PREPARATION OF CUBIC BORON NITRIDE FILMS BY RF BIAS SPUTTERING

Osamu Tsuda, Yukiko Yamada, Yoshinao Tatebayashi
and Toyonobu Yoshida

Department of Metallurgy and Materials Science, Faculty of Engineering, TheUniversity of Tokyo, 7-3-1 Hongo, Bunkyo-ku Tokyo, 113 Japan

Abstract

Cubic boron nitride (cBN) films were successfully prepared by the phase-regulated rf bias sputtering with the aid of magnetic field. The effects of the substrate bias voltage (V_S), the working gas pressure (p) and the deposition time were investigated systematically. Cubic phase was formed in the films deposited with V_S above the threshold which depended on p. Even at p = 0.4 mTorr, cBN films were grown with V_S above 100 V. The prepared cBN films had a double-layered structure which consists of an initially deposited layer of sp^2 phase and a layer of cubic phase subsequently grown. The maximum growth rate of the cubic layer was estimated to be approximately 1 nm/s. Stress measurements of the cBN films were also carried out, revealing that the cBN films had compressive stress of a few GPa.

1. INTRODUCTION

Cubic boron nitride (cBN), which is thermodynamically stable under high pressure and high temperature similar to diamond [1], has unique and attractive properties such as high hardness, strength, chemical stability and wear resistance. In addition, in some properties, such as thermal stability in oxygen atmosphere, chemical inertness with ferrous materials, and possibility of n type doping, cBN is a superior material to diamond. Recently, several researchers have reported the deposition of cBN films by PVD [2,3] or CVD [4,5] methods with ion bombardment to a growing surface. Rf bias sputtering is one of the techniques utilized for cBN synthesis [6,7], in which negative rf self-bias is applied to the substrate in order to enhance the ion bombardment. In rf bias sputtering, interference and dephasing between the two rf power inputs may disturb the energy distributions of charged particles and affect deposition process assisted by ions and/or electrons, particularly for the case of using two rf sources with almost an identical frequency [8]. The authors have developed an rf sputtering system having synchronizable rf sources and regulated the difference of the phase angles of the rf voltages. By this technique it was revealed that the phase angle difference is one of the deposition parameter which affect cBN formation [9]. Additionally, an unbalanced magnetic field was employed in this study in order to confine the plasma and enhance the ion flux [10] because high ion flux to the substrate is expected to be an important condition for cBN formation.

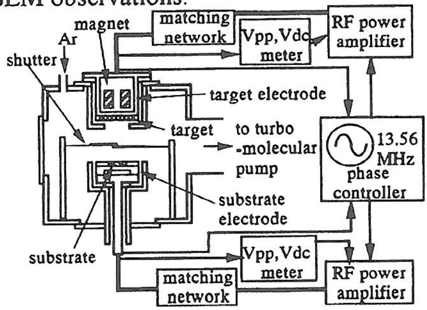
In the present work, using the phase-regulated rf bias sputtering enhanced by a magnetic field, we have investigated influences of the substrate bias voltage, the working gas pressure and the deposition time on cBN formation, and the internal stress in the cBN films.

2. EXPERIMENTAL

TABLE I. Experimental conditions

Rf power input	
(target electrode, P_t)	600, 1000, 2000 W
(substrate electrode, P_s)	30 ~ 500 W
Negative substrate bias voltage ($-V_s$)	100 ~ 500 V
Working gas pressure (p)	0.4 ~ 16 mTorr
Gas flow rate (Ar)	~ 40 sccm
Distance between the electrodes	40 mm
Phase angle difference ($\Delta\phi$)	0°
Magnetic field (at the center of the substrate electrode)	150 G
Deposition time	0 ~ 210 s

Figure 1(a) is a schematic diagram of the apparatus used here, which is basically an rf bias sputtering equipment. A phase shifter was used to synchronize the two rf sources with its internal quartz oscillator (13.56 MHz) and to regulate the difference of phase angles between the rf voltages of the two electrodes ($\Delta\phi$). $\Delta\phi$ was regulated to be 0°, namely in phase, which was the angle that yielded highest content of cBN in the previous work [9]. The target was a ϕ90 mm sintered hexagonal BN disk (>99.7 wt%). 32x32 mm Si (100) wafers were used as substrates. A cylindrical permanent magnet was inserted behind the target electrode to confine the plasma. The magnetic field was about 150 G at the center of the substrate surface (Fig. 1(b)). The base pressure of the chamber was less than 1×10^{-5} Torr. The target and the substrate were presputtered in a pure Ar discharge for 30 min at p = 16 mTorr with the shutter closed. Then the films were deposited on the substrates under the conditions shown in Table I. Judging from the color of the substrate surface, the substrate temperature was estimated to be above and below 600 °C for P_t = 2000 W(dark red heat) and 600, 1000 W (dark), respectively. The specimens were examined mainly by transmission Fourier transform infrared spectroscopy(FTIR). Cubic BN is an IR-active material showing an absorption peak near 1065 cm^{-1} and sp^2-bonded BN shows absorption peaks at 1380 cm^{-1} and 800 cm^{-1} corresponding to B-N stretching mode and B-N-B bending mode, respectively [11,12]. These absorption peaks were used for quantitative analysis of cubic and sp^2-bonded phases. Transmission electron diffraction(TED) and X-ray photoelectron spectroscopy (XPS) were also used for structural analysis and for compositional analysis, respectively. Internal stress in the films was estimated from the radius of the curvatures of Si substrates using a surface profilometer. The stress was calculated using Stoney's equation [13]. Film thickness measurements were made by cross sectional SEM observations.



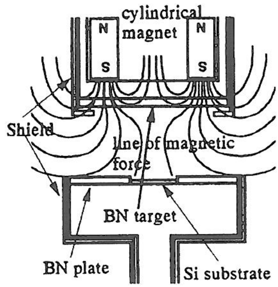


Fig. 1 (a) Schematic diagram of the rf bias sputtering apparatus. (b) Schematic drawing of the permanent magnet inserted behind the target electrode, and the magnetic field.

3. RESULTS AND DISCUSSIONS

Effects of bias voltage

Figure 2 shows the dependence of the IR absorbances of the BN films upon V_s ranging from -100 V to -500 V. The films were deposited with p = 16 mTorr and P_t = 2000 W for 120 s. The absorbance of *sp*^{2} phase decreased gradually with the increase of V_s up to 200 V. At V_s = 250 V the absorbance decreased rapidly, and kept a nearly constant value with V_s above 300 V. The cubic phase was grown for V_s above the threshold of 200 V. For V_s above 300 V the absorbance of cubic phase decreased. This dependence upon the bias voltage was also reported in other works [2,14-16] and qualitatively in good agreement with them.

Figure 3 shows the TED pattern of the same specimen. All the rings except the innermost one are indexed as cubic phase, and the innermost was indexed as hBN (002). This result means that the film consisted of cubic and *sp*^{2} phases, and is consistent with that of the IR measurement (Fig. 2). The dark field image using cBN(111) reflection indicated that the cBN film consisted of small crystallites less than 100 nm. Compositional measurements by XPS revealed that the chemical composition ratio N/B of the same specimen was almost stoichiometric (unity) in comparison with a CVD-grown pyrolytic BN plate as a standard. The cBN film contained a few % of oxygen and 1 % argon. No other impurities such as carbon were detected in the film.

Effects of deposition time

Figure 4 shows the deposition time dependence of the IR absorbances and the film thickness (V_s = 300 V and P_t = 2000 W). The absorbance of cubic phase increased linearly with the deposition time after 30 s, while that of *sp*^{2} phase had an almost constant value of about 0.035. Such a tendency was also observed in the films prepared at V_s = 250 V. Figure 5 shows the IR absorbance changes at the initial growth stage of a BN film deposited at V_s = 300 V. The rf power input to the target was reduced into 600 W to lower the deposition rate. The figure clearly shows the growth process of the cBN film with a layered structure. These results mean that the films containing cBN had a layered structure of sp^2 and cubic phases and that the upper layer containing only a single cBN phase can be grown after the initial sp^2-bonded layer is deposited adjacent to the substrate, although Fig. 2 seemingly shows that the films deposited with Vs just above the threshold (200 V) had mixed layer of two phases. The layered structure of the cBN films was also reported by other workers [18,19]. So the presence of the initial sp^2 layer is not dependent on the deposition techniques and their procedures. From the thickness change in Fig. 4, the growth rates of the cubic phase was calculated to be 0.98 nm/s. IR absorption coefficient of the cubic phase and the thickness of the initial sp^2-bonded layer were also calculated to be 30000 cm^{-1} and 40 nm, respectively. The cBN films with the thicknesses more than about 210 nm were easily peeled off from the substrates. After the delamination, the IR absorption peak at about 1080 cm^{-1} shifted toward lower wave number by 20 cm^{-1}. This suggests that the cBN films on Si substrates had compressive stress and that the stress was relieved by the delamination

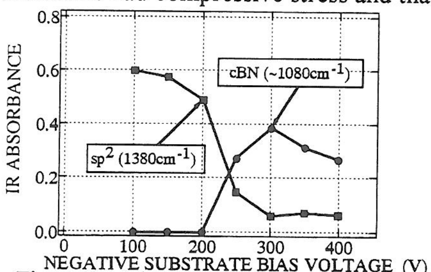


Fig. 2 IR absorbances of the films deposited with P_t = 2000 W for 120 s as a function of the substrate bias voltage ($-V_s$).

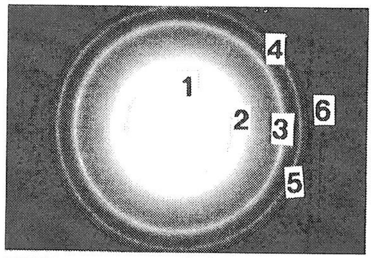


Fig. 3 TED pattern of the cBN film (V_s=200 V, P_t=2000 W, 210 s). 1:h(002), 2:c(111), 3:c(220), 4:c(311), 5:c(222), 6:c(400).

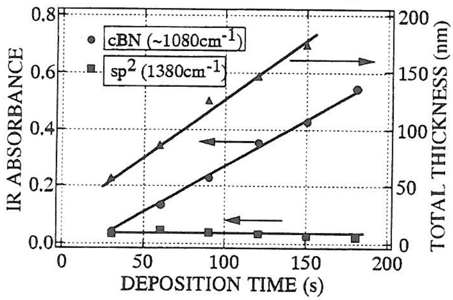


Fig. 4 Deposition time dependence of the IR absorbances and the film thickness. (Vs = 300 V and Pt = 2000 W)

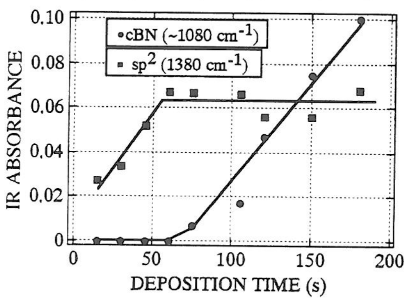


Fig. 5 Initial growth stage of the cBN film deposited with Vs = 300 V and Pt = 600 W

Effects of working gas pressure

Figures 6 (a) and (b) shows working gas pressure dependence on cBN formation. All the samples shown in the figure were deposited with P_t = 1000 W for 180 s. For the case of p = 0.4 mTorr and 16 mTorr, V_s windows for cBN formation were 125 V - 350 V and 200 V - 400 V, respectively. The decrease of the V_s threshold with p may be caused mainly by less collisional motion of ions in the sheath. This kind of ion motion is also expected in the target sheath. In fact, the deposition rate increased from 0.60 nm/s to 0.83 nm/s inversely with the working gas pressure. In contrast to the results reported by Mieno et al. [16], even at p = 0.4 mTorr cBN films were grown with V_s above 100 V in the present study. This can be probably explained by the difference of ion fluxes. In our case, the deposition rate was about a few times as high as that reported by Mieno et al, and this suggests the ion fluxes to the substrate and the target were much larger in this system. The V_s threshold of 100 V is as low as that reported by magnetron sputtering with an ECR ion source (104 V) [20]. However, it should be noted that ion energy is dependent on the plasma potential and the motion in the sheath as well as V_s. Thus, further investigation of the plasma potential (which is typically a few tens of volts) or direct measurements of ion energy will be required to discuss in terms of threshold energy of ions. The difference between the V_s threshold values in Figs. 2 and 6 may be due to the different deposition rates which resulted from the different rf power inputs (P_t = 2000 W for Fig. 2 and 1000 W for Figs. 6).

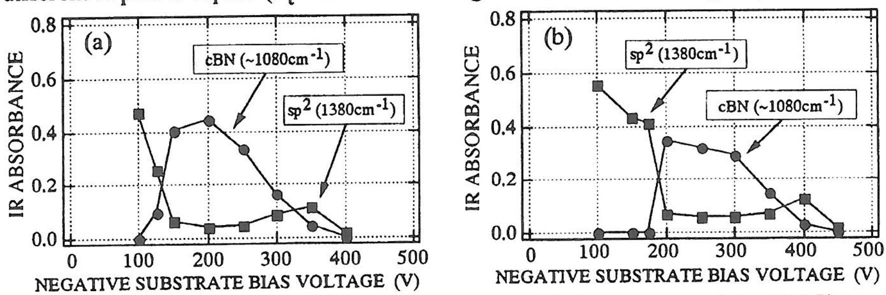


Fig. 6 The effects of the working gas pressure on IR absorbances of the BN films deposited with P_t = 1000 W for 180 s. (a) p = 0.4 mTorr, (b) p = 16 mTorr.

Stress measurements of BN films

The stress measurements revealed that the cBN films had relatively high compressive stress of a few GPa while the BN films containing only sp^2 phase had the stress around 1 GPa. The compressive stress is the same order with those reported by other workers [3,21,22] who used ion plating and ECR-PECVD with substrate biasing. It may be caused by the ion bombardment effects, such as peening effect of Ar ions or forward sputtering of the deposits. A further exploration is required for the clarification of the stress generation mechanism, which is considered to be closely related to cBN formation [22].

4. CONCLUSION

cBN films were successfully prepared by the phase-regulated rf bias sputtering with the aid of magnetic field. Cubic phase was formed in the films deposited with the substrate bias voltage above the threshold. No mixed phase layer was formed for V_s even just above the threshold. The cBN films had a layered structure which consists of an initially deposited layer of sp^2 phase and a layer of cubic phase subsequently grown. The threshold decreased with the working gas pressure. Even at p = 0.4 mTorr, cBN films were grown with V_s above 100 V. The maximum growth rate of cubic phase was estimated to be approximately 1 nm/s for V_s = 300 V, P_t = 2000 W and p = 16 mTorr. The cBN films had compressive stress of about a few GPa, and the stress was relieved by the delamination from the substrate.

5. ACKNOWLEDGMENTS

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