

Influences of C₇H₈, Ar and H₂ additions on the formation of BCN:O,H films using trimethylborate and N₂ gases by bipolar-type plasma based ion implantation

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The preparation of B-C-N films are attempted using trimethylborate (TMB: BO₃(CH₃)₃) and N₂ gases by a bipolar-type plasma based ion implantation method, and the influences of C₇H₈, Ar and H₂ additional gases on the possibility of film formation are examined. It is found that no film is obtained using only TMB or TMB and N₂ gases (TMB+N₂). In the case of C₇H₈ addition to TMB+N₂ system, the films composed of B, C, N and O are deposited. However, the deposition rate is significantly decreased as compared with the deposition of diamond-like carbon films using only C₇H₈ gas under the same deposition condition. As for Ar addition to TMB+N₂ system, it is possible to deposit the films. However, FT-IR results suggest that BO_x:H films are formed. On the other hand, H₂ addition to TMB+N₂ system makes the deposition of BCN:O,H films achievable, although the deposition rate is relatively low. In current experiments, O atoms still remain in the films even as a reduced gas of H₂ uses. However, these results suggest that the film deposition using TMB+N₂ system is strongly affected by the additional gases.

Key words: bipolar-type PBII, BCN:O,H film, trimethylborate, C₇H₈, Ar, H₂

1. INTRODUCTION

Recently, Boron-Carbon-Nitrogen (BCN) films have attracted much attention because of excellent mechanical properties as diamond-like carbon (DLC) films. Moreover, it is expected that BCN films have higher thermal stability in the air and more optical transparency as compared with DLC films due to the presence of B-N bonding. Many studies on the preparation of BCN films have been carried out with various methods, such as sputtering [1, 2] and CVD techniques [3-10].

On the other hand, plasma based ion implantation (PBII) has attracted much interest in industrial application because of the capability of surface coating for 3 dimensional workpieces. The authors have investigated on the deposition of DLC films on various substrates using a bipolar-type PBII equipment developed by Miyagawa et al [11, 12]. It is also expected that the PBII system should be applicable for another material coating, such as BCN film. So, we start to study the deposition of BCN films by the bipolar-type PBII system. To achieve this purpose, it is required that the gas source including B element is inlet to the PBII chamber like CVD methods. In the case of CVD, various gas source was used such as B₂H₆ [3, 4], BCl₃ [5, 6], C₃H₁₂B₃N₃ [7-10] and C₈H₁₈BN [8-10]. As well known, however, B₂H₆ and BCl₃ are very toxic and the others are less toxic but much expensive. Therefore, they are not always suitable for the industrial use. After searching suitable source gases, we eventually selected trimethylborate (TMB: BO₃(CH₃)₃) as a source gas of B because of convenience in handling due to liquid phase at atmospheric pressure, less toxic and relatively cheap.

In the case of TMB use, O atoms are included in the precursor of TMB. Therefore, the process is more complicated due to the presence of O decomposed of the precursor. The presence of O may act as a brake upon the

deposition on the substrate so that the use of TMB does not always assure of BCN film deposition.

On the other hand, it is reported by S. Ulrich and coworkers [11, 12] that thick c-BN:O films which have low residual stress and enough mechanical properties comparable to those of c-BN films can be obtained by purposely inletting O₂ gas under the deposition condition of c-BN films. According to them, the presence of O in process is not always pessimistic outlook also in the case of BCN film deposition. It is believed to be worth using TMB as an attempt of the deposition of BCN:O films instead of BCN films, even though the effects of O in TMB on the deposition are unclear.

Moreover, it is pointed out in the literature [3, 4, 8-10] that additional gases, such as Ar and H₂, are used as a process gas which may help and enhance the deposition of BCN films by CVD methods. By analogy with them, the deposition of the films using TMB also must be affected by the additional gases, although the roles of the additional gases are not always clarified. Naturally, one can expect that the use of H₂ gas may cause O extracting from deposited films. In any event, the control of the O concentration in the films is needed as far as using TMB source gas. To make sure of the process to control the composition of the films, it should be necessary to understand the roles of the additional gases.

In this study, we venture to use TMB as a source gas and focus on the possibility of the film deposition by the bipolar-type PBII system for the first time experiment, and also check up on the influences of the additional gases on the deposition of the films. From the results of current experiment, some interesting aspects for the deposition of the films from TMB are obtained as mentioned and discussed in section 3, although BCN:O,H and BO_x:H films are deposited against our purpose of BCN films. In a next

step, we will aim at improving the way of experiment by aid of these aspects to get the purposing BCN films.

2. EXPERIMENTAL

There are 2 PBII equipments using different pumping system in our laboratory. One is evacuated by a turbo molecular pump (PBII A) and the other is evacuated by a diffusion oil pump (PBII B). The PBII B was used when H₂ gas was flowed because the pumping speed to H₂ gas of the turbo molecular pump is not enough to verify the ratio of H₂ to other gases. Figure 1 shows the common illustration of the bipolar-type PBII system [13, 14]. The films were prepared on Si(100) substrates which were held on the center of the cylindrical vacuum chamber. Positively and negatively pulsed voltages (V_p and V_n) were applied to the substrate through a high-voltage feed-through. The each chamber was evacuated to less than 10^{-3} Pa by the turbo molecular pump (PBII A) or the diffusion oil pump (PBII B). Typical preparation conditions are listed in Table I. Trimethylborate (TMB: $\text{BO}_3(\text{CH}_3)_3$), N₂ and the additional gases (C₇H₈, Ar and H₂) were inlet to the chamber and the flow rates of the gases were varied as listed in Table I. Deposition pressures were kept 0.2 Pa in PBII A and 1.2 Pa in PBII B, respectively. Deposition times for the TMB+N₂+C₇H₈ case and the others (TMB+N₂+Ar and TMB+N₂+H₂) were 30 min and 120 min, respectively. Respective pulse frequencies were also 3 kHz and 4 kHz.

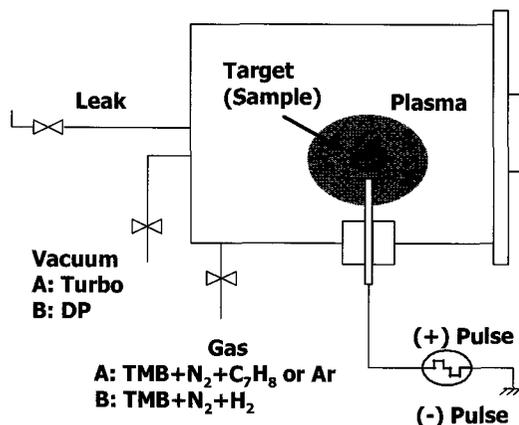


Fig. 1. Illustration of bipolar-type PBII system.

Substrate temperature was measured by a chromel-alumel thermocouple located at the center of the substrate holder and covered with a stainless steel sheet of 0.1 mm thick. The measured substrate temperature for each experiment was also listed in table I. The substrate holders of 15 and 10 cm in diameter were employed in PBII A and in PBII B, respectively.

Film thickness was measured by a surface profilometer (Kosaka Laboratory Ltd., ET300). The microstructure of the films were examined by a Fourier transformation infrared spectroscopy (FT-IR, Perkin Elmer GX), and the compositional analysis was performed by an energy dispersive X-ray spectroscopy (EDX, Philips XLS30).

3. RESULTS AND DISCUSSION

Figure 2 shows (a) the deposition rate of the films prepared for 30 min using TMB+N₂+C₇H₈ source gases as a function of V_p and V_n . For comparison, (b) the deposition rate of diamond-like carbon (DLC) films prepared for 30 min using only C₇H₈ source gas under the same conditions of V_p and V_n . The change in the deposition rate of the films is different from that of DLC films. The deposition rate is relatively low as compared with that of DLC films. In addition, it is not significantly changed as the V_p increases but slightly decreased with increasing V_n .

Figure 3 shows typical results of EDX measurements of the deposited films at different V_n using the TMB+N₂+C₇H₈ source gases under $V_p = +4$ kV. The results clearly show that the films are composed of B, C, N and O and the concentration of N and O is decreased with increasing V_n . This result suggests that ion bombardment may cause the release of N and O in the films. The concentration of H was not measured in this experiment. However, it is reported by H. Ahn et al [9, 10] that H is included more than 25 % in the BCN films prepared by plasma assisted CVD using liquid organic compounds. According to their report, H is also believed to be included in current films, so that the deposited films are able to be denoted by BCN:O,H.

To examine the ion bombardment effect, Ar gas was used as an additional gas instead of C₇H₈. Figure 4 shows the change in the deposition rate of the films using TMB+N₂+Ar. In the samples a and b, it is indicated that no deposition is occurred using TMB only and TMB+N₂. On the other hand, in the samples c and d, the films are clearly deposited using TMB+Ar and TMB+N₂+Ar. However, when using TMB+N₂+Ar, further increase of N₂ gas ratio (or flow rate) causes no deposition again in the sample e.

Table. I. Typical condition for deposition of the films by bipolar-type PBII system.

System	Gas	Flow rate (sccm)	Pressure (Pa)	Pulse frequency (kHz)	Positively pulsed voltage (kV)	Negatively pulsed voltage (kV)	Substrate temperature (°C)	Deposition time (min)
PBII A (Turbo)	TMB	2	0.2	3	2 - 4	5 - 15	250 - 400	30
	N ₂	2						
	C ₇ H ₈	2						
PBII B (DP)	TMB	2, 4	1.2	4	2	2.5	250	120
	N ₂	2, 4						
	Ar	2						
PBII B (DP)	TMB	7	1.2	4	1.6	3.6	< 130	120
	N ₂	5, 10						
	H ₂	10						

Figure 5 shows the FT-IR spectra of the samples a – e corresponding to those of Fig. 3. For the samples a, b and e, no specific signal is observed in the spectra, indicating that no detectable phase, such as SiO_x, is formed on the surface of the substrate. For the samples c and d, however, 3 peaks appear around 1190, 1430 and 3200 cm⁻¹, respectively. These peaks can be assigned to B-O deformation (1192 cm⁻¹), B-O stretching (1435 cm⁻¹) and BO-H (3230 cm⁻¹) vibration modes, respectively [15]. These results suggest that BO_x:H films are obtained using TMB+Ar or TMB+N₂+Ar gases. This is also supported by the fact that the films were dissolved in the water.

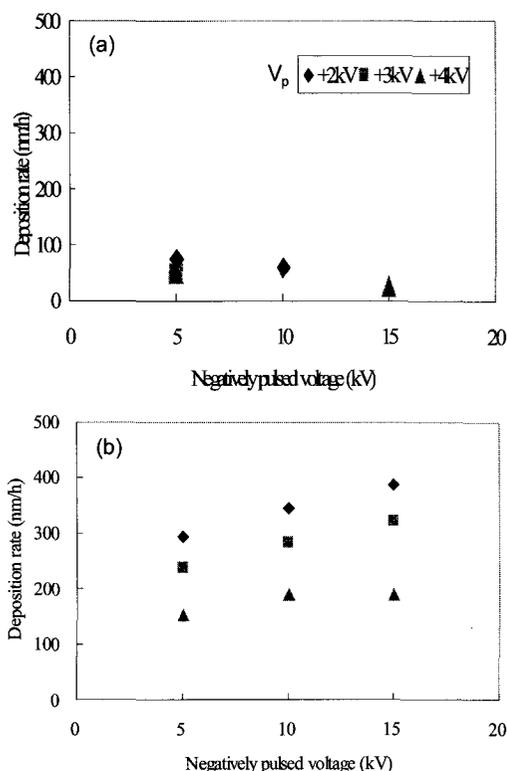


Fig. 2. Deposition rate of (a) the films and (b) DLC films as a function of positively and negatively pulsed voltages. Source gases are (a) TMB+N₂+C₇H₈ and (b) C₇H₈, respectively.

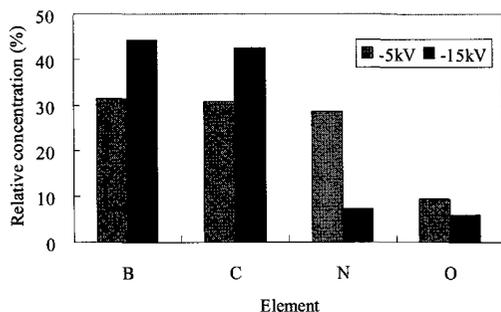


Fig. 3. Change in relative concentration of the films using a source gas of TMB+N₂+C₇H₈ as a function of V_n at V_p = +4 kV.

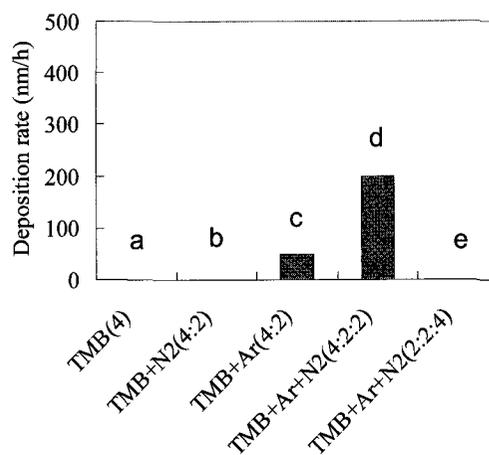


Fig. 4. Deposition rate of the films using a source gas of TMB+N₂+Ar. The ratio of flow rates is also indicated in parentheses.

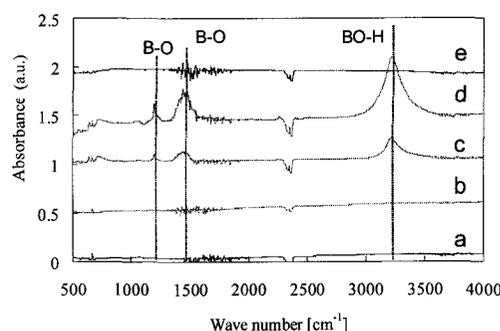


Fig. 5. FT-IR spectra of the films using a source gas of TMB+N₂+Ar. The samples of a – e correspond to those of Fig. 4.

As shown in Fig. 4, Ar addition has much effect on the increase of the deposition rate of the films, which may be caused by Ar ion bombardment. However, BO_x:H films are formed as shown in Fig. 5. To deoxidize the deposited film is attempted by H₂ addition instead of Ar gas. The deposition of the films was performed by PBII B and owing to circumstances, H₂ flow rate is kept constant of 10 sccm. Figure 6 shows the deposition rate of the films using TMB+N₂+H₂ as a function of (a) N₂ flow rate and (b) peak current when applying V_p, respectively. The deposition of the films takes place in the range of N₂ flow rate 0 – 10 sccm although the deposition rate is relatively low. The deposition rate is also slightly increased with increasing the peak current. The results of EDX analysis showed that the relative concentration of B, C, N and O were 44.4, 34.9, 17.7 and 3.0 %, respectively. This indicated that BCN:O:H films are also obtained. The concentration of N was increased and that of O was decreased, but O still remained in the films.

The results of the case of TMB+N₂+C₇H₈ indicate that the deposition rate is decreased and the concentrations of N and O are also decreased with increasing V_n. This suggests that the ion bombardment affects on the composition and deposition of the films. While, the results of TMB+N₂+Ar case indicate that BO_x:H films are obtained but the increase of N₂ gas ratio causes no deposition of the film. This fact

suggests that Ar ion bombardment causes the reduction of C and N in the films, leading to the formation of BO_x:H films, and increasing N ion bombardment may disturb thin film condensation on the substrate. From these results, it is considered that ion bombardment may play an important role and some suitable condition of ion bombardment is necessary for the film deposition. H. Ann and coworkers [8 – 10] also pointed out that in the PACVD process at low temperature, an important part is played by ion bombardment assistance of the plasma chemistry and thin film condensation.

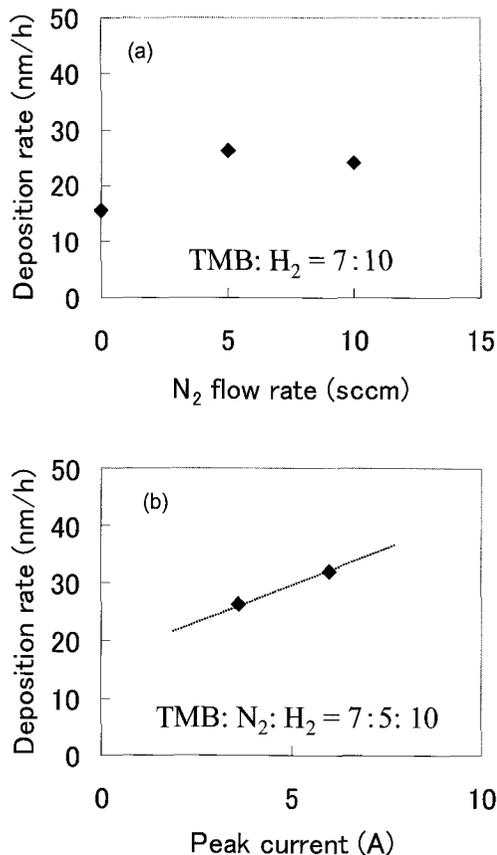


Fig. 6. Deposition rates of the films using a source gas of TMB+N₂+H₂ as a function of (a) N₂ gas flow rate and (b) peak current when applying positively pulsed voltage, respectively.

On the other hand, the deposition of the films is possible in spite of the increase of N₂ gas ratio in the case of TMB+N₂+H₂, and the deposition rate is slightly increased with increasing peak current when applying V_p, as shown in Fig. 5. These results suggest that the presence of H₂ is also effective for the enhancement of the film deposition. Yokomichi et al. [5] suggested that reactive hydrogen atoms play an important role in the deposition of BCN films by hot-filament CVD methods. In our experiment, reactive hydrogen atoms also should be generated and increased in amount at high peak current. Therefore, it is believed that the increase of reactive hydrogen atoms generated by the decomposition of additional H₂ may terminate the surface and keep high reactivity so that the sticking probability of the reactive species is increased on the growing surface, resulting in enhancement of the film formation. Tendency of

the increase in N concentration is also consistent with the result reported by Yokomichi et al [5]. In any event, however, the deposition rate is still low and the difficulty of the composition control in the films remains. To explore more available deposition condition, further investigation is underway.

4. SUMMARY

The experiment with the deposition of the films was carried out using TMB+N₂+additional gases (C₇H₈, Ar or H₂) by the bipolar-type PBII A and B systems. It was found that the BCN:O,H films can be deposited although the deposition rate is relatively low, otherwise no deposition was obtained. In addition, the additional gases strongly affected to the deposition of the films. The influences of the additional gases are summarized as follows:

(1) TMB+N₂+C₇H₈

The concentrations of N and O in BCN:O,H films were reduced and the deposition rate of the films was also decreased with increasing V_n.

(2) TMB+N₂+Ar

BO_x:H films were obtained when using TMB+Ar and TMB+N₂+Ar. However, the increase of N₂ gas ratio caused no deposition of the films.

(3) TMB+N₂+H₂

The deposition was possible when N₂ gas ratio was increased. The deposition rate was slightly increased with increasing peak current. The concentration of N was increased but O still remained in the films.

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