modulus of the films were obtained by Berkovich type nanoindenter (ENT-2100, Elionix) measurement. Maximum indentation depth for each sample was varied from 20 – 60 nm according to the film thickness. Loading and unloading times were 10 s and hold time was 5 s.
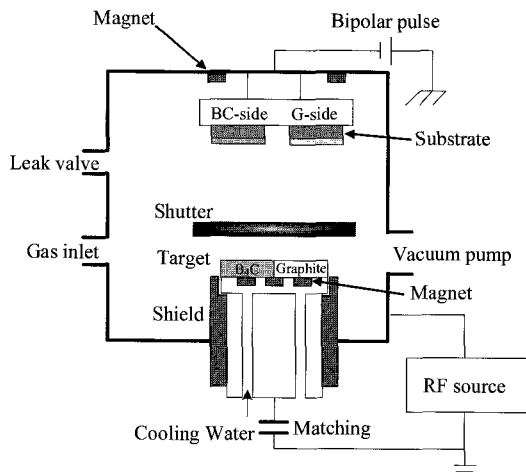
3. RESULTS AND DISCUSSION

FE-SEM observation revealed that the surfaces of the films were very smooth and featureless for all samples. However, the composition of the films was gradually changed according to the sample position from BC-side to G-side. In a previous study [6], the difference of the composition was at most within 5% if the area was selected within 10 x 10 mm^2. In this experiment, the Si substrates were set carefully at the same position for all depositions and the all measurements were carried out within 10 x 10 mm^2. Therefore, it is believed that this procedure makes the composition deference smaller and the conclusion is not significantly affected by the composition difference. Figure 2 shows that the changes in composition of the BC-side (a) and G-side (b) films obtained from EDX analysis. The signals from B, C, N and O elements are only observed so that the films are composed of B, C, N and O atoms without any other element. In the case of BC-side films (a), the concentrations of B, C and N is approximately 50%, 33% and 12%, respectively. No significant dependence of V_n is observed. However, the concentration of O is decreased with increasing V_n. On the other hand, in the case of G-side films (b), the concentrations of B, C, and N are approximately 40%, 46% and 12%, respectively. The concentration of O is also decreased with increasing V_n. A similar compositional variation of BC-side and G-side films was obtained at different V_p. These results suggest that the composition of the films is mainly determined by sample position except for O atoms.

Fig. 1. Illustration of an RF-magnetron sputter equipment.

Table I. Typical sputtering conditions.

Substrate	Si(100)	
Target	B_4C,	Graphite
RF power	200	(W)
Gas	Ar (10%) + N_2	
Pressure	0.3	(Pa)
Deposition time	30	(min)

Table II. Typical conditions for substrate bias voltage.

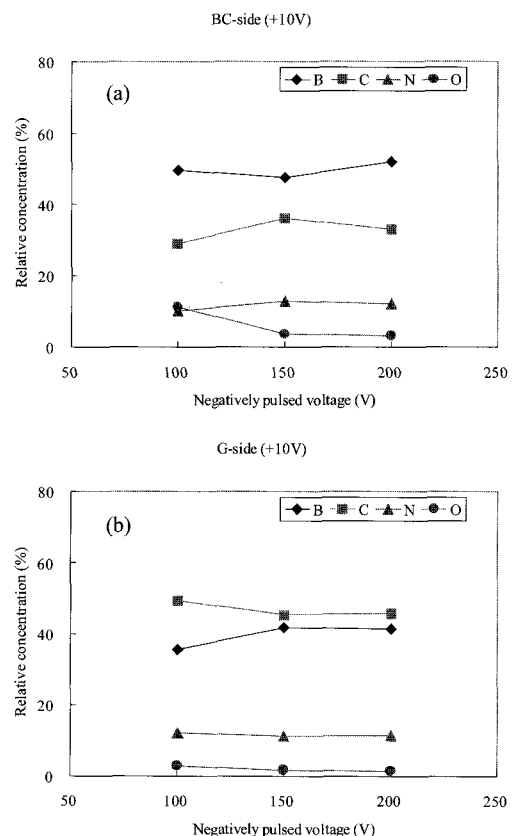| Positively pulsed voltage	+10, +30, +50	(V)
Negatively pulsed voltage	-100, -150, -200	(V)
Frequency	1	(kHz)
Duty cycle	0.5	(ms)

Fig. 2. Change in composition of BC-side films (a) and G-side films (b) prepared under the different negatively pulsed voltages at positively pulsed voltage of +10V.

Figure 3 shows FT-IR spectra of BC-side films (a) and G-side films (b) prepared under the different V_n at V_p of +10 V. The valley around 1550 cm^{-1} is observed for all spectra due to the air so that it should be neglected. In BC-side films (a), several broad peaks appear and the assignment is relatively complicated. At V_n of -100 V, broad peaks at 670 cm^{-1}, 1050 cm^{-1}, 1250-1390 cm^{-1}, 1650 cm^{-1}, 2200cm^{-1}, 3200cm^{-1} and 3350 cm^{-1} are observed. These peaks may be assigned to B-O-B bending, B-O stretching in BO$_4$ unit, B-O asymmetric stretching [8], N-H bending, C $\equiv$ N stretching [2], BO-H stretching [8] and N-H stretching [2] vibrations. With increasing V_n, however, a shoulder peak at 760 cm^{-1} appears and the peak broadened and centered at 1340 cm^{-1} is observed. The change of the peak shape should be caused by the decrease of B-O vibrations and the increase of h-BN vibration (760 cm^{-1} and 1380 cm^{-1}), C-C, B-C, C-N vibrations (1100 - 1300 cm^{-1}) and C=C, C=N vibrations (1500 - 1600 cm^{-1}) [2,6]. In addition, the increase of C$\equiv$N peak at 2200 cm^{-1} and the decrease of BO-H peak at 3200 cm^{-1} also observed. A similar result is obtained in G-side films (b). These results suggest that B-O bonds are decreased with increasing V_n. This tendency was also observed for all samples prepared at different V_p.
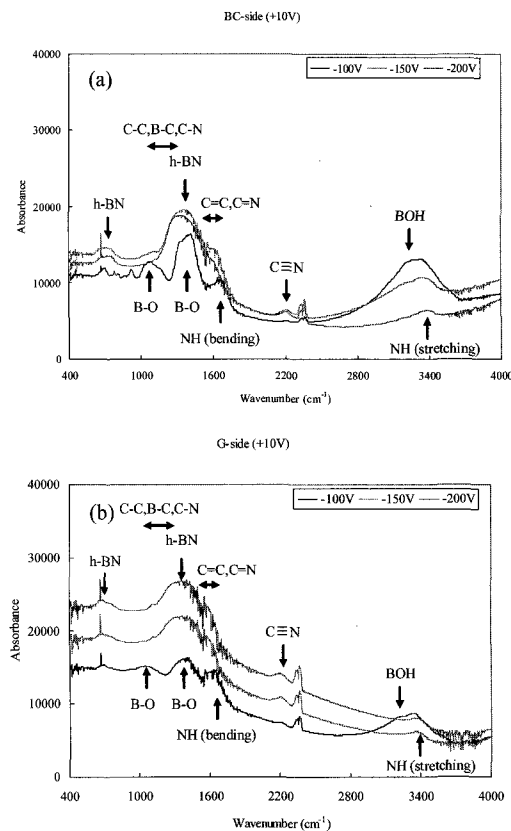

Fig. 3. FT-IR spectra of BC-side films (a) and G-side films (b) prepared under the different negatively pulsed voltages at positively pulsed voltage of +10V.

To examine the crystal structure in the films, thin film XRD measurements were carried out. At low V_p, no

significant peak was observed in spite of different V_n. Considering with the FE-SEM observation which shows the smooth and featureless surfaces of the films, this suggested that the films are presumably amorphous structure or composed of small crystallites. However, the increase of V_p caused the appearance of small bumps in XRD patterns. Figure 4 shows XRD patterns of BC-side films prepared under different V_n at V_p of +50 V. At V_n of -100 V, no apparent peak is observed. With increasing V_n, however, small bumps appear at 36.2° and 41.5° except for Si (111) peak at 28.4°. These peaks are also confirmed by slow scan XRD measurement, as shown in Fig. 4(a) and 4(b), and may arise from B$_4$C (021) and h-BN (100) planes. From these results, it is suggested that the crystallization may occur at higher V_p and V_n.
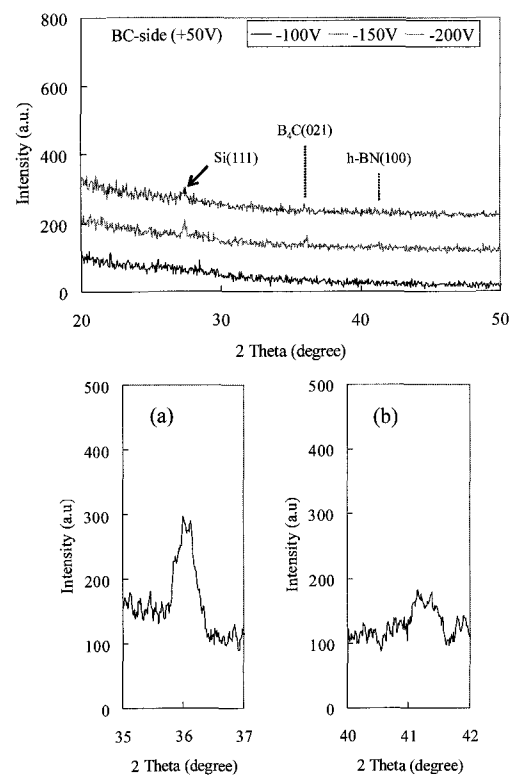

Fig. 4. XRD patterns of BC-side films prepared under the different negatively pulsed voltages at positively pulsed voltage of +50V.(a) and (b) indicate the results of slow scan XRD measurements for the film at -200 V.

Figure 5 shows the change in hardness of BC-side films (a) and G-side films (b) prepared under the different conditions of V_p and V_n. In BC-side films (a), the hardness is approximately 0.9 GPa at V_n of -100 V. However, the hardness is increased with increasing V_n. In addition, the hardness is also slightly increased with increasing V_p. Maximum value of 7.1 GPa is obtained when applying V_p of +50 V and V_n of -200 V. On the other hand, in G-side films (b), the hardness is increased with increasing V_p and V_n, too. However, the hardness appears to tend to approximately 6.5 GPa at higher V_n. Figure 6 shows the change in young modulus of BC-side

films (a) and G-side films (b). In BC-side films (a), the young modulus is increased with increasing V_n but appears to approach to approximately 60 GPa. In G-side films, the young modulus is also increased with increasing V_n from 40 to 80 GPa. These results show that the V_p and V_n clearly have much effect on the mechanical properties, such as hardness and young modulus, and the effectiveness of V_p and V_n is different between BC-side and G-side films which may arise from the difference in composition.
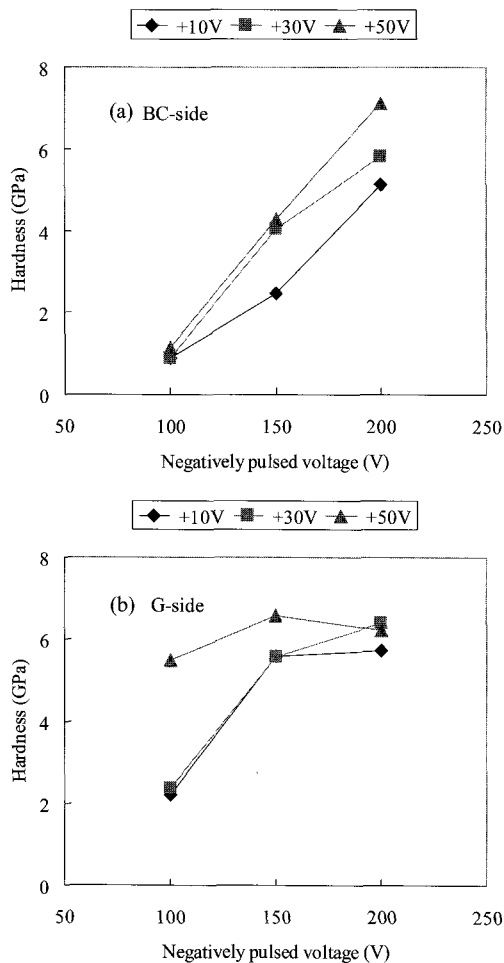

Fig. 5. Change in hardness of BC-side films (a) and G-side films (b) prepared under the different negatively and positively pulsed voltages.

The increase of V_n means the increase in ion energy. Thus, high-energy ion bombardment should take place at high V_n. The high-energy ion bombardment is believed to make the films dense. The EDX analysis shows the concentration of O is decreased with increasing V_n, as shown in Fig. 2. There are 2 possibilities: one is the oxidation during deposition, the other is the oxidation in the air after deposition. It is noted that the back pressure of the sputtering is less than 1 mPa and the purity of the Ar-N$_2$ gas is 99.999%, as mentioned in section 2. Considering with the fact that the samples were kept in the air for 135 – 161 days before the EDX and FT-IR measurements, it is believed that the oxidation during

deposition might proceed but the effect may be obviously low and the incorporation of O into the films mainly should occur in the air, and then the oxidation might be saturated after the samples are taken out from the chamber. This consideration is supported by the presence of BOH bonds, as shown in Fig. 3, which may be formed by the reaction with H$_2$O in the air. Although one might expect that the H concentration was quantitatively estimated by FT-IR peaks of BOH and NH bonds, it is difficult to calculate from the peak intensity by Lambert-Beer's law since the molar extinction coefficient at the observed wavenumbers for BCN material including BOH and NH bonds are unknown. However, it should be said that the H concentration is not beyond the O and N concentrations as far as assuming BOH and NH bonds. From the EDX analysis, as shown in Fig. 2, the concentrations of both O and N in the film are about 10 %. Therefore, the H concentration in the film is at most estimated to about 20 %, which is comparable to typical DLC films prepared by bipolar-type plasma based ion implantation technique [9]. It is noted that the value of 20 % is presumably overestimated as the above assumption that all O and N bond to H in the film is not realistic.
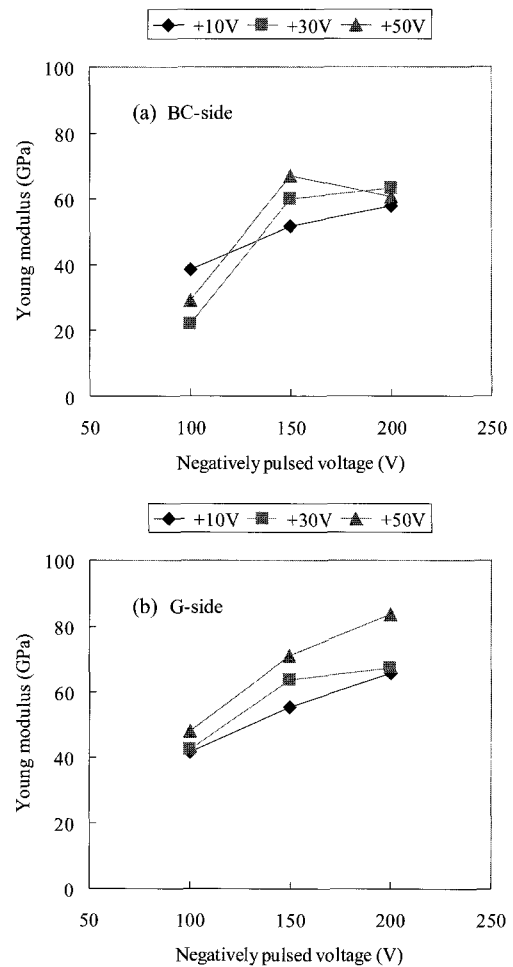

Fig. 6. Change in young modulus of BC-side films (a) and G-side films (b) prepared under the different negatively and positively pulsed voltages.

At higher V_n, however, dense structure may be formed so that the oxidation of the films does not proceed. In addition, increasing V_n causes the increase in hardness and young modulus of the films, as shown in Figs. 5 and 6. It is noted that bonding states are not significantly different between the films at V_n of -150 V and -200 V, as shown in Fig. 3. Judging from these results, it might be concluded that the increase in hardness and young modulus also should be caused by the densification of the films due to high-energy ion bombardment at high V_n.

On the other hand, the increase of V_p indicates the increase in electron energy, thus the high-energy electron irradiation may take place at higher V_p. It is expected that high-energy electron irradiation causes the sample heating. The results of XRD measurements show that the crystallization of h-BN and B_4C phases occurs at high V_p, as shown in Fig. 4. This fact is considered to be caused by electron heating at high V_p.

In the previous study [7], it was reported that the hardness was 8 GPa for BC-side film and 16 GPa for G-side film prepared at $V_p = +10V$ and $V_n = -100V$ at 2 Pa by RF sputtering before reforming to magnetron-type. In this experiment, however, the hardness was decreased to 1 GPa for BC-side film and 2 GPa for G-side film at the same bipolar pulsed voltages at 0.3 Pa by the reformed RF magnetron sputtering. The results were unexpected and the reason why the films were so softened is not known. The hardness of BCN films prepared by before-reforming RF sputtering was abruptly decreased to 4 GPa after thermal annealing at 600 °C in the air for 1 h [6]. Judging from this result, the oxidation might account for the softening of the films. To make clear this point of view, further study is underway.

The hardness of the BCN film is increased up to about 6 GPa in this experiment. A possible application is the passivation film on the semiconductor as a low k material, where the hardness of 6 GPa is enough to use. However, the value is relatively low as compared with that of DLC film (typically about 17 GPa) [10]. From the results of this experiment, indicating that the hardness is increased at least for BC-side films as V_n increases, it is believed that further increase of the substrate bias voltages must cause the increase of the hardness of the BCN films more and more. Then, high power bipolar pulse source will be applied to our RF magnetron sputtering system in future.

4. SUMMARY

BCN films are prepared by RF magnetron sputtering and the microstructure and mechanical properties (hardness and young modulus) are examined as a function of positively and negatively pulsed voltages (V_p and V_n). Our findings are as follows:

1. The surface is very smooth and featureless for all samples. The films are composed of B, C, N and O elements. The composition of the films are varied according to the sample position faced to semicircle B_4C (BC-side) and graphite (G-side) targets and do not apparently depend on V_p and V_n except for O atoms which are decreased at higher V_n.

2. B-O bonds are observed at low V_n of -100 V but decreased as V_n increases for both BC-side and G-side films. These films may be amorphous structure. However, the crystallization of h-BN and B_4C phases is observed at high V_p.

3. The hardness and young modulus of the films tend to be increased with increasing V_n. The effectiveness of V_p and V_n is different between BC-side and G-side films.

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