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# CHEMICAL VAPOR DEPOSITION OF HEXAGONAL BORON NITRIDE FILMS IN THE REDUCED PRESSURE

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## ABSTRACT

Hexagonal boron nitride (h-BN) films were deposited onto a graphite substrate in reduced pressure by reacting ammonia and boron tribromide at 800– 1200°C. The growth rate of h-BN films was dependent on the substrate temperature and the total pressures. The growth rate increased with increasing the substrate temperature at the pressure of 2 kPa, while it showed a maximum value at the pressures of 4 and 8 kPa. The temperature at which the maximum growth rate occurs decreased with increasing total pressure. With increasing the substrate temperature and total pressure, the apparent grain size increased and the surface morphology showed a rough, cauliflower-like structure. © 2000 *Elsevier Science Ltd* 

KEYWORDS: A. ceramics, A. nitrides, B. vapor deposition, D. microstructure

## **INTRODUCTION**

Hexagonal boron nitride (h-BN), which in its crystalline form is analogous to graphite, has been extensively investigated in the last few decades. More recently, considerable interest has arisen in possible applications of h-BN due to excellent thermal conductivity, extremely high electrical resistivity, microwave and infrared transmittance, and chemical stability [1–4].

Chemical vapor deposition (CVD) techniques have been used to prepare h-BN films from various gaseous precursors, such as boron trifluoride (BF<sub>3</sub>) [5], boron trichlorides (BCl<sub>3</sub>) [6], and diborane (B<sub>2</sub>H<sub>6</sub>) [7], with a mixture of ammonia (NH<sub>3</sub>) and hydrogen (or inert gases). Among the boron sources, boron trichloride and diborane have been used most frequently because the former yields a high deposition rate and the latter decreases the process temperature to as low as 600°C. With boron trichloride as a boron source, high substrate

temperature is required in order to obtain crystalline h-BN; otherwise, amorphous BN is deposited. On the other hand, with diborane the deposition rate is comparatively much lower than other boron sources. Recently, Takahashi et al. [8] succeeded in preparing h-BN films at a temperature as low as 700°C. However, they found that the films obtained below 1000°C were amorphous, and obtained crystalline films only after annealing them at much higher temperature.

Another potential source of h-BN deposition comes from the reaction of boron tribromide (BBr<sub>3</sub>) and ammonia. As would be expected from the periodicity of boron halides, boron tribromide is thermodynamically more unstable than boron trifluoride or boron trichloride, thus it can produce reactive boron containing chemical species at much lower temperature [9]. Furthermore, the danger caused by the inflammability of boron trichloride is less. However, there has been little information in the literature on chemical vapor deposition of h-BN from the BBr<sub>3</sub>–NH<sub>3</sub>–H<sub>2</sub> gas system. Therefore, the objective of the present study was to use boron tribromide as a new boron source and investigate the effect of process parameters on the CVD of h-BN films.

#### EXPERIMENTAL

Hexagonal boron nitride films were deposited in a cold-wall-type quartz reactor heated by infrared radiation lamps. The temperature of the substrate was measured using a thermocouple, which was in contact with the substrate pedestal. A coaxial double tube was used as a reactor, and the air was pumped in between the tubes in order to prevent deposition on the reactor wall. Graphite plates  $(10 \times 10 \times 1 \text{ mm})$  and cylindrical graphite were used as substrate and susceptor, respectively. A mixture of ammonia and hydrogen was introduced into the uppermost part of the reactor, while the boron tribromide vapor, saturated at 0°C with argon bubbling gas, was supplied separately through a different inlet tube, 2 cm apart above the substrate. The total flow rate and molar fraction of NH<sub>3</sub>/BBr<sub>3</sub> was adjusted with a mass flow controller and meters. A rotary vacuum pump was used to adjust the total gas pressure in the reaction chamber between 2 and 12 kPa. Prior to deposition, the reactor was pumped out and flushed with argon, and the experiment was finished by bypassing the reactants. A schematic diagram of the experimental apparatus is illustrated in Figure 1.

The growth rate of the h-BN was estimated by measuring the weight gain during deposition periods. The deposited films were identified with infrared spectroscopy and X-ray diffraction. The as-grown deposits surface morphology and cross-sectional microstructure were examined with scanning electron microscopy.

## **RESULTS AND DISCUSSION**

The deposition processing parameters investigated are substrate temperature and total pressure of the reactor. In the chemical vapor deposition of h-BN with  $NH_3_BX_3$  gas system, where X is F, Cl, or Br, the depletion of ammonia concentration above the substrate is unavoidable by the formation of ammonium halides ( $NH_4X$ ), therefore  $NH_3/BBr_3$  value higher than 1.0 is required [10,11]. Our previous work [12] found that the optimum deposition could be obtained at  $NH_3/BBr_3 = 3.0$ . Therefore, the  $NH_3/BBr_3$  ratio was kept at 3.0 throughout the experiment.



FIG. 1 Schematic diagram of the apparatus for h-BN deposition.

The dependence of the growth rate on the substrate temperature is shown in Figure 2. The total pressure of the reactor was 2, 4, or 8 kPa, and the time of vapor deposition was 20 min. As can be seen in Figure 2, at the total pressure of 2 kPa, the growth rate increased continuously with increase in the substrate temperature, while in the case of 4 or 8 kPa, the rate reached a maximum and further increase in the temperature decreased the growth rate.



FIG. 2

Dependence of growth rate on the substrate temperature and total pressure ( $NH_3/BBr_3 = 3.0$ , deposition time = 20 min).



FIG. 3

Scanning electron micrographs of the surfaces grown at (a) 800°C, (b) 900°C, (c) 1000°C, and (d) 1100°C (total pressure = 2 kPa). The scale for all figures is the same.

The maximum rate occurred at 1100 and 1000°C at the pressure of 4 and 8 kPa, respectively. In the low temperature region, an increase in total pressure led to an increase in the number of the reactant gas molecules, and as a consequence, deposition was promoted. The decrease of growth rate at 4 and 8 kPa at high temperatures is considered to be caused by a depletion of reactants due to increase of vapor phase reaction, which is promoted by high reactant concentration combined with high substrate temperature.

The effect of temperature on the as-grown surface of deposits is shown in Figure 3. The total pressure was 2 kPa and  $NH_3/BBr_3$  ratio was 3.0. The h-BN surface obtained at 800°C was composed of small particles. It can be seen from Figure 3 that the apparent grain size increases as the substrate temperature increases.

Figure 4 shows the effect of total pressure on the surface of deposits, where substrate temperature was 1000°C. With increasing total pressure, the apparent grain size increases and the surface deposited at high total pressure shows a rough, cauliflower-like structure. The effects of substrate temperature (Fig. 3) and total pressure (Fig. 4) on the surface morphology show a similar tendency. These results are considered to be related to the growth rate, that is, the surface grows into a rough, cauliflower-like structure when the atoms on the film have adequate surface mobility at high temperature and the concentration of reactants above the substrate is high.

Films deposited under various conditions were identified by IR spectrometry and XRD. Figure 5 shows IR spectra of the film deposited at 800°C. Two main absorption peaks, typical of the h-BN structure, appear at 1380 cm<sup>-1</sup>, the B–N stretching vibration, and a weak band near 790 cm<sup>-1</sup>, the B–N–B bending vibration. The two weak broad absorptions at approximately 3250 cm<sup>-1</sup>, N–H vibration, and 3400 cm<sup>-1</sup>, O–H vibration, are attributed to the humidity sensitive nature of h-BN. After a few days of exposure to a ambient environment,



FIG. 4

Scanning electron micrographs of the surfaces grown at (a) 2 kPa, (b) 4 kPa, (c) 8 kPa, and (d) 12 kPa (substrate temperature =  $1000^{\circ}$ C). The scale for all figures is the same.

the transparent h-BN films turned opaque. The expected N–Br or B–Br absorptions were not detected, indicating completion of  $BBr_3$  decomposition.

The results of X-ray diffraction showed that the main phase of the deposits was h-BN. A typical X-ray diffraction pattern of the deposits is presented in Figure 6. Strong (002) peaks





IR spectrum of h-BN film deposited at 800°C (total pressure = 4 kPa, substrate temperature = 1000°C, deposition time = 20 min.).



FIG. 6

X-ray diffraction pattern of h-BN film deposited at  $800^{\circ}$ C (total pressure = 4 kPa, substrate temperature =  $1000^{\circ}$ C, deposition time = 20 min).

of h-BN and weak (110) and (101) peaks are evident. The patterns were similar regardless of the temperature. These results show that the h-BN films were well-crystallized even at temperature as low as 800°C.

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