

The effects of substrate bias mode (DC, uni- and bipolar pulse) on the microstructure and mechanical properties of BCN films prepared by RF sputtering

Jongduk Kim, Setsuo Nakao, Junho Choi and Shojiro Miyake*

National Institute of Advanced Industrial Science and Technology (AIST), 2266-98 Anagahora, Shimosidami, Moriyama-ku, Nagoya 463-8560

Fax: 81-52-736-7406, e-mail: nakao.s@aist.go.jp

* Nippon Institute of Technology, 4-1 Gakuendai Miyashiro-machi Minamisaitama-gun Saitama 345-8501

Fax: 81-480-33-7745, e-mail: saburo@nit.ac.jp

Boron-Carbon-Nitrogen (BCN) films are deposited on Si (100) substrates by RF sputtering with a mixture of Ar and N₂ gases using a target of graphite combined with semi-circled boron carbide (B₄C). A couple of the films located at the positions faced to B₄C (BC) and graphite (G) sides are prepared at the same time, and their microstructure and mechanical properties are examined against the substrate bias modes, DC, uni- and bipolar pulses. The films are also examined as a function of the duty cycle in unipolar pulse. The results show that the concentration of C in the G side films is larger than those of the BC side films. For the unipolar pulse mode, the composition and the surface morphology are not significantly affected by the duty cycle. However, the maximal of the mechanical properties of the G side film in hardness and wear resistance are obtained at the duty cycle of 500 μ s. For the bipolar pulse mode, h-BN phase is increased in amount as compared with the unipolar pulse mode. In addition, the B concentration is increased and the mechanical properties are decreased in the BC side films, while, the N concentration is increased and the mechanical properties are increased in the G side films. These effects of the bipolar pulse mode are similar to those of the negative DC mode.

Key words: RF sputtering, BCN film, unipolar pulse, bipolar pulse, h-BN, nanoindentation

1. INTRODUCTION

The ternary B-C-N films have attracted considerable attention in recent years for the potentially interesting properties of this system. The films are classified as super hard coatings, and even their amorphous films also have excellent mechanical and optical properties. Several methods of preparing BCN films have been reported, such as sputtering [1-7] and chemical vapor deposition (CVD) [8]. In the case of CVD, various source gases including B element are used, but they are usually very toxic otherwise very expensive. Therefore, the CVD process to deposit BCN films is not always convenience in handling in industrial application. In contrast to the CVD process, solid phase targets including B, such as h-BN and B₄C, combined with graphite are usually used in the sputtering deposition. This indicates that the sputtering process is safer and more convenience in handling than the CVD process. Therefore, it is believed that the sputtering is suitable to the BCN coatings. However, to control the microstructure and mechanical properties by changing deposition parameters still remain difficult in synthesizing BCN compounds by sputtering method. In particular, synthesis of cubic BCN structure is not realized up to date.

Substrate bias voltage is considered to be an important parameter in sputtering method. In fact, it is reported [9] that cubic BN films can be formed when applying negative DC bias voltage at high temperature. By analogy, negative DC bias voltage has also been applying to the substrate in the BCN film deposition by several researchers [1-3]. In a previous paper [1], it was reported that the hardness of BCN films deposited at negative DC bias voltage of -100 V is higher than that at no bias voltage when using a target of graphite and semicircle B₄C in RF sputtering. This suggests

that ion bombardment is effective to the improvement of the mechanical properties of the films. However, in DC bias voltage, the growing surface of the films should be charged up since BCN compound is electrical insulator. The charge-up-effect may prevent to assure of the control of the microstructure and mechanical properties of BCN films by the substrate bias voltage. Attempts of RF substrate bias were made [5,6], but the films were decreased in thickness with increasing RF power due to sputtering effect. On the other hand, one may expect that pulse bias mode, such as uni- and bipolar pulse voltages, is able to reduce the charge-up-effect on the growing surface of the films as compared with DC bias mode. However, the preparation of BCN films applying pulse bias voltage has rarely been attempted [7] as far as our knowledge.

In this work, BCN films are prepared under the different substrate bias modes, DC, uni- and bipolar pulse voltages, by RF sputtering method. The BCN films are characterized by energy dispersive X-ray spectroscopy (EDX), Fourier transform infrared spectroscopy (FT-IR), atomic force microscopy (AFM), nanoindentation and nanowear test.

2. EXPERIMENTAL

Figure 1 shows the schematic illustrations (a) the RF sputtering equipment and (b) the position relation between samples and sputtering target. The chamber was evacuated at approximately 2×10^{-4} Pa prior to the deposition using a turbo molecular pump. Then, a mixture gas of Ar 10% - N₂ 90% was inlet to the chamber. The working pressure was kept about 3 Pa during the deposition. The RF power was 300 W at a frequency of 13.56 MHz. The deposition time was 1 hour. The distance between the target and the

substrate was kept at 50 mm. The sputtering target was composed of a B₄C semicircle-disk of 40 mm in radius put on a graphite circle-disk of 80 mm in diameter. Two Si substrates (2×1.5 cm²) were attached to the substrate holder and faced to each side of B₄C (BC side) and graphite (G side) of the target. The bias voltages of DC, uni- and bipolar pulses were applied to the substrate through the substrate holder. The substrate bias conditions are listed in Table I. The frequency of pulses was kept at 1 kHz so that the cycle period was 1 ms. The potential of unipolar pulse was -100 V and the duty cycle was varied in the range of 250 to 750 μs. In the case of bipolar pulse mode, +10 V was applied for 500 μs, and consequently -100 V was done for 500 μs. The DC bias voltage was -100 V. These substrate bias modes were denoted by P1, P2, P3, P4 and DC, respectively. The thicknesses of the films of BC and G sides were also listed in Table I.

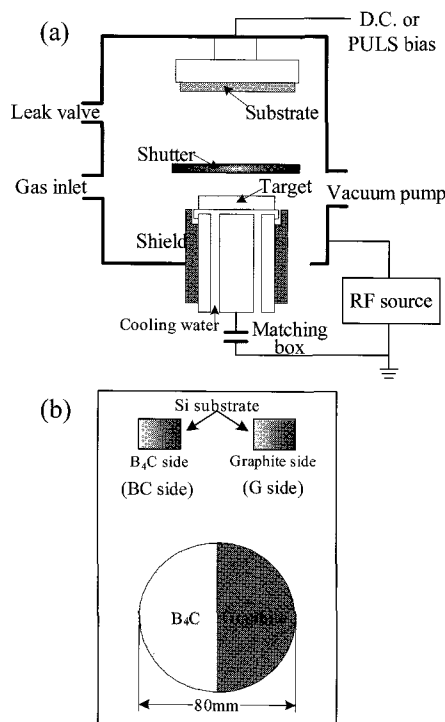


Fig. 1. Schematic illustrations of (a) the RF sputtering equipment and (b) the position relation between samples and sputtering target.

Table I. Conditions on the substrate bias mode and thicknesses of the deposited films.

No.	Substrate bias mode	Voltage (V)	Frequency (kHz)	Duty cycle (μs)	Thickness (nm)	
					BC side	G side
P1	unipolar pulse	-100	1	250	490	540
P2	unipolar pulse	-100	1	500	680	680
P3	unipolar pulse	-100	1	750	580	690
P4	bipolar pulse	+10, -100	1	500, 500	810	320
DC	direct current	-100	-	-	800	680

FTIR (Spectrum GX, Perkin-Elmer) was used to characterize the phase structure at the transmission mode in the range of 500 - 2000 cm⁻¹. The background spectrum of

an uncoated Si substrate was also measured to calculate the absorption coefficient, α (cm⁻¹) of the deposited films. The composition of the films was evaluated by EDX (XLS30, Philips) which was able to detect elements from B to U. The surface images of the films were obtained by AFM system (SPA300, Seiko Instrument Inc.) and the root mean square (rms) roughness was determined in the scan area of 2 μm x 2 μm. Nanowear tests were also conducted using the AFM system by dry sliding of a 100-nm-radius diamond-coated Si tip applying a constant normal load of 40 μN on the sample surface in scans. The scan area was 500 nm x 500 nm and the tip-sliding frequency was 2 Hz. After nanowear testing, the surface images of the wear craters were taken again by the AFM mode. Nanoindentation tests were carried out by nanomechanical test instrument (TriboScope, Hysitron Inc.) equipped with AFM system. The hardness and elastic modulus were evaluated from the loading-unloading curves. A fused quartz with a reduced elastic modulus of 69.6 GPa was used to calibrate the area function of the Berkovitch indenter tip.

3. RESULTS AND DISCUSSION

A couple of the films were prepared at the same time, as shown in Fig. 1(b). According to the sample positions (BC and G sides), the composition of the deposited films was significantly changed. Figure 2 shows typical EDX spectra of BC and G side films deposited at the substrate bias mode of P1. For the both spectra, the signals of B, C, N and O are observed, indicating that the both films are composed of B, C, N and O. The concentration of each element is obtained from the peak intensity, as shown in Fig. 3 and mentioned next paragraph. For the G side film, the concentrations of B and N are decreased and that of C is increased in comparison with the BC side film. On the other hand, the concentration of O is independent of the sample position and merely 0.4% for the both films. Therefore, O is extrinsic element which may be adsorbed on the surface of the films during sample handling in the air. Hereafter, the concentration of O is neglected and the relative concentration of B, C and N are discussed simply.

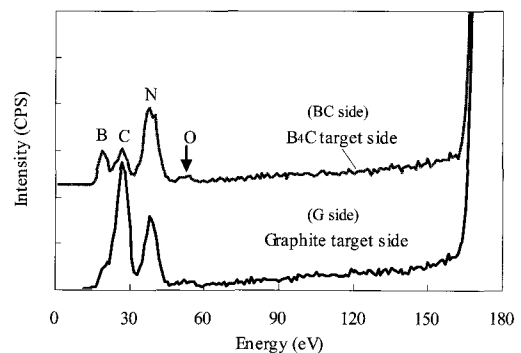


Fig. 2. EDX spectra of the films prepared at the substrate bias mode of P1.

Figure 3 shows the change in the relative concentration of B, C and N of the (a) BC and (b) G side films obtained from EDX spectra against the various substrate bias modes,

as listed in Table I. For the unipolar pulse modes, P1 – P3, the concentrations of B, C and N are not significantly changed against the duty cycle in the BC side films. The same trend is also observed in the G side films. However, the concentrations are apparently changed for the bipolar pulse mode, P4, in comparison with the unipolar pulse mode. The B concentration is increased in the BC side film, and the N concentration is increased in the G side film. A similar tendency is also observed in the respective side films for the DC mode.

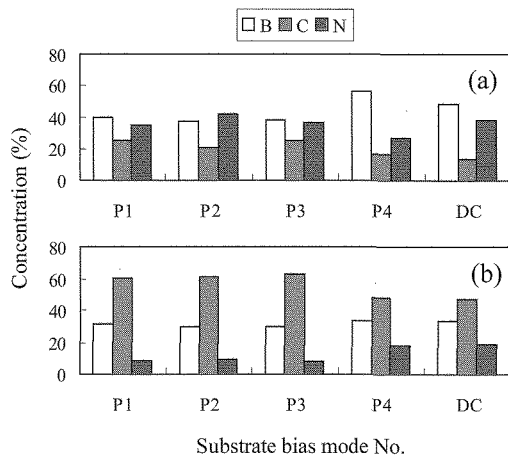


Fig. 3. Relative concentration of B, C and N of the (a) BC and (b) G side samples obtained from EDX spectra against the substrate bias modes.

Figure 4 shows the FT-IR spectra of the (a) BC and G side films deposited under the different substrate bias modes. In the BC side films (a), a small peak at 780 cm^{-1} and an apparent peak at 1400 cm^{-1} are observed for all of the substrate bias modes. These peaks are assigned the out-of-plane B-N-B bending vibration and the in-plane B-N stretching vibration of h-BN structure, respectively [1-3]. However, the peak at 1400 cm^{-1} of the films is broader than that of h-BN bulk sample. Two shoulder peaks, indicating by A and B in Fig. 4, are recognized at around 1200 cm^{-1} and 1580 cm^{-1} , respectively. The shoulder peak A can be assigned the overlap of the peaks of B-C (1174 cm^{-1}) and C-N (1272 cm^{-1}) vibrations, and the shoulder peak B can be assigned the overlap of the peaks of C=N (1540 cm^{-1}) and C=C (1600 cm^{-1}) vibrations [1-3]. In the BC side films for the unipolar pulse mode, any significant difference is not observed among the spectra of P1 – P3. However, for the bipolar pulse mode, P4, the peak of h-BN is increased in intensity as well as for the DC mode. In the G side films (b), the peak of h-BN is decreased in intensity for all of the films as compared with the BC side films. This fact is consistent with the results of EDX measurement, showing that the C concentration is increased in the G side films, although the change of IR signals from C=C bonds is little due to low IR sensitivity. The similar tendency against the substrate bias modes is observed among the spectra of P1 – P4 and DC also in the G side films.

The fact that the IR signal from h-BN is increased in intensity for P4 and DC indicates that h-BN phase in the both side films is increased in amount as compared with P1 – P3. This result is also consistent with the results, showing the increase of B and N in the BC and G side films,

respectively, for the bipolar pulse and DC modes.

Figure 5 shows the AFM images of the BC and G side films deposited under the different substrate bias modes. The root mean square (rms) values of the surface roughness are also indicated. For the unipolar pulse mode, the both BC and G side films appear to be composed of many grains of 66.5 nm in average. Significant difference of the duty cycles in surface morphology among the BC and/or G side films is not observed, although the rms values are relatively scattered so that the relationship between the rms values and the duty cycle or the sample position is unclear. For the bipolar pulse mode, the both side films also appear to be composed of many grains of 77.1 nm in average. It is noted that the surface of G side film is very smooth, showing the lowest rms value of 1.2 nm . On the other hand, for the DC mode, many grains are also observed and the size of the grains is increased to 109.8 nm in average as compared with those for the uni- and bipolar pulse modes. These results suggest that the substrate bias mode evidently has effect on the surface morphology of the films.

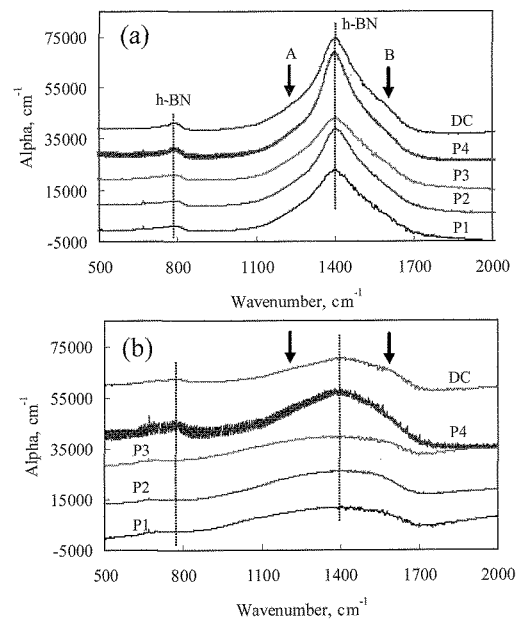


Fig. 4. FT-IR spectra of the (a) BC and (b) G side samples prepared under the different substrate bias modes.

Figure 6 shows the hardness and elastic modulus of the BC and G side films against the substrate bias modes of P1 – P4 and DC. For the unipolar pulse modes of P1 – P3, the hardness of BC and G side films are not significantly different and ranged from $9.2\text{ -- }11.2\text{ GPa}$ except for the G side film of P2 (13.6 GPa). This result suggests that the maximal value of the hardness in the G side films is obtained at the duty cycle of $500\text{ }\mu\text{s}$. For the bipolar pulse mode, the hardness of the BC side film is decreased to 8.2 GPa and that of the G side film is increased to 16.0 GPa . The same trend as the divergence of the difference in hardness is also observed in the DC mode. The variation of the elastic modulus against the sample positions and the substrate bias modes is found to be similar to that of the hardness.

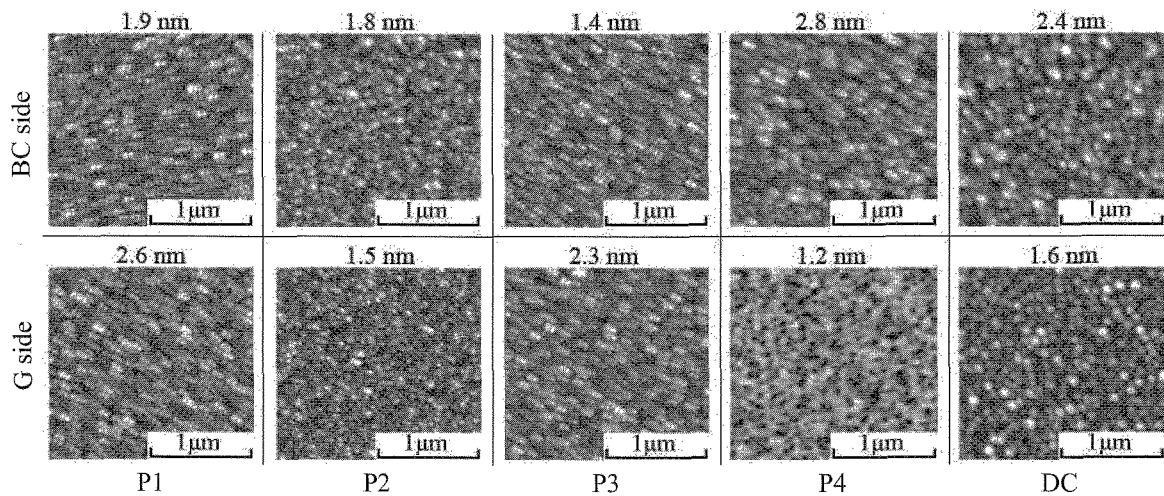


Fig. 5. AFM images of the BC (up side) and G (down side) side samples prepared under the different substrate bias modes. The root mean square (rms) values of the surface roughness are also indicated on the top of the respective images.

Figure 7 shows the results of the nanowear tests on the BC and G side films against the substrate bias modes. For the unipolar pulse modes, P1 – P3, the maximal and minimal values are observed in the BC and G side films deposited at the substrate bias mode of P2 (the duty cycle of 500 μ s), respectively. The difference in wear depth between the BC and G side films is further diverged for the bipolar pulse mode. In contrast to the bipolar pulse mode, the wear depth of the both side films is decreased for the DC mode. It is common sense that the wear resistance property is related to the hardness and the friction coefficient of the surface. The BC side films do not always indicate significant difference in hardness as shown in Fig. 6. Therefore, the differences of the BC side films in wear depth mainly arise from the different friction coefficients of the samples. From these results, it is assumed that the duty cycle and the substrate bias mode may affect not only the hardness but also the friction coefficient of the deposited films.

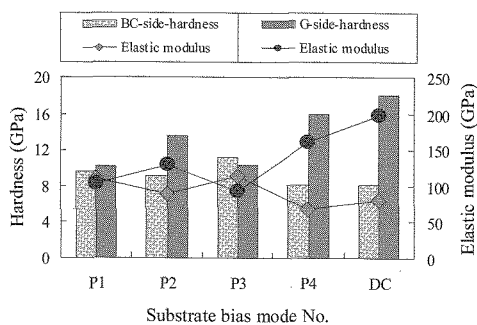


Fig. 6. Hardness and elastic modulus of the BC and G side samples measured by nanoindentation test against the substrate bias modes.

In the case of the unipolar pulse mode, the composition and the bonding state estimated from FT-IR spectra are not significantly changed by the duty cycle, as shown in Figs. 3 and 4. In addition, the surface morphology is similar for all of the BC and G side films, as shown in Fig. 5. In the mechanical properties, however, the G side film deposited

at the duty cycle of 500 μ s indicates the maximal hardness and minimal wear depth among the films of P1 – P3, as shown in Figs. 5 and 6. These results suggest that the mechanical properties are more sensitive to the duty cycle than the composition and the bonding state of the films, especially in the G side films. It is believed that the charge-up-effect is reduced with decreasing the duty cycle. However, the effective negative voltage is also decreased as the duty cycle decreases, resulting in the reduction of ion bombardment effect on the improvement of the mechanical properties. From above consideration, it is reasonable that the maximal of the mechanical property is obtained at the duty cycle of 500 μ s. Considering with the previous reports [1,2] indicated that the mechanical properties may be closely related to not only the C concentration but also the dense structure of the films, it is assumed that the improvement of the mechanical properties of the G side films may arise from the dense structure formed by the efficient ion bombardment at the duty cycle of 500 μ s.

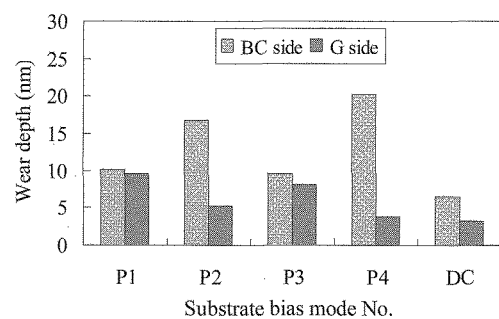


Fig. 7. The results of nanowear test on the BC and G side samples using sliding of diamond-coated Si tip against the substrate bias modes.

In comparison with the unipolar pulse mode, the variation of the composition, FT-IR spectra and the hardness of the films for the bipolar pulse mode are similar to those for the DC mode, as shown in Figs. 3, 4 and 6. Slight differences between the films for the bipolar pulse and DC modes are obtained in the surface morphology and

the wear resistance property, as shown in Figs. 5 and 7. It is noted that the effective negative voltage of the bipolar pulse is only the half of negative DC voltage, i.e., the duty ratio of 50%. In spite of this, it is interesting that the bipolar pulse mode causes the similar effect of the DC mode. Since the bipolar pulse mode is also believed to reduce the charge-up-effect as compared with the DC mode, it might be said that the mechanical properties of the films are improved by efficient ion bombardment in the case of the bipolar pulse mode. This consideration is consistent with the fact that the concentration of N is increased in the G side films, possibly caused by N ion implantation. The effect of the positive pulse voltage of the bipolar pulse mode is not known but the observed slight differences in surface morphology and mechanical properties may be due to the positive pulse voltage. To make sure this point of view, further investigation on the bipolar pulse mode is in progress.

4. SUMMARY

BCN films are deposited on Si substrates by RF sputtering using the target of graphite and semicircle B₄C in an Ar-N₂ gas mixture. A couple of the films, faced to the respective target sides of B₄C (BC side) and graphite (G side), are obtained at the same time. The microstructure and mechanical properties of the both BC and G side films are examined against the different substrate bias modes, DC, uni- and bipolar pulses. In the case of unipolar pulse mode, the effects of the duty cycle are also examined. Our findings are as follows:

- (1) the substrate bias mode
 - (A) In the BC side films, the B concentration is increased together with the increase of h-BN phase, and the decrease of the mechanical properties in hardness and wear resistance is observed for the bipolar pulse mode as compared with the unipolar pulse mode. The surface morphology is similar between the uni- and bipolar pulse modes.
 - (B) In the G side films, on the other hand, the C concentration is larger than that in the BC side films.

In addition, the N concentration is increased also together with the increase of h-BN phase, and the increase of the mechanical properties is observed for the bipolar pulse mode. The smooth surface of 1.2 nm in rms is obtained at the bipolar pulse mode.

- (C) The effects of the DC mode are similar to those of the bipolar pulse mode, although the slight differences in surface morphology and mechanical properties are observed.
- (2) the duty cycle

Any significant difference is not always observed in the composition, the FT-IR spectra and the surface morphology of the films due to the difference of the duty cycle for the unipolar pulse mode. However, the maximal value of the hardness and the increase of wear resistance are found in the G side film prepared at the duty cycle of 500 μ s.

Judging from the results, it is concluded that the pulse bias voltages evidently have effect on the microstructure and mechanical properties of the BCN films.

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(Received December 10, 2006; Accepted May 15, 2007)