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SYNTHESIS OF BN FILMS BY THE PLASMA CVD WITH VARIOUS SOLIDS: BH_3NH_3, H_3BO_3 AND $NaBH_4$

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Summary

We have studied the formation conditions of cubic boron nitride (c-BN) formed by the dissociation of BH_3NH_3, H_3BO_3 and $NaBH_4$ in the reactive gases H_2 or NH_3, and also by the plasma excitement of the dissociated gases using r.f. induction and tungsten filament heating. It was found in these deposition processes that the tungsten filament heating greatly contributes to the formation of c-BN as compared with the contribution of r.f. induction.

The deposition ratio c-BN/amorphous BN (a-BN) in the films deposited with BH_3NH_3–H_2 changes with the change of the emission intensity ratio $I(H\alpha)/I(H_2{}^*)$ in the gas plasma, where the wavelengths of the Hα and $H_2{}^*$ photoemissions are 656 nm and 603 nm respectively. In particular, when the ratio $I(H\alpha)/I(H_2{}^*)$ becomes maximum, the deposition rate of c-BN also becomes maximum. In the H_3BO_3–NH_3 and $NaBH_4$–NH_3 systems, it was found that the deposition ratio c-BN/a-BN varies with the emission intensity ratio $I(N_2{}^+)/I(NH_3{}^*)$ and $I(N_2{}^*)/I(NH_3{}^*)$, where the wavelengths of the $N_2{}^+$, $N_2{}^*$ and $NH_3{}^*$ photoemissions are 391 nm, 406 nm and 564 nm respectively.

1. Introduction

The synthesis of cubic boron nitride (c-BN) from hexagonal BN (h-BN) catalyst systems was first announced by Wentorf [1] in 1957. Subsequently, c-BN was obtained by the direct transformation from h-BN by Bundy and Wentorf [2]. BN films have been synthesized by various processes such as boron evaporation with $N_2{}^+$ ion-beam bombardment [3], activated reactive evaporation using the hollow cathode discharge [4] and ECR plasma chemical vapor deposition (CVD) [5]. In the plasma CVD method, various raw materials and reactive gases such as $B + N_2$ [3, 6], $B + N_2 + Ar$ [4, 7], $B_2H_6 + NH_3 + H_2$ [8] and $B_3N_3H_6$ [9] have been used for the synthesis. The c-BN structure, however, used to be formed partially in the amorphous or turbostratic BN (a-BN) structure.

We have investigated the synthesis of c-BN and found a new method

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using r.f. plasma CVD thermally assisted by a tungsten filament [10]. In the case of synthesis with $B_2H_6 + NH_3 + H_2$, it was found that the deposition ratio c-BN/a-BN depends on the conditions of the r.f. power, filament temperature and gas pressure. The c-BN structure was especially formed under conditions when the tungsten filament temperature was higher than 1600 °C and the r.f. power was higher than 50 W. Thus, it is necessary to the formation of c-BN that hydrogen radicals are excited into higher activated energy levels in the gas plasma [10].

In the present report, relations between formation conditions and crystal structures of BN with respect to various solids, *i.e.* BH_3NH_3, H_3BO_3 and $NaBH_4$, as raw materials will be described and discussed.

2. Experimental procedure

Figure 1 shows a schematic diagram of the apparatus for thermally assisted r.f. plasma CVD. The system is composed of two main parts, *i.e.* a plasma chamber and a substrate heating chamber with a tungsten filament situated just above the substrate. The solid raw material (0.1 g) is placed in a ceramic boat in the plasma chamber. In a typical run, the metal chamber is evacuated to a pressure of 1.3 mPa using the diffusion pump system. After heating the substrate to a temperature of 800 °C, the solid raw material is evaporated and a reactive gas is induced. The evaporated solid raw material and the induced gas then make a gas mixture. The mixed gas is excited into the plasma state by the r.f. induction of 13.56 MHz. The excited plasma is further thermally activated by the heating of the tungsten filament. The reactive gases used here were selected corresponding to the raw solid materials: hydrogen (H_2) for BH_3NH_3, and NH_3 for H_3BO_3 and $NaBH_4$. The BN films were deposited on silicon wafers. The deposition conditions are summarized in Table 1.

The crystal structure analyses of as-deposited films were made by transmission electron microscope (TEM) observation and infrared (IR)

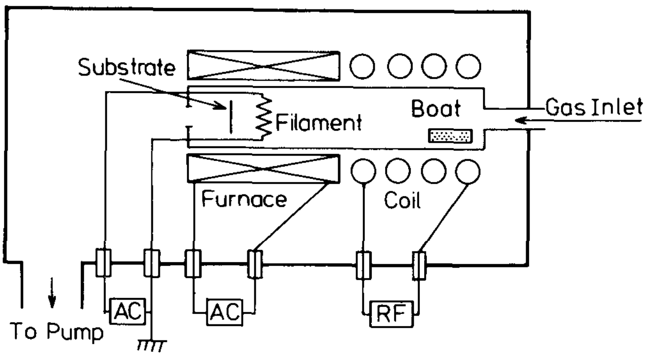

Fig. 1. Schematic diagram of the r.f. plasma CVD apparatus.

TABLE 1

Deposition conditions

filament temperature	1100 - 1700 °C
r.f. power	0 - 200 W
gas pressure	20 - 500 Pa
substrate temperature	800 °C
substrate	silicon
deposition time	0.5 h

absorption measurement. The c-BN and a-BN have strong absorption bands at 1080 cm^{-1} and 1380 cm^{-1} (c plane) respectively. The deposition ratio of c-BN/a-BN can be obtained by the intensity ratio of the IR absorption bands, since the absorption intensity is a function of the film thickness. In this work, the deposition ratio was obtained by this method. The photoemission spectra of the plasma with and without tungsten filament heating were measured in the visible range by optical emission spectroscopy.

3. Results and discussion

3.1. BH_3NH_3–H_2 system

In this system, c-BN was always synthesized under the conditions of filament temperature greater than 1600 °C and r.f. power greater than 60 W. The reactive gas pressure was found to affect the c-BN deposition rate. Figure 2 shows the IR absorption spectra measured for films deposited at filament temperatures from 1100 to 1700 °C. The r.f. power and the gas pressure were kept constant at 100 W and 70 Pa respectively. The films deposited below 1500 °C have no absorption peak; however, those deposited at

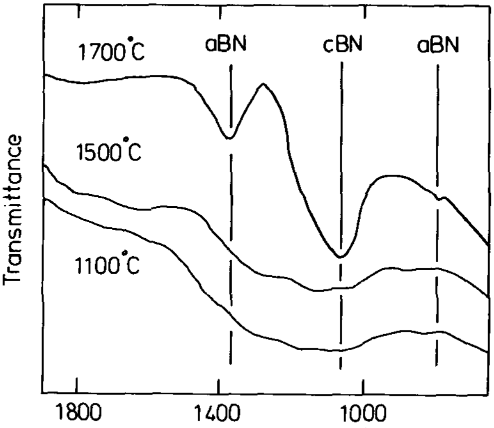

Fig. 2. IR absorption spectra of the films deposited with BH_3NH_3–H_2.

1700 °C show several absorption peaks. A strong peak near 1080 cm^{-1} corresponds to the F_2 vibrational mode of c-BN, and a medium absorption peak at 1380 cm^{-1} and a weak one at 800 cm^{-1} are assigned to the E_{1u}(*c* plane) and A_{2u}(out of *c* plane) vibrational modes of a-BN respectively. According to the TEM observation of the films deposited at a filament temperature of 1700 °C, many aggregates of crystalline particles with a particle size of about 30 nm were embedded in the amorphous structure. The mean size of the aggregates and their average distance were about 500 nm and 700 nm respectively. Electron diffraction patterns from the amorphous region showed halo-rings corresponding to those of a-BN or turbostratic BN. However, diffraction patterns of the zinc-blende-type structure having a lattice constant of $a_0 = 0.362$ nm were observed in the crystalline region. Thus, the a-BN and c-BN structures were recognized in the films deposited at a filament temperature of 1700 °C.

The IR absorption spectra were measured for the films deposited at r.f. powers from 0 to 200 W. The filament temperature and the gas pressure were kept constant at 1700 °C and 70 Pa. Intensity ratios $A_{c\text{-BN}}(1080\ cm^{-1})/A_{a\text{-BN}}$ (1380 cm^{-1}) for the IR absorption spectra are shown in Fig. 3. Both the a-BN and c-BN structures were recognized in the films deposited at r.f. powers above 80 W, but the c-BN was not formed in the films deposited at 0 W. The ratio $A_{c\text{-BN}}/A_{a\text{-BN}}$ increases with increasing r.f. power since the deposition rate of c-BN increases rapidly, contrary to that of a-BN which decreases above 100 W.

When the reactive gas pressure was changed, the IR absorption intensity ratio changed as shown in Fig. 4, where the r.f. power and filament temperature were kept constant at 200 W and 1700 °C respectively. The ratio increases with increasing gas pressure up to 70 Pa and then decreases rapidly with a further increase of gas pressure. The increase of the ratio is caused by the increase of the deposition rate of c-BN as compared with that of a-BN. The decrease of the ratio resulted from the rapid increase of the deposition rate of a-BN above 70 Pa.

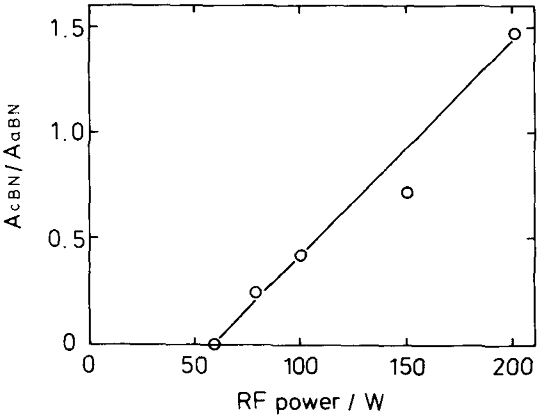

Fig. 3. IR absorption intensity ratio as a function of r.f. power.

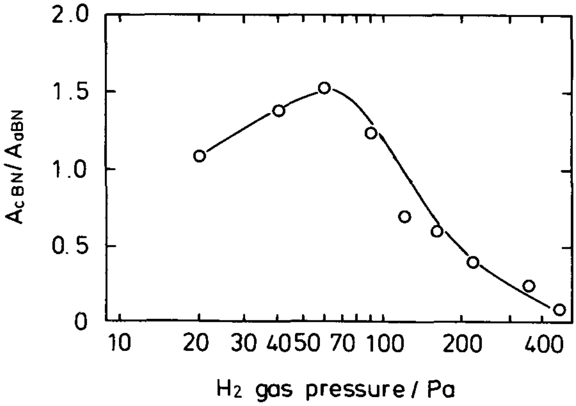

Fig. 4. IR absorption intensity ratio as a function of gas pressure.

According to these results, it was found that the deposition ratio c-BN/a-BN depends upon deposition conditions such as the filament temperature, r.f. power and gas pressure.

According to the plasma photoemission spectrophotometry, photoemissions from several radicals such as H_2^* (hydrogen molecule radical) and H (atomic hydrogen) were observed in the reactive gas plasma throughout the whole visible region. In particular, photoemissions with wavelengths of 603 nm and 656 nm, corresponding to the radicals H_2^* and Hα respectively, are very strong. Figure 5 shows the emission intensity ratio $I(H\alpha)/I(H_2^*)$ and $I(H\alpha)/I(H\alpha_0)$ as a function of filament temperature, where $I(H\alpha_0)$ is the constant emission intensity of atomic hydrogen excited by r.f. induction only (without filament heating). The ratio $I(H\alpha)/I(H_2^*)$ is nearly constant below 1500 °C, but becomes much stronger above that temperature. This is because

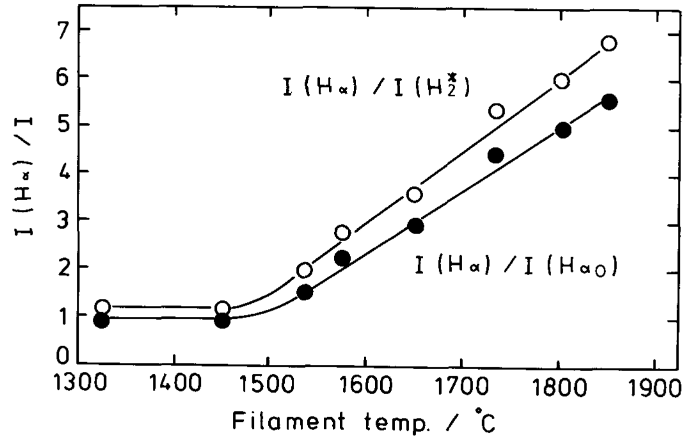

Fig. 5. Photoemission intensity ratios $I(H\alpha)/I(H_2^*)$ and $I(H\alpha)/I(H_2^*)$ as a function of filament temperature: r.f. power; 100 W; gas pressure; 70 Pa.

the degree of dissociation of hydrogen increases rapidly with increasing temperature above 1500 °C. In the higher temperature region (greater than 1500 °C), dissociation by filament heating is found to be predominant.

The emission intensity ratio $I(\mathrm{H}\alpha)/I(\mathrm{H}_2{}^*)$ as a function of r.f. power is shown in Fig. 6. The emission intensities begin to stabilize above 30 W. The hydrogen molecule is thought to be a little dissociated to the hydrogen atom by r.f. power higher than 30 W. The ratio $I(\mathrm{H}\alpha)/I(\mathrm{H}_2{}^*)$ increases slightly with increasing r.f. power.

The ratio $I(\mathrm{H}\alpha)/I(\mathrm{H}_2{}^*)$ as a function of gas pressure is shown in Fig. 7. The ratio shows the gradual decrease with increasing gas pressure to 600 Pa. The decrease of the ratio results from the decline of the dissociation rate, that is to say, the decrease in the amount of radicals.

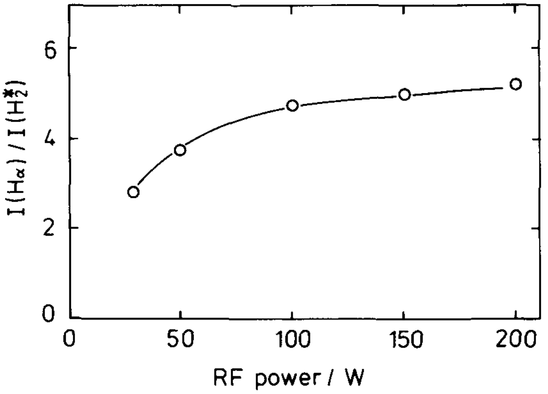

Fig. 6. Photoemission intensity ratios $I(\mathrm{H}\alpha)/I(\mathrm{H}_2{}^*)$ as a function of r.f. power: filament temperature; 1700 °C; gas pressure; 70 Pa.

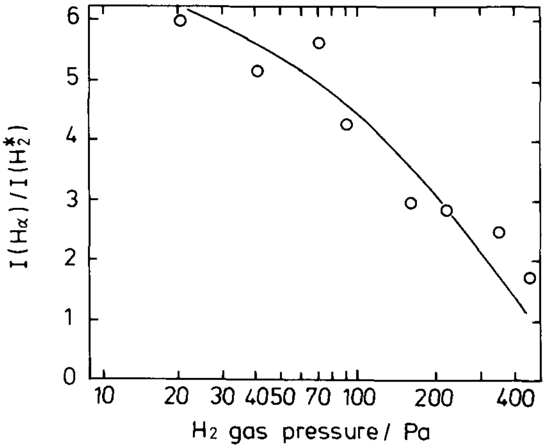

Fig. 7. Photoemission intensity ratios $I(\mathrm{H}\alpha)/I(\mathrm{H}_2{}^*)$ as a function of gas pressure: filament temperature; 1700 °C; r.f. power; 100 W.

According to the above results, it was found that the deposition ratio c-BN/a-BN is closely related to the emission intensity ratio $I(\mathrm{H}\alpha)/I(\mathrm{H}_2^*)$. In particular, when the ratio $I(\mathrm{H}\alpha)/I(\mathrm{H}_2^*)$ becomes maximum, the deposition rate of c-BN also becomes maximum.

3.2. H_3BO_3–NH_3 and $NaBH_4$–NH_3 systems

The IR absorption intensity ratios for these systems change almost in the same manner as shown in the case of the BH_3NH_3–H_2 system with increasing r.f. power and gas pressure. The ratios in these systems $A_{\text{c-BN}}/A_{\text{a-BN}}$ are shown in Fig. 8 as a function of r.f. power. Both the a-BN and c-BN structures were characterized in the films deposited at various conditions including a condition without r.f. induction. For gas pressure, the intensity ratios are shown in Fig. 9(a). The ratios have broad maxima in the gas pressure range between 20 and 50 Pa. The result of plasma spectrophotometry of NH_3 excited by both r.f. induction and filament heating is shown in Fig. 9(b). The photoemission intensity ratios $I(\mathrm{N}_2^+)/I(\mathrm{NH}_3^*)$ and $I(\mathrm{N}_2^*)/I(\mathrm{NH}_3^*)$ have broad maxima in the gas pressure range between 10 and 100 Pa. By comparison, it is found that the deposition ratio c-BN/a-BN depends upon the emission intensity ratios $I(\mathrm{N}_2^+)/I(\mathrm{NH}_3^*)$ and $I(\mathrm{N}_2^*)/I(\mathrm{NH}_3^*)$.

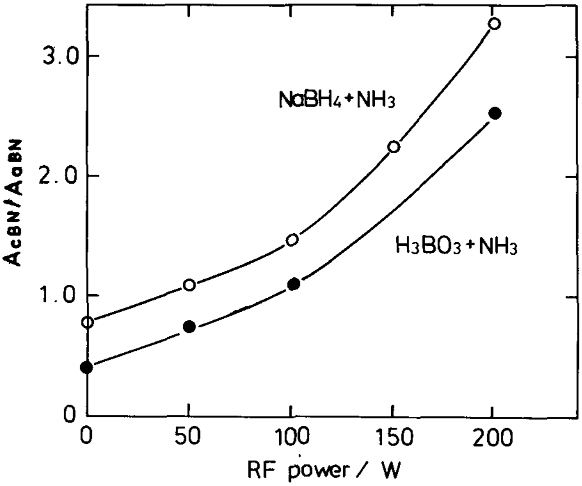

Fig. 8. IR absorption intensity ratios of the films deposited at a filament temperature of 1700 °C and a gas pressure of 40 Pa as a function of r.f. power.

4. Conclusion

We have studied the formation conditions of c-BN formed by the dissociation of BH_3NH_3, H_3BO_3 and $NaBH_4$ in the reactive gases H_2 or NH_3, and also by plasma excitement of the dissociated gases using r.f. induction and tungsten filament heating.

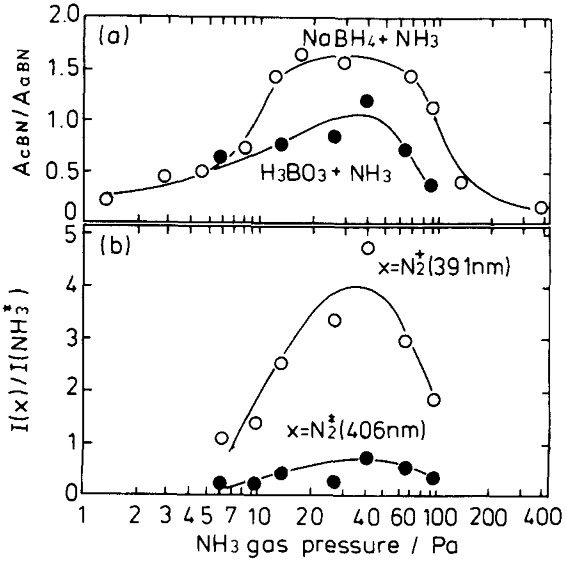

Fig. 9. (a) IR absorption intensity ratios of the films deposited at a filament temperature of 1700 °C and a r.f. power of 100 W as a function of gas pressure. (b) Photoemission intensity ratios of the reactive gas plasma as a function of gas pressure.

It was found in these deposition processes that the tungsten filament heating greatly contributes to the formation of c-BN as compared with the contribution of r.f. induction.

The deposition ratio c-BN/a-BN in the films deposited with BH_3NH_3–H_2 changes with the change of the emission intensity ratio $I(H\alpha)/I(H_2^*)$ in the gas plasma. In particular, when the ratio $I(H\alpha)/I(H_2^*)$ becomes maximum, the deposition rate of c-BN also becomes maximum. In the H_3BO_3–NH_3 and $NaBH_4$–NH_3 systems, it was found that the deposition ratio c-BN/a-BN varies with the emission intensity ratio $I(N_2^+)/I(NH_3^*)$ and $I(N_2^*)/I(NH_3^*)$.

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