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Deposition of B-C-N films by Sputtering and their Mechanical Properties

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Ternary Boron-Carbon-Nitrogen (BCN) thin films were deposited onto silicon substrates by RF sputtering with a mixture gas of nitrogen and argon. Carbon contents of the BCN films were changed using a carbon (C) target combined with a semi circled born carbide (B_4C) target. The fine BCN structure and mechanical properties were examined by Fourier transformation infrared spectroscopy (FT-IR), microwear test and nanoindentation hardness measurements. The FT-IR analysis for as-deposited film proved the presence of partially crystallized h-BN. The structure did not change after thermal annealing at 400 and 600℃. Hardness was varied in the range of 8-18 GPa, and it was increased as the carbon content increased.
Key words: RF sputter, BCN film, h-BN, nanoindentation, microwear

1. INTRODUCTION

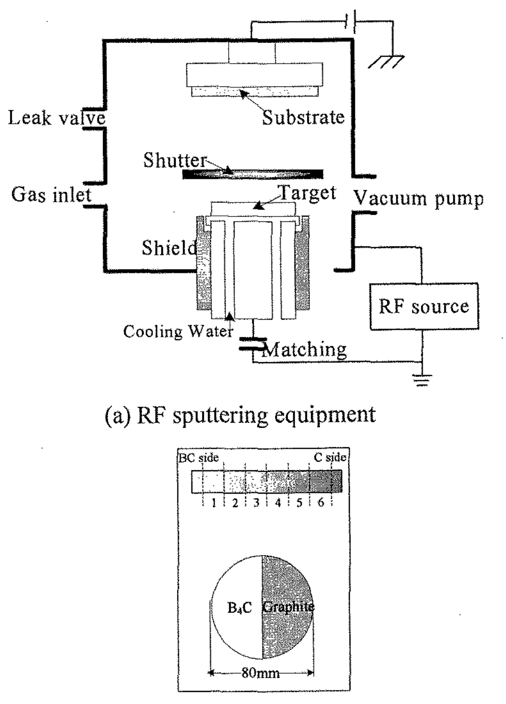
Very thin films deposited on the surface of other materials are extremely important to many technology-base industries. Recently, high attention is paid to the preparation of diamond-like carbon (DLC) film owing to its excellent characteristics and practical use in advanced technologies [1-3]. However, when DLC film is deposited on ferrous materials, the required properties are not achieved due to the diffusion and carbon transfer during application. Moreover, it is difficult to apply them as protective film on plastics optical components like lenses since these films are opaque [4].

Therefore, it is a high demanded on super hard film for ferrous materials. One of the candidates is boron-carbonitride (BCN) film. Higher stability at elevated temperatures compared to DLC films is expected for BCN coatings. In addition, B, C and N are the light elements of super hard materials like diamond (C), cubic boron nitride (c-BN), and carbon nitride (β-C_3N_4). If the nano-structure of BCN is controlled mechanical properties for BCN films are expected to be better than those for DLC films [5-7]. It is reported to obtain the BCN film with the mechanical property without inferiority compared with the DLC film by used the targets of h-BN and graphite so far [8]. However, stability in the high temperature atmosphere of the BCN film has not been reported up to now.

The aim of this work is to prepare a stable BCN thin film with excellent mechanical properties and high temperature stability. In this report, influence of the annealing in the air and the mechanical property by the change in the amount of C was examined.

2. EXPERIMENTAL

Figure 1 shows a schematic illustration of the RF sputtering equipment used in this experiment. The deposition conditions are summarized in Table I. An 80 mm diameter target of sintered boron carbide (B_4C) target was used. The RF power was 100 W, 200 W and 300 W. Moreover, two semicircle graphite (C) and B_4C targets were used in order to change content of carbon in the film. System base pressure prior to deposition was approximately $1\text{-}2\times10^{-4}$ Pa. Thin films were deposited on a Si (100) wafer (2×8 cm^2) using N_2 or the mixture of N_2 and Ar (90%:10%) gas. A working pressure of about 3 Pa was fixed during sputtering. The distance from



(a) RF sputtering equipment

(b) Position of targets and sample

Fig. 1. Schematic illustration of the RF sputtering equipment used in this experiment.

the substrate to the target was about 50 mm. The deposition time were varied in the range of 1-4 h, so that the thickness of the films also was varied from 0.7-1 μm. The nanoindentation hardness of the films using an AFM (atomic force microscope) with a Berkovich-type diamond indenter under a load of 300 μN at an indentation time of 6 s. To evaluate the microwear properties, we used AFM with a very sharp diamond tip of nearly 0.1 μm radius with 10–90 μN load. The film composition was measured with Rutherford backscattering spectroscopy (RBS) and Energy Dispersive X-ray (EDX). Electric furnace was used for annealing at 400, 600, and 800℃ for each 1 h in the air.

Table I. Deposition Conditions for BCN films by RF sputtering.

Target	B_4C, B_4C+C
RF Power(13.56MHz)	100~300W
Substrate	Si(100)
Gas Pressure	3.0Pa
Gas flow ratio	3~5sccm
Substrate DC bias	0 ~ -100V
Deposition time	60~240 min
Thinkness of films	700 ~1000 nm

3. RESULTS AND DISCUSSION

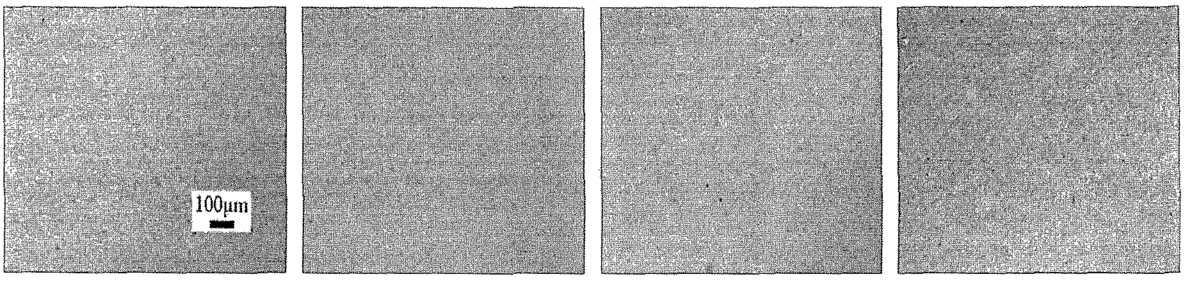
3.1 BCN films that used boron carbide target

The optical micrographs of heat-treated films are shown in Fig. 2. These films were deposited in N_2 plasma at the RF power of 300 W. The thickness of the film was 1.0 μm. There is no visible difference between the as deposited and annealed BCN films at different temperatures. Peeling of the deposited layer was partially observed after annealing at 800℃.

The influence of RF power (100, 200 and 300 W) and annealing temperature on the microstructure of BCN film analyzed by FT-IR spectroscopy is shown in Fig. 3. The peaks of h-BN at 790 cm^{-1} and 1400 cm^{-1} are visible in as grown and annealed samples up to 600℃. The peaks are broader as the annealing temperature increase. These peaks nearly disappear after annealing at 800℃ as show in Fig. 3a. The h-BN peaks are sharper in the film deposited at 300 W as compared with the films deposited at 100 and 200 W, while SiO_2 peaks are weaker. On the other hand, the absorption peaks of SiO_2 appear at 800℃.

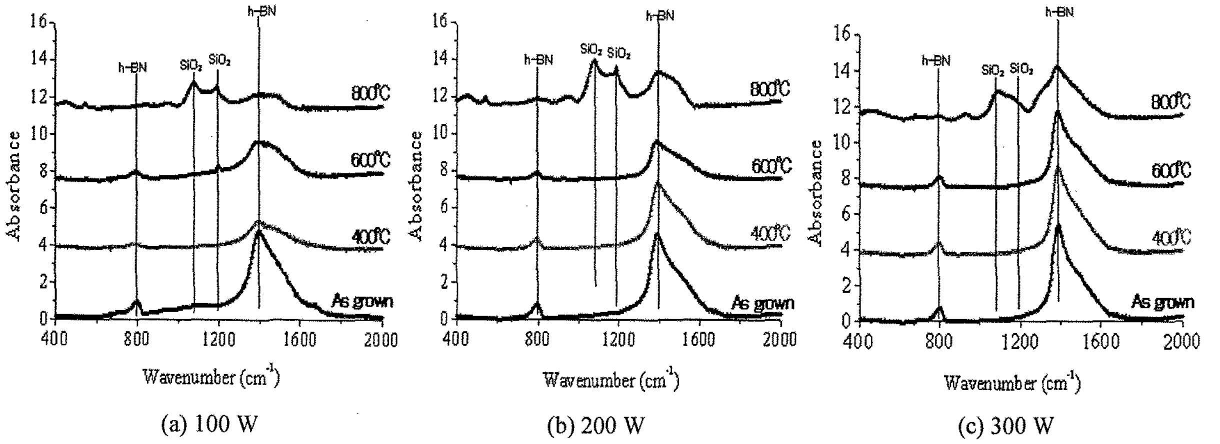
The results of RBS composition analysis of BCN film deposited at 300 W are shown in Fig. 4. The areal density of carbon is about 1/4 of those of nitrogen and boron. With increasing annealing temperature, the areal densities of B, C and N are decreased. The signal of Si is not detected until 600℃, although it is detected at 800℃ from Si substrate as the film is partially peeled. This suggests that the film is stable until 600℃ in the air.

The results of nanoindentation hardness of these BCN films were 5-9 GPa. The mechanical properties of the BCN films were influenced by the amount of carbon [9-10].



(a) As grown (b) 400℃ (c) 600℃ (d) 800℃

Fig. 2. Optical micrographs of BCN films before and after heat treatment.



(a) 100 W (b) 200 W (c) 300 W

Fig. 3. Changes of FT-IR spectra of BCN films due to annealing temperature. The films were deposited at (a) 100 W, (b) 200 W and (c) 300 W.

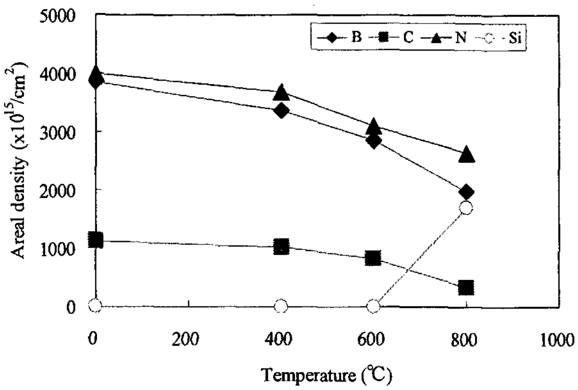
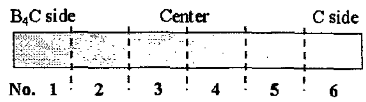


Fig. 4. Compositional change of BCN films due to annealing temperature measured by RBS.



·Model of measured sample

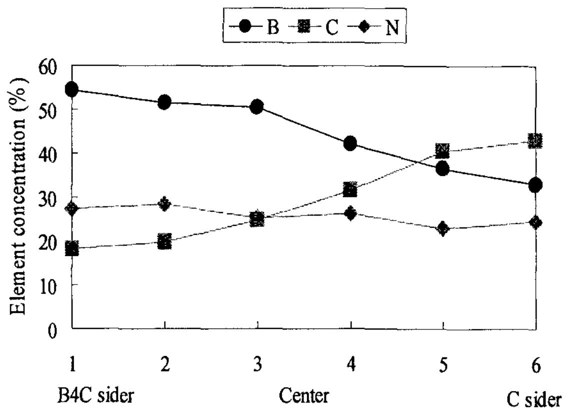


Fig. 5. The EDX quantitative analysis on the BCN films deposited by semicircular (C and B_4C) targets.

3.2 BCN films that used boron carbide and graphite targets

As for the BCN film as mentioned in section 3.1, the amount of C is relatively small in comparison with B and N in the case of B_4C target alone. BCN films were deposited by a semicircular target of B_4C on to graphite target (Fig. 1b).

Figure 5 shows the qualitative analysis of the BCN film by Energy Dispersive X-ray (EDX). The boron showed about 55% on B_4C target side, about 50-40% in the center. And, there is a tendency to decrease 32% on C target side. The carbon is about 18% on B_4C target side, about 20-30% at the center, and 43% on C target side. The element content of the carbon shows the tendency to increase on the carbon target side in the film. The nitrogen content is 20-30% in each film.

Figure 6 shows the FT-IR spectrum of these samples. The peaks of h-BN at 790 cm^{-1} and 1400 cm^{-1} are visible in all samples. Small peaks at 790 cm^{-1} indicate B-N-B vibrates in h-BN, and belong to the B-N vibrations in h-BN of strong peaks at 1400 cm^{-1} [11]. Therefore, the made film obviously contains B-N bond. It is thought that

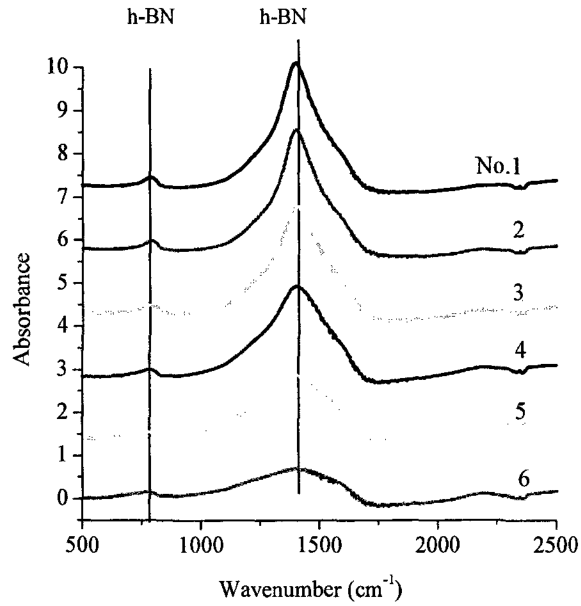


Fig. 6. FT-IR spectra of the BCN films in the differentamount of carbon.

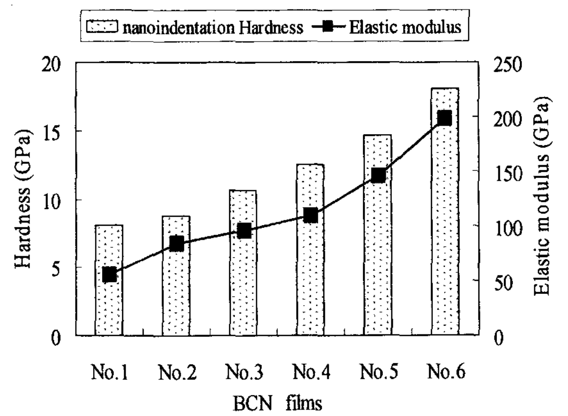


Fig. 7. Nanoindentation hardness of BCN films in the different amount of carbon.

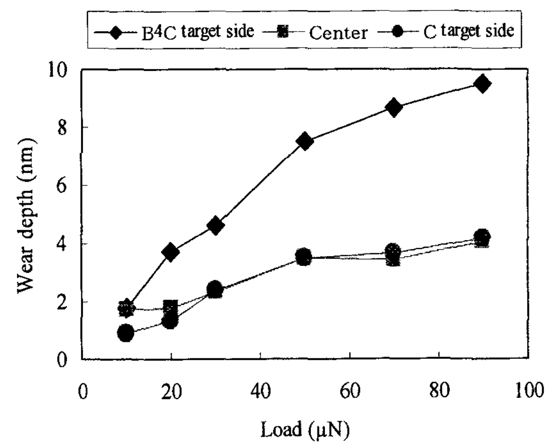


Fig. 8. Microwear depth of BCN films deposited by semicircular C and B_4C targets.

1400 cm^{-1} peaks are considerably wide compared with only BN, and bonding other than B-N bond exist, too. The h-BN peak becomes a broad on the carbon side though the peak is clear on B_4C side. This is because a lot of carbon elements are contained in the film on the carbon target side.

Figure 7 shows the nanoindentation hardness of BCN films at 6 parts of a film (as show in Fig. 5). The nanoindentation hardness is about 8 GPa on B_4C side. However, it increases about 11 GPa in the center and about 18 GPa on C side. The amount of the carbon on the hardest C side was 43%. Moreover, elastic modulus also increases with hardness increases. It is found from this result that the hardness of the film is high when the amount of carbon is large.

Figure 8 shows the microwear depth of BCN films deposited by semicircular C and B_4C targets. The BCN film on the center and B_4C target side became 1.7 nm microwear depth of with 10 μN. The BCN film on C targets side was the lowest value of 0.8 nm. The center and C side are almost the same microwear depth in load 30-90 μN. On the other hand, the microwear depth of B_4C side depends for the load and 9.5 nm in microwear depth is shown with 90 μN. The microwear depth shows a similar tendency to nanoindentation hardness.

4. CONCLUSIONS

Ternary Boron-Carbon-Nitrogen (BCN) thin films were deposited onto silicon substrates by RF sputtering. And, their mechanical property was evaluated. These results are summarized as follows.

- The thermal annealing up to 600℃ did not have an effect on the composition of the film. But, degradation of the BCN film was observed after annealing at 800℃.
- Hardness and wear resistance were improved as the amount of the carbon increases in the BCN film.

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