

Stability to moisture for chemically vapour-deposited boron nitride

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Chemically vapour-deposited boron nitride (CVD-BN) plates prepared by use of the $\text{BCl}_3\text{-NH}_3\text{-H}_2$ gas system were investigated as to their stability to moisture. Infrared (IR) spectroscopic measurement, chemical analysis and thermal gravimetric analysis were used in this study. The synthesis conditions of CVD-BN plates have a large influence on their stability to moisture. The stability of CVD-BN plates prepared under a total gas pressure (P_{tot}) of 10 to 60 torr degraded as the deposition temperature (T_{dep}) was lowered. The CVD-BN plates with transparent and isotropic properties, which were prepared at below 1400°C and above 10 torr, showed poor stability to moisture. The CVD-BN plates synthesized under 5 torr had high moisture-resistance, even at a T_{dep} as low as 1400°C . An IR absorption spectral study revealed that the unstable species existing in CVD-BN plates had changed to ammonium borate hydrates by reacting with moisture in the atmosphere. The stability to moisture for CVD-BN plates degraded as the deposition rate was raised, especially for the CVD-BN plates prepared at 1400°C .

1. Introduction

Because boron nitride prepared by chemical vapour deposition (CVD-BN) is a valuable material for electronic and high temperature applications, many reports on the subject of deposition of CVD-BN have been published. These reports point out that some deposits produced by the reaction of NH_3 with BCl_3 or B_2H_6 gases are unstable when they are exposed to moisture or water. There are some disagreements, however, with respect to the relationships between synthesis conditions and moisture resistance. Basche [1] reported that deposits formed from the $\text{BCl}_3 + \text{NH}_3$ system at 1450°C or below were soluble in water. While Sano and Aoki [2] studied a deposition of BN from the $\text{BCl}_3 + \text{NH}_3 + \text{Ar}$ system at $600\text{--}1100^\circ\text{C}$ and noted that the thin film obtained below 900°C was unstable. According to Motojima *et al.* [3] who prepared BN thin film in a temperature range of $250\text{--}700^\circ\text{C}$, the deposits obtained below 600°C were attacked when immersed in water. In these reports the stability criterion was based on whether or not the deposits obtained contain water-soluble elements. None of these reports have considered the reaction of unstable elements with moisture in the atmosphere.

The present author has reported on the structure [4], density and deposition rates [5] of chemically vapour-deposited BN (CVD-BN) plates synthesized on a graphite substrate under the $\text{BCl}_3 + \text{NH}_3 + \text{H}_2$ system in a cold wall type CVD reactor. This report will focus on the issue of the stability of CVD-BN plate to moisture.

2. Experimental procedure

Synthesis conditions of CVD-BN plates are shown in Table I. Details of the synthesis procedures have been

described in a previous paper [4]. A powder specimen was prepared by reducing CVD-BN plate ($30\text{ mm} \times 10\text{ mm} \times 0.2 \sim 1\text{ mm}$) to powder with a vibratory mill for 15 sec. This specimen was subjected to the following test measurements.

Infrared (IR) absorption spectra were obtained (a) immediately after powdering (denoted as fresh powder) and (b) after being stabilized by being left to stand under atmospheric conditions of relative humidity 65–80% at room temperature for 60 days (denoted as stabilized powder). For both cases the KBr pellet measurement technique was used.

Chemical analysis was used to determine the boron (B) and nitrogen (N) content in the stabilized powder. The neutralization titration method with the mannitol reagent was used for boron determination and the steam distillation method for nitrogen determination.

Thermal gravimetric analysis (TGA) was performed on the stabilized powder with a heating rate of 5°C min^{-1} in an argon atmosphere.

3. Results and discussion

3.1. Change in IR spectrum by reaction with moisture

In Fig. 1 the IR spectrum of stabilized powder (broken line) is compared to the IR spectrum observed immediately after powdering (solid line). Figure 1a shows the IR spectrum of the specimen synthesized at a deposition temperature (T_{dep}) of 2000°C and total gas pressure (P_{tot}) of 10 torr, while Figs 1b and c are for specimens obtained under 5 and 10 torr, respectively at 1400°C . The spectra in Figs 1a and b were consistent with that of BN having sp^2 bonding [6]. There were no significant changes during the 60-day stabilization period.

TABLE I The synthesis conditions of CVD-BN plates

Deposition temperature, T_{dep}	1200–2000°C
Total gas pressure, P_{tot}	5–60 torr
Gas flow rate, FR(NH_3)	90 $\text{cm}^3 \text{min}^{-1}$
FR(BCl_3)	140 $\text{cm}^3 \text{min}^{-1}$
FR(H_2)	670 $\text{cm}^3 \text{min}^{-1}$
Deposition time, t	1–9 h

On the other hand, in the specimen obtained at 1400°C and 10 torr, there was a large difference between the spectra of the fresh powder and the stabilized powder (Fig. 1c). In the IR spectrum shown in Fig. 1c the absorption due to the NH_2 group was observed at about 3200 cm^{-1} together with the one due to BN. In addition, the stabilized powder gave new absorption peaks at 1100, 1020, 920 and 690 cm^{-1} (broken line). These peaks were identified as originating from ammonium borate hydrates since they were consistent with the spectrum of an $(\text{NH}_4)_2\text{O} \cdot 5\text{B}_2\text{O}_3 \cdot 8\text{H}_2\text{O}$ reagent (Wako Pure Chemical Industries, Ltd). Furthermore, the X-ray diffraction pattern of the stabilized powder contained the main reflections of $(\text{NH}_4)_2\text{O} \cdot 5\text{B}_2\text{O}_3 \cdot 8\text{H}_2\text{O}$ (JCPDS 12-638) and $(\text{NH}_4)_2\text{O} \cdot 4\text{B}_2\text{O}_3 \cdot 6\text{H}_2\text{O}$ (JCPDS 19-72), together with the reflections of turbostratic BN (t-BN). In the IR peaks at about 3200 cm^{-1} and about 800 cm^{-1} , some differences were observed between IR spectra of the fresh powder prepared at 2000°C–10 torr and 1400°C–5 torr and at 1400°C–10 torr. It was noted that the CVD-BN plate synthesized at 1400°C and 10 torr emitted a NH_3 odour during the powdering

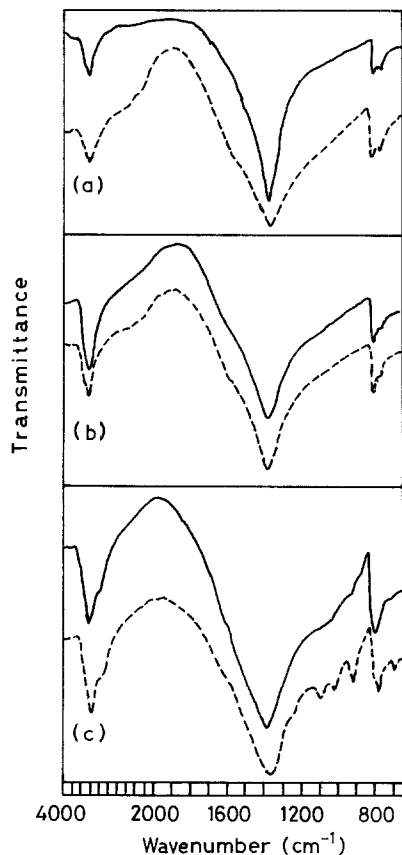


Figure 1 IR spectra measured immediately after the powdering process (solid lines) and after being left to stand under atmospheric conditions for 60 days (broken lines). (a) $T_{\text{dep}} = 2000^\circ\text{C}$, $P_{\text{tot}} = 10$ torr; (b) $T_{\text{dep}} = 1400^\circ\text{C}$, $P_{\text{tot}} = 5$ torr, (c) $T_{\text{dep}} = 1400^\circ\text{C}$, $P_{\text{tot}} = 10$ torr.

process. This observation suggests some changes in the composition of the deposit have taken place in the powdering process and thus explains the differences observed in IR spectra mentioned above. Consequently, it can be concluded that the CVD-BN plate obtained at 1400°C and 10 torr changes its character reacting with moisture not only while in the process of being reduced to powder but also during the time it is allowed to stand under atmospheric condition.

Gebhardt [7] synthesized CVD-BN from B-trichloroborazole ($\text{Cl}_3\text{B}_3\text{N}_3\text{H}_3$) at 1100–1800°C. The IR spectrum of the deposit prepared at 1200°C was reported by Gebhardt as having exactly the same features as the one shown as a broken line in Fig. 1c. He suggested that IR peaks other than that of BN originated from “undecomposed species” trapped in the deposit. However, the present study makes it clear that those peaks are due to ammonium borate hydrates which may be formed during handling. Chlorine content in the stabilized powder shown in Fig. 1c was no more than 0.06 wt %. This result suggests that undecomposed species are little included in the unstable CVD-BN plates. Unstable species altered to ammonium borate hydrates may have unstable sight such as the dangling bond in amorphous materials. In another study Rand and Roberts [8] showed that boric acid is formed when thin film produced from the $\text{B}_2\text{H}_6 + \text{NH}_3 + \text{N}_2$ (or He) system at 600–800°C was allowed to stand for 1–2 wk under atmospheric condition. In the present study, it was observed that the CVD-BN plates being unstable to moisture were partly changed into ammonium borate hydrates. The causes for the disagreement between our observations and those of Rand and Roberts have not as yet been clarified.

3.2. Effects of synthesis conditions on the stability to moisture

Stability of CVD-BN plates synthesized under various synthesis conditions was quantitatively evaluated by determining the chemical composition of the stabilized powder. Figs 2 and 3 show the effects of synthesis conditions on the (B + N) content and the B/N atomic ratio, respectively. Analyses of a commercial h-BN powder (Wako Pure Chemical Ind., Ltd) and a CVD-BN plate (Union Carbide Corp., denoted as UCC-BN) are also included in both figures for comparison purposes.

As seen from Fig. 2, the CVD-BN plate synthesized at a P_{tot} of 5 torr has a (B + N) content of about 95%. This value is very close to those of the commercial h-BN powder and the UCC-BN plate. On the other hand, for the stabilized powder prepared from the transparent CVD-BN plates [4] produced at above 10 torr and below 1400°C, the (B + N) content is less than 70 wt %.

The results in Fig. 3 indicate that the specimens prepared at 5 torr show B/N atomic ratios nearly equal to the stoichiometric value of 1, independent of T_{dep} . Whereas, those synthesized at a P_{tot} above 10 torr and at low T_{dep} show distinctively the existence of excess amounts of boron.

A comparison of the results in Figs 2 and 3 reveals

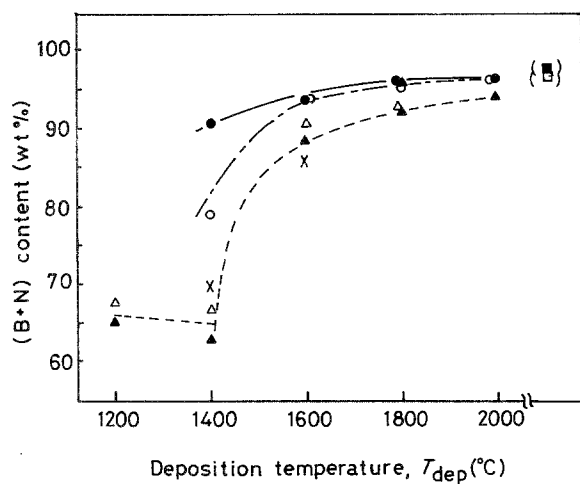


Figure 2 Effect of T_{dep} on the boron and nitrogen contents of the stabilized powder. Commercially obtainable boron nitride; (■)h-BN powder, (□)UCC-BN. Values of P_{tot} (torr) are (●) 5; (○) 10; (x) 20; (▲) 30; (△) 60.

that the stabilized powder containing excess boron has a low (B + N) content.

Fig. 4 shows the relation between the (B + N) content and the B/N atomic ratio. Each broken line indicates a calculated curve for a different mixture of BN (m mol %) and an ammonium borate hydrate (n mol %) or a mixture of BN and boric oxide. As shown in Fig. 4, the results for the stabilized powder are closely approximated by curves (b), $m\text{BN} + n(\text{NH}_4)_2\text{O} \cdot 4\text{B}_2\text{O}_3 \cdot 6\text{H}_2\text{O}$, and (c), $m\text{BN} + n(\text{NH}_4)_2\text{O} \cdot 5\text{B}_2\text{O}_3 \cdot 8\text{H}_2\text{O}$. These findings are consistent with the present results of the IR spectrum measurements described above. These results suggest that the CVD-BN plate obtained at a P_{tot} above 10 torr and low T_{dep} tends to change into ammonium borate hydrates as a result of the reaction with moisture encountered during the powdering and stabilization processes.

Two conclusions can be drawn from Figs 2 and 3. First, the stability of the CVD-BN plates synthesized at 10–60 torr degraded as the deposition temperature was lowered. Secondly, the CVD-BN plates obtained at 5 torr showed high resistance to moisture, even at a T_{dep} as low as 1400 °C (cf. Fig. 1b).

TGA curves for some stabilized powders are shown in Fig. 5. As clearly shown in Fig. 5 the stabilized powders prepared from the CVD-BN plates at a T_{dep} of 1400 °C and at P_{tot} of 30 and 10 torr showed weight

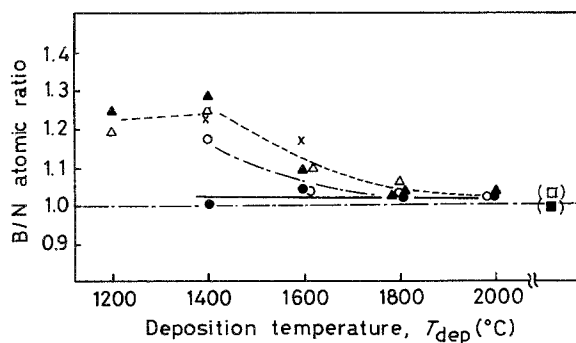


Figure 3 Effect of T_{dep} on the B/N atomic ratio of the stabilized powder. Commercially obtainable boron nitride; (■)h-BN powder, (□)UCC-BN. Values of P_{tot} (torr) are (●) 5; (○) 10; (x) 20; (▲) 30; (△) 60.

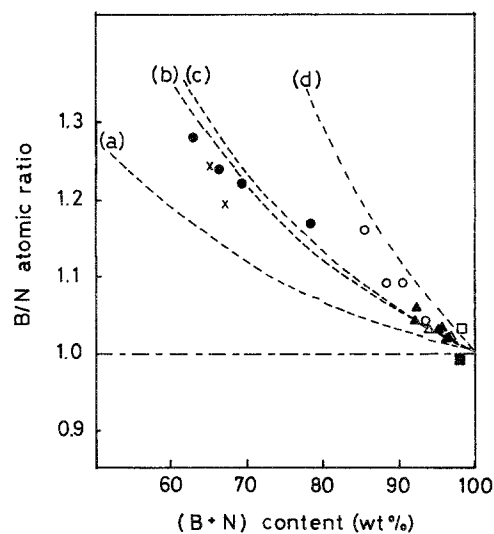


Figure 4 Correlation between the (B + N) content and the B/N atomic ratio. Commercially obtainable boron nitride; (■)h-BN, (□)UCC-BN. Broken line indicates the calculated values for the mixture of; (a) $m\text{BN} + n(\text{NH}_4)_2\text{O} \cdot 2\text{B}_2\text{O}_3 \cdot \text{H}_2\text{O}$, (b) $m\text{BN} + n(\text{NH}_4)_2\text{O} \cdot 4\text{B}_2\text{O}_3 \cdot 6\text{H}_2\text{O}$, (c) $m\text{BN} + n(\text{NH}_4)_2\text{O} \cdot 5\text{B}_2\text{O}_3 \cdot 8\text{H}_2\text{O}$, (d) $m\text{BN} + n\text{B}_2\text{O}_3$. T_{dep} (°C) = (x) 1200; (●) 1400; (○) 1600; (▲) 1800; (△) 2000.

losses of 17 and 10 wt % at beyond 500 °C, respectively. These powders had low (B + N) content and high B/N atomic ratio. The gradual weight loss takes place up to a temperature of 500 °C, as shown in Fig. 5. When the stabilized powder was assumed to be either a mixture of BN and $(\text{NH}_4)_2\text{O} \cdot 4\text{B}_2\text{O}_3 \cdot 6\text{H}_2\text{O}$ (Mixture-A) or a mixture of BN and $(\text{NH}_4)_2\text{O} \cdot 5\text{B}_2\text{O}_3 \cdot 8\text{H}_2\text{O}$ (Mixture-B), the weight loss of the mixture due to heating can be calculated by considering thermal decomposition of ammonium borate hydrate as follows:

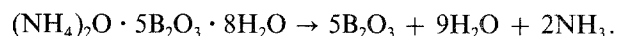
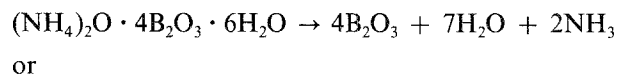


Fig. 6 illustrates the calculated values of weight loss as a function of the (B + N) content. The broken line represents Mixture-A and the solid line Mixture-B. The closed circles indicate the observed values of the stabilized powder obtained from TGA and chemical analysis. It can be seen from Fig. 6 that the observed values nearly fit to the calculated values. Therefore,

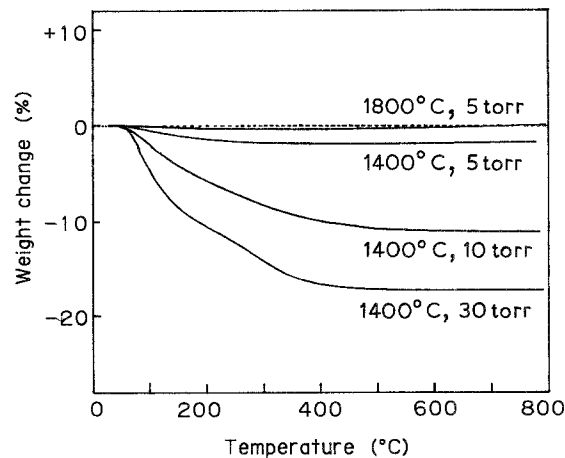


Figure 5 TGA curve of the stabilized powder in argon atmosphere.

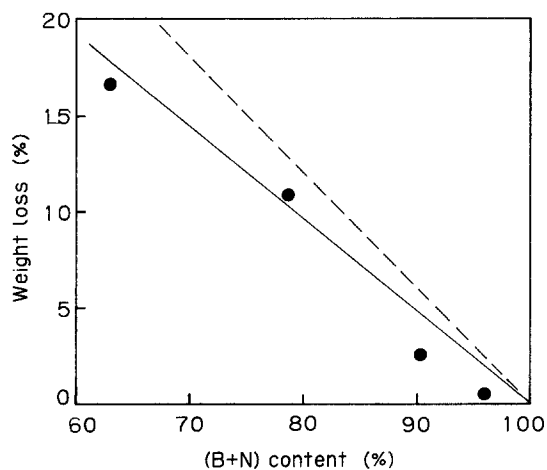


Figure 6 Correlation between the (B + N) content and the weight loss (at 500°C) of the stabilized powder. Solid and broken lines indicate the calculated values for the mixture of BN and $(\text{NH}_4)_2\text{O} \cdot 5\text{B}_2\text{O}_3 \cdot 8\text{H}_2\text{O}$ and for the mixture of BN and $(\text{NH}_4)_2\text{O} \cdot 4\text{B}_2\text{O}_3 \cdot 6\text{H}_2\text{O}$, respectively.

the vapourization of H_2O and NH_3 , which is generated by thermal decomposition of ammonium borate hydrates in the stabilized powder, is determined to be the cause of the weight loss. Takahashi *et al.* [9] prepared transparent BN thick film on iron substrate at 1250°C and 1 atm by using the $\text{BCl}_3\text{-NH}_3\text{-Ar-N}_2$ system. Their TGA data showed a similar weight loss up to 500°C reaching 14 wt % for their BN thick film. This large weight loss may be due to ammonium borate hydrates formed during handling.

Gebhardt [7] described that the quantity of unstable species (undecomposed species) trapped in the deposit is determined not only by T_{dep} but also by the gas concentration and deposition rate. To confirm this idea the relationship between the deposition rate and the stability of the CVD-BN plates synthesized in this study was examined. The stability to moisture for CVD-BN plate has been able to evaluate with the value of (B + N) content in Fig. 2. Figure 7 shows the relation between the (B + N) content of stabilized powder and the deposition rate of CVD-BN plate [5]. At a T_{dep} below 1600°C the (B + N) content decreases as the deposition rate increases. One of the reasons for obtaining the stable BN thin film to

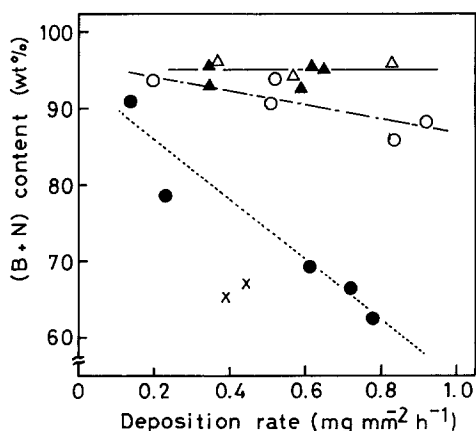


Figure 7 Correlation between the deposition rate of CVD-BN plate and the (B + N) content of the stabilized powder. T_{dep} (°C) = (Δ) 2000; (\blacktriangle) 1800; (\circ) 1600; (\bullet) 1400; (\times) 1200.

moisture at low T_{dep} may be due to its low deposition rate.

O'Connor [10] has point out that t-BN powder tends to undergo hydrolysis. Also, Economy and Anderson [11] reported that a BN fibre consisting of t-BN with $c_0/2$ of 0.341 nm incurred a weight loss of several per cent after being immersed in boiling water for 16 h. As shown in Fig. 2, CVD-BN prepared at low T_{dep} composed of t-BN with $c_0/2$ of 0.350 nm or greater has shown a large change in its (B + N) content due to the moisture. On the other hand, t-BN with $c_0/2$ of 0.344 nm which was synthesized at 2000°C and 10 torr, was not influenced by moisture.

The BN fibre with $c_0/2$ of 0.341 nm had a density of about 1.8 g cm^{-3} which is smaller than that of our CVD-BN plate with $c_0/2$ of 0.344 nm (density 2.1 g cm^{-3}). As described in previous work [5], the density of CVD-BN plate closely correlated with the value of $c_0/2$. These findings indicate that the stability of CVD-BN plates against moisture may also depend on the density and the value of $c_0/2$. This conclusion is suggested that the existence of unstable species or unstable sites in deposit leads to a decrease density.

4. Conclusions

The following is a summary of the results.

1. The synthesis conditions greatly affected the stability of CVD-BN plate to moisture. The CVD-BN plate obtained at 5 torr and 1400–2000°C had a high moisture resistance.
2. The stability of the CVD-BN plates prepared at 10–60 torr degraded as the T_{dep} was lowered. Particularly, the transparent isotropic CVD-BN plate obtained at above 10 torr and below 1400°C showed poor moisture resistance.
3. Poor moisture resistant unstable species (or unstable sites) contained in CVD-BN plate were changed to ammonium borate hydrates as a result of the reaction with moisture.

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