

the society for solid-state and electrochemical science and technology

# **Chemical Vapor Deposition of Boron Nitride**

N. Patibandla and K. L. Luthra

*J. Electrochem. Soc.* 1992, Volume 139, Issue 12, Pages 3558-3565. doi: 10.1149/1.2069121

**Email alerting** service Receive free email alerts when new articles cite this article - sign up in the box at the top right corner of the article or click here

To subscribe to *Journal of The Electrochemical Society* go to: http://jes.ecsdl.org/subscriptions

© 1992 ECS - The Electrochemical Society



Fig. 10. Activation enthalpies for lithium diffusion in  $Li_n\{x(A_2O)\cdot WO_3\}$  (A = Na<sup>+</sup>, NH<sup>+</sup><sub>4</sub>) and Li\_nWO\_3; (a) Li\_n\{0.14(Na\_2O)\cdot  $WO_3$  (b)  $Li_n[0.051\{(NH_4)_2O\} \cdot WO_3]$ , and (c)  $Li_nWO_3$ .

WO<sub>3</sub>. Moreover, the hexagonal oxides showed a good charge-discharge cycling behavior at lower capacity below n = 0.5 in  $\text{Li}_n \{ x(A_2O) \cdot WO_3 \}$  (A = Na<sup>+</sup>, K<sup>+</sup>, NH<sup>+</sup><sub>4</sub>).

## Acknowledgment

The authors thank Professor Y. Umetz for flame photometric analysis.

Manuscript submitted March 4, 1992; revised manuscript received Aug. 3, 1992.

Iwate University assisted in meeting the publication costs of this article.

#### REFERENCES

- 1. M. S. Whittingham, This Journal, 123. 315 (1976).
- M. Green, W. C. Smith, and J. A. Weiner, *Thin Solid Films*, 38, 89 (1976).
- 3. K. H. Cheng and M. S. Whittingham, Solid State Ionics, 1, 151 (1980).
- 4. N. Kumagai and K. Tanno, Denki Kagaku, 49, 599 (1981).
- N. Kumagai, N. Kumagai, and K. Tanno, Electrochim. Acta, 32, 152 (1987).
- N. Kumagai, N. Kumagai, and K. Tanno, J. Appl. Electrochem., 18, 857 (1988).
   N. Kumagai, N. Kumagai, and K. Tanno, Appl. Pys.,
- A49, 83 (1989).
- N. Kumagai, Y. Matsuura, Y. Umetzu, and K. Tanno, Solid State Ionics, 53-56, 324 (1992).
- G. Gerand, G. Nowgrocki, J. Guenot, and M. Figlarz, J. Solid State Chem., 29, 429 (1979).
   N. Kumagai and K. Tanno, Denki Kagaku, 48, 601
- (1980).
- 11. Naoaki Kumagai, K. Tanno, and Nobuko Kumagai, Electrochim. Acta, 27, 1087 (1982).
- 12. C. Ho, I. D. Raistrick, and R. A. Huggins, This Journal, 127, 343 (1980).
- S. Basu and W. L. Worrell, Fast Ion Transport in Solids, J. N. Mundy, P. D. Vashita, and G. K. Shenoy, Edi-tors, p. 149, North-Holland, Amsterdam (1979).
   A. S. Nagelberg and W. L. Worrell, J. Solid State Chem., 29, 345 (1979).
   S. D. Pasiatish, and R. A. Hugging, Solid State
- 15. S. Joo, I. D. Raistrick, and R. A. Huggins, Solid State Ionics, 17, 313 (1985).
- 16. W. Weppner and R. A. Huggins, A. Rev. Mater. Sci., 8, 269 (1978)
- 17. W. Dieterich, Solid State Ionics, 5, 21 (1981).

# **Chemical Vapor Deposition of Boron Nitride**

# N. Patibandla<sup>a</sup> and K. L. Luthra<sup>\*</sup>

General Electric Corporate Research and Development, Schenectady, New York 12301

#### ABSTRACT

Thermodynamics and kinetics of boron nitride deposition from BCl<sub>3</sub>-NH<sub>3</sub> gas mixtures were studied in the temperature range 850 to  $1050^{\circ}$ C at pressures between 1.1 and 3.5 Torr. A wide range of deposition rates, as high as  $1 \, \mu$ m/min, were measured. The rate of depositon was controlled by an interface reaction with an activation energy of  $35 \pm 3$  kcal/mol. The deposition rate constant essentially was independent of the partial pressure of  $NH_3$  and showed a close to first-order dependence on the partial pressure of  $BCl_3$ . The rate-limiting step of the interface reaction may be the dissociative adsorption of  $BCl_3$  onto the substrate surface. The deposited BN was of theoretical density, turbostratic structure, and contained about 12 atomic percent oxygen.

The high electrical resistivity and low dielectric constant of boron nitride make it a useful material for several electronic applications.<sup>1-3</sup> Also, the lubricative characteristics of its laminar structure make it a uniquely qualified material for fiber coatings in ceramic matrix composites (CMC). Boron nitride is a useful fiber coating in SiC fiber reinforced SiC,4 mulite,5,6 and zirconia-based7 matrix composites. Chemical vapor deposition (CVD) is used extensively in producing semiconductor devices and fiber coatings. Dense uniform continuous films of high purity can be obtained using CVD.

Gas mixtures containing BCl<sub>3</sub> and NH<sub>3</sub> are widely used gaseous precursors in CVD of BN.8-19 Å comprehensive thermodynamic analysis on the CVD of BN conducted by

\* Electrochemical Society Active Member.

\* Present address: Center for Composite Materials and Structures, Rensselaer Polytechnic Institute, Troy, NY 12180.

Hannache et al.<sup>14</sup> and a general review on the experimental BN-CVD reported by Lackey et al.<sup>18</sup> are available in the literature. Many of the earlier studies<sup>8-15</sup> reported on the technique and/or the characteristics of the deposit, thus restricting the applicability to certain empirically established conditions that were arrived at by individual researchers. In other studies,  $BCl_3$ -NH $_3$  and  $H_2$  <sup>16</sup> or  $BCl_3$ -NH $_3$ and  $N_s^{17}$  mixtures were used to address the governing principles of the deposition process. According to the aforementioned thermodynamic analysis,<sup>14</sup> presence of free hydrogen in the initial gas mixture can lead to codeposition of free boron. The effect of nitrogen is unknown. A comprehensive kinetic analysis was published recently by Lee et al. 19 This study addresses BN deposition on alumina substrates over a limited range of reactant partial pressures.

Here our principle objective is to understand the thermodynamics and kinetics of low pressure CVD of BN on several substrates from BCl<sub>3</sub> and NH<sub>3</sub> gas mixtures and further identify the role of H<sub>2</sub> and N<sub>2</sub>. Using several substrates is important as BN has become a useful fiber coating in CMCs. The use of low pressures facilitates infiltration of fiber bundles and preforms.<sup>20</sup> Closed system thermodynamic analysis is conducted to obtain information complementary to other published work.<sup>14</sup> The kinetics of BN deposition are studied as a function of several experimental variables on flat coupon samples to identify the rate-limiting steps of the deposition process. The experimental setup and the parameters are chosen such that the effect of gas transport rates, if any, can be calculated and accounted for and thereby the conditions for interfacial-reaction-controlled deposition can be identified.

#### Thermodynamic Analysis

A thermodynamic analysis was conducted using the data from JANAF tables.<sup>21</sup> All the compounds of B-N-Cl-H system listed in the JANAF tables were considered. Thermodynamic calculations were performed using a computer program that finds the equilibrium conditions by free-energy minimization. A complete description of the calculation procedure is available in Ref. 22. For the present case, the nature of the calculations is identical to the one described in Ref. 14. First, deposition of boron nitride from a gaseous mixture of BCl<sub>3</sub> and N<sub>2</sub> was considered. In this B-N-Cl system, the overall chemical reaction can be written as

$$2BCl_3(g) + N_2(g) = 2BN(s) + 3Cl_2(g)$$
[1]

The thermodynamic yield of BN with respect to inlet  $BCl_3$  concentration ( $Y_B$ ) represents the moles of BN formed per mole of  $BCl_3$ . It is similar to that defined in Ref. 14 and can be written as

$$Y_{\rm B} = \frac{100 < \rm BN>_{eq}}{[\rm BCl_3]_{in}}$$
[2]

where the angular brackets represent the mole concentration of condensed phase and the square brackets refer to that of a gaseous species. The subscripts eq and in refer to the equilibrium and the initial concentrations, respectively.

The yield calculated according to Eq. 2 at a temperature of 1000°C and a total pressure of 1 Torr varies between 0.015 and 0.043% for a N/B ratio of one and eight ( $N_2/BCl_3$  ratio of 0.5 and 4.0), respectively. These yields are plotted as a function of N/B ratio in Fig. 1. This yield had only a small dependence on the total pressure, slightly decreasing with increasing pressure. The equilibrium constant of reaction 1 may be written as

$$K_{\rm eq}^{(1)} = \frac{a_{\rm BN}^2 p_{\rm Cl_2}^3}{p_{\rm N_2} p_{\rm BCl_3}^2}$$
[3]

According to this equilibrium constant, the activity of BN and hence the thermodynamic yield of BN varies inversely with the partial pressure of  $Cl_2$ . The  $Cl_2$  partial pressure reaches its equilibrium value at low yields of BN. Therefore,  $BCl_3/N_2$  mixtures cannot be used to deposit BN. To reduce the partial pressure of  $Cl_2$ , one may introduce a gas that readily reacts with  $Cl_2$ , such as  $H_2$ . In this B-N-Cl-H system, the overall reaction may now be written as

$$2BCl_3(g) + N_2(g) + 3H_2(g) = 2BN(s) + 6HCl(g)$$
[4]

Thermodynamic yield of BN with respect to inlet gas  $BCl_3$  concentration ( $Y_B$ ) for this system also can be calculated according to Eq. 2 and is shown in Fig. 1 as a function of inlet N/B ratio for several  $H_2/N_2$  ratios. The yield of BN increases with both N/B and H/N ratios. For a  $H_2/N_2$  ratio of three, an N/B ratio of 1.5 or higher gives a thermodynamic yield better than 95%.

Thermodynamically, there is no difference between a 3:1  $H_2$  to  $N_2$  gas mixture and ammonia ( $NH_3$ ) gas because at the temperatures of interest  $NH_3$  dissociates into  $N_2$  and  $H_2$ . Hence reaction 4 may be rewritten as



Fig. 1. Thermodynamic yield of BN with reference to  $BCl_3(Y_B)$  of  $BCl_3-N_2-H_2$  gas mixtures as a function of N/B ratio for several H/N ratios at 1000°C between 1 and 760 Torr.

$$BCl_3(g) + NH_3(g) = BN(s) + 3HCl(g)$$
[5]

For this reaction, yield of BN with respect to initial BCl<sub>3</sub> concentration ( $Y_B$ ) may be calculated according to Eq. 2. The yield with respect to initial NH<sub>3</sub> concentration ( $Y_N$ ) represents the moles of BN formed per mole of NH<sub>3</sub> and can be expressed as

$$Y_{\rm N} = \frac{100 < \rm BN >_{eq}}{[\rm NH_3]_{in}}$$
 [6]

Yields with reference to both  $BCl_3$  and  $NH_3$  are plotted in Fig. 2. An  $NH_3/BCl_3$  ratio of 1.5 is sufficient to give a yield of more than 95% with reference to  $BCl_3$  and a yield of more than 65% with reference to  $NH_3$ . At higher  $NH_3/BCl_3$  ratios, yield with reference to  $BCl_3$  increases marginally but the yield with respect to  $NH_3$  drops rapidly to about 50% at a N/B ratio of 2. Hence,  $NH_3/BCl_3$  ratios close to but not less than 1.5 are used in the present work.

## Experimental

The kinetics of BN deposition were measured on flat samples  $(2.5 \times 1.25 \times 0.1 \text{ cm})$  suspended freely in a flowing gas in the temperature range 850 to 1050°C at pressures of 1.1 and 3.5 Torr for STP gas velocities between 0.13 and 1.43 cm/s. Such a sample geometry provides a well defined flow past the sample and allows calculation of gas phase transport rates. The gas velocities are normalized to STP conditions for ease of comparison and were calculated by dividing the volume of gas input (cm<sup>3</sup>/s) by the cross-sectional area of the reactor tube (4.91 cm<sup>2</sup>). Most of the experiments were conducted using BCl<sub>3</sub> and NH<sub>3</sub> gas mixtures. A few additional experiments were conducted using BCl<sub>3</sub>, NH<sub>3</sub> plus H<sub>2</sub> or N<sub>2</sub> gas mixtures to understand the deposition mechanism.

To monitor the deposition process continuously, a thermogravimetric balance (Cahn-1000) was interfaced with a vertical hot-wall low pressure CVD reactor. A schematic of this setup is shown in Fig. 3. The sample can be heated by a Pt-resistance furnace that can be moved up and down. The sample can be loaded when the furnace is in the down



Fig. 2. Thermodynamic yield of BN with reference to  $BCl_3(Y_B)$  and  $NH_3(Y_N)$  of  $BCl_3$ - $NH_3$  gas mixtures as a function of N/B ratio at 1000°C between 1 and 760 Torr.

position, and in the up position the constant temperature hot zone of the furnace surrounds the sample. The reaction gases (BCl<sub>3</sub> and NH<sub>3</sub>) pass through separate tubes located beside the reaction tube and enter it at the bottom and therefore the gases are heated before mixing with each other. Although the temperature of the gases at the time of mixing depends on the flow rates and is unknown, it is believed to be high enough to avoid formation of solid am-



Fig. 3. A schematic diagram of the experimental setup used for chemical vapor deposition of BN.

monium chloride (NH<sub>4</sub>Cl) before the gases pass over the sample. After exiting the reactor, the gases pass through a series of filters and traps that help in trapping white powdery  $NH_4Cl$  that forms at low temperatures. A counterflow of argon from the balance to the reaction tube prevents the corrosive gases from entering the balance.

In a typical run, a sample was suspended from the TGA inside the reactor to about 10 cm above the reaction gas inlets. After the initial setup, the system was flushed with Ar (entering through the balance) and  $N_2$  (flowing through the BCl<sub>3</sub> line) for about 60 min at the experimental pressure. The NH<sub>3</sub> line was opened and the preheated furnace was raised to heat the sample. After the sample reached the deposition temperature and the balance stabilized beyond the initial buoyancy, BCl<sub>3</sub> was allowed to pass through. A typical deposition run was between 30 and 60 min. The deposition reaction was stopped by closing the gas inlets. The weight gain measured by TGA was verified by measuring the initial and the final weights of the sample and the quartz hook. The error in the TGA weight gain due to deposition on the quartz hook was less than 5%. At a given temperature and pressure, the gas velocity (V) was changed by changing the total gas input (BCl<sub>3</sub> + NH<sub>3</sub>) into the system from 37.5 cm<sup>3</sup>/min to 420 cm<sup>3</sup>/min at STP. The partial pressures were changed by changing the inlet gas ratio of NH<sub>3</sub> to  $BCl_3$  between 1.5 and 20 and also by addition of  $N_2$  or  $H_2$ . The bulk of the experimentation was conducted on graphite samples. The deposition rates also were measured on quartz, alumina, and silicon carbide substrates for comparison.

After deposition selected samples were sectioned along their length parallel to the gas flow direction to measure the coating thickness using optical microscopy. Particular attention was paid to inspecting the thickness uniformity of these coatings. The surface microstructure of the coatings was examined also. The chemistry of the coatings was obtained by conducting an elemental analysis using x-ray photoelectron spectroscopy (XPS). The degree of crystallinity of the coating was inspected by x-ray diffraction (XRD). An uncoated substrate also was scanned by XRD for comparison.

#### Results

Plots of weight gain vs. time measured on graphite samples at 50°C intervals between 850 and 1050°C are shown in Fig. 4. This set of experiments was conducted using 45 cm<sup>3</sup>/min NH<sub>3</sub> and 30 cm<sup>3</sup>/min BCl<sub>3</sub> (*i.e.*, N/B = 1.5 and V = 0.25 cm/s at STP) at an average pressure of  $1.4 \pm 0.1$  Torr. A slight increase, about 5% per h in pressure was observed during each run. The weight gain is linear with respect to time indicating that the deposition rate (K) is independent of time. The rate of deposition measured at 950°C (Fig. 4) is  $0.045 \pm 0.005$  mg/cm<sup>2</sup> min. This corresponds to a rate of  $0.2 \pm 0.02 \ \mu$ m/min, if the deposited BN is of theoretical density (2.25 g/cm<sup>3</sup>). The thickness of the coating on a sample



Fig. 4. Deposition kinetics of BN from BCl<sub>3</sub>-NH<sub>3</sub> gas mixtures between 850 and 1050°C at 1.4  $\pm$  0.1 Torr and an NH<sub>3</sub>/BCl<sub>3</sub> ratio of 1.5.



Fig. 5. An optical micrograph showing cross section of a BN coated graphite sample after coating for 45 min at 1050°C, 1.4 Torr and an NH<sub>3</sub>/BCl<sub>3</sub> ratio of 1.5.

after 45 min at 950°C was measured to be 9.0  $\mu$ m, in excellent agreement with 9.0 ± 0.9  $\mu$ m calculated from the above rate confirming that the deposited BN was indeed of theoretical density. These results demonstrate that a TGA facility can be used to measure the deposition rates with a high accuracy. Figure 5 shows a cross-sectional view of the deposit after 45 min at 1050°C, 1.4 Torr and N/B = 1.5. The thickness of the deposit is about 28  $\mu$ m in excellent agreement with the 27 ± 2  $\mu$ m calculated from the data shown in Fig. 4. In addition, the thickness of the coatings was uniform along the entire length of the samples, *i.e.*, parallel to the gas flow direction.

Another set of experiments was conducted at  $950^{\circ}$ C,  $1.4 \pm 0.1$  Torr, and NH<sub>3</sub>/BCl<sub>3</sub> ratio of 1.5 and at different gas velocities to evaluate whether the deposition rates are influenced by transport rate across the gas boundary layer. The kinetics of deposition measured in these experiments are plotted in Fig. 6. The ratio of deposition is independent of gas velocity.

The effect of total pressure on deposition rates is shown in Fig. 7. The experiments were conducted at two different pressures (1.4 and 3.5 Torr) while keeping all other conditions (*T*, *V*, and precursor composition) the same. Increasing the pressure by a factor of 2.5 increased the deposition rate by about the same factor. The effect of pressure can be seen more profoundly in Fig. 8, where the deposition kinetics measured at 1.4 and 3.5 Torr between 850 and 1050°C are summarized as an Arhenius plot. The deposition rates comply with an exponential dependence on the temperature. The kinetics measured at 1.4 Torr conform to an activation energy of  $32 \pm 2$  kcal/mol and those measured at 3.5 Torr conform to an activation energy of  $37 \pm 2$  kcal/mol.



Fig. 6. Effect of gas velocity on the deposition kinetics of BN from BCl<sub>3</sub>-NH<sub>3</sub> gas mixtures.



Fig. 7. Effect of pressure on the deposition kinetics of BN from BCl<sub>3</sub>-NH<sub>3</sub> gas mixtures.

Although there is a slight change in the activation energy with pressure, an average value of  $35 \pm 3$  kcal/mol provides a reasonable fit for all the data as shown by the dashed lines. At all the temperatures of measurement, the deposition rates measured at 3.5 Torr are consistently higher by a factor of about 2.5 (3.5 Torr/1.4 Torr) than those measured at 1.4 Torr indicating a linear dependence of K on P. Therefore, the rate constant for BN deposition on graphite can be expressed by the following equations

$$K(g/cm^2 s) = 1.1 \pm 0.1(P) \exp\left(\frac{-35 \pm 3 \text{ kcal/mol}}{RT}\right)$$
 [7]

$$K(\mu m/s) = 4.9 \pm 0.5 \times 10^{3} (P) \exp\left(\frac{-35 \pm 3 \text{ kcal/mol}}{RT}\right)$$
 [8]

where, P is the total pressure in Torr, either 1.4 or 3.5 for the data shown in Fig. 8.

To test the dependence of K on the substrate chemistry, deposition was studied on several different substrates at  $950^{\circ}$ C, using an inlet gas mixture of 45NH<sub>3</sub>-30BCl<sub>3</sub> between 1.3 and 1.5 Torr. The pressure control within each experiment was better than  $\pm 0.03$  Torr. The data presented in Fig. 9 suggest that the deposition rate is independent of substrate chemistry. Also deposition rates were measured on quartz samples between 900 and  $1050^{\circ}$ C. The data are compared with those measured on graphite in Fig. 10. The deposition rates measured on quartz show an activation energy of about  $39 \pm 3$  kcal/mol, within the experimental error to that measured on graphite substrate. Excellent



Fig. 8. The BN deposition rate constant as a function of temperature (K in g/cm<sup>2</sup> s).



Fig. 9. Deposition kinetics of BN from BCl<sub>3</sub>-NH<sub>3</sub> gas mixtures measured on different substrates.



Fig. 10. The BN deposition rate constants measured on graphite and quartz substrates as a function of 1/T.

agreement between the two sets of data, for graphite and quartz, suggests that the substrate chemistry has little or no influence on the kinetics of deposition. This is not surprising because after deposition of a few atomic layers, BN is deposited on itself but not on the original substrate.

As previously indicated, from a thermodynamic standpoint, deposition with  $NH_3$ - $BCl_3$  mixture is equivalent to that with  $N_2$ - $H_2$ - $BCl_3$  mixture with a H/N ratio of 3. To evaluate kinetic effects, additional experiments were conducted on graphite substrates in which  $NH_3$  was substituted by a mixture of  $H_2$  and  $N_2$ . However, no deposit was seen on the substrates suggesting that the presence of ammonia is necessary.

Table I. Deposition of BN from NH<sub>3</sub>-BCl<sub>3</sub>-{N<sub>2</sub>/H<sub>2</sub>/Ar} mixtures at 950°C.

Inlet gas composition <sup>a</sup> (cm <sup>3</sup> /min)	Total pressure P (Torr)	p <sub>NH</sub> (Torr)	p <sub>BCL</sub> (Torr)	Deposition rate k (mg/cm²/min) <sup>b</sup>
NH./BCl.				
400/20	1.40	1.33	0.07	0.028
200/10	1.38	1.31	0.07	0.020
140/14	1.69	1.54	0.15	0.038
60/15	1.37	1.10	0.27	0.041
90/60	1.17	0.70	0.47	0.046
60/30	1.55	1.03	0.52	0.045
45/30	1.33	0.80	0.53	0.045
22.5/15	1.43	0.86	0.57	0.046
60/15	3.20	2.56	0.64	0.110
70/20	3.10	2.40	0.70	0.110
60/30	3.18	2.12	1.06	0.149
45/30	3.12	1.87	1.25	0.150
45/30	3.50	2.10	1.40	0.123
NH <sub>3</sub> /BCl <sub>3</sub> /H <sub>2</sub>				
22.5/15/200	1.57	0.15	0.10	0.015
45/30/175	1.36	0.25	0.16	0.027
45/30/175	2.08	0.37	0.25	0.035
45/30/50	1.65	0.60	0.40	0.039
NH <sub>2</sub> /BCl <sub>2</sub> /N <sub>2</sub>				
22.5/15/200	1.38	0.13	0.09	0.019
22.5/15/200	1.85	0.18	0.12	0.016
45/30/175	1.35	0.24	0.16	0.024
NH <sub>3</sub> /BCl <sub>3</sub> /Ar				
22.Š/15/Ž00	1.65	0.16	0.10	0.020
45/30/175	1.46	0.26	0.18	0.023
			. <u> </u>	

<sup>a</sup> 100 cm<sup>3</sup>/min corresponds to a gas velocity of 0.34 cm/s at STP. <sup>b</sup>  $K(\mu m/min) = K(mg/cm^2 min) \times 4.44$ .

To understand the dependence of K on the partial pressures of the reaction gases, additional experiments were conducted at 950°C over a range of NH<sub>3</sub>/BCl<sub>3</sub> ratios and also with gas mixtures containing BCl<sub>3</sub>, NH<sub>3</sub> plus H<sub>2</sub> or N<sub>2</sub> or Ar. The rates of deposition measured in these runs and the corresponding partial pressures of the gaseous species in the inlet mixture are listed in Table I. A complete analysis of the data is presented in the Discussion. To examine the influence of HCl partial pressure, we attempted to conduct some experiments with BCl<sub>3</sub>-NH<sub>3</sub>-HCl gas mixtures. In these experiments large amounts of white powdery deposits formed at gas inlets and outlets of the reactor, outside the heated zone, and plugged the gas flows within a few minutes, thus preventing the kinetics measurements.

The surface morphology of the deposits was investigated by optical microscopy. Figure 11 shows the surface microstructure at two different magnifications. The low magnification image shows the uniformity of the deposit on the substrate surface and the high magnification image shows an orange-peel type structure. The crystallinity of the deposit was verified by x-ray diffraction. An intensity vs. 20 plot is shown in Fig. 12. The sharp peak located at  $26.5^{\circ} - 20$  is from the substrate, and the broad hump between 18 and 30° is from the coating. Similar x-ray patterns, reported in the literature, <sup>10,11,19</sup> have been suggested to represent a turbostratic structure. The chemical composition of the deposit was obtained using XPS. The elemental analysis of the deposit showed presence of B, N, and O.

Fig. 11. Surface topography of BN deposited at 950°C and 1.4 Torr on graphite at different magnifications.



Fig. 12. A typical XRD pattern of BN deposited using  $BCl_3$ -NH $_3$  gas mixtures.

Presence of oxygen in CVD-BN in amounts as high as 10 to 15 atomic percent (a/o), as  $BO_xN_y$  species, was reported to be common by Naslain *et al.*<sup>23</sup> Our deposits showed about 12 a/o oxygen. The B-1S peak, shown in Fig. 13, could be resolved into peaks at binding energies corresponding to BN and a compound with lower binding energy for boron.<sup>24</sup> Although additional work is needed to identify this boron compound, the oxygen may be present as  $BO_xN_y$  species as suggested by Naslain *et al.*<sup>23</sup>

#### Discussion

To comprehend the kinetics of the deposition process fully, let us look at the steps involved. At a substrate, deposition of a coating, such as BN, can occur via two modes (*i*) gas-phase nucleation and growth of BN into solid particles, followed by transport of BN particles to the surface, referred to as homogeneous nucleation of the deposit, (*ii*) gas-phase transport of the gaseous reactants to the surface, followed by an interface reaction, followed by transport of the gaseous reaction products away from the surface, referred to as heterogeneous nucleation of the deposit. The homogeneous nucleation process normally leads to formation of a powdery and flaky deposit that is nonadherent.<sup>16,18,19,25</sup> The dense and adherent nature of the deposits formed in the present study indicates heterogeneous nucle-





Fig. 13. A typical XPS pattern of BN deposited using  $\text{BCl}_3\text{-}\text{NH}_3$  gas mixtures.

ation. The rate of deposition then is controlled by either transport of reactants and/or products referred to as mass transport control or by a surface reaction referred to as interface reaction control.

First, let us consider the possibility of a mass transport control. For the sample arrangement used in the present experiments, the equations for mass transport rate calculations are well developed.<sup>26-28</sup> For flow past a freely suspended sample, the boundary-layer thickness starts from zero and gradually builds up to a finite thickness along the length of the sample. If the deposition is gas-phase-diffusion controlled, the thickness of the deposit varies along the length of the sample: maximum at the front end of the sample where the boundary layer thickness is zero. Our results show that the thickness of the deposit is constant along the length of the sample, suggesting that the deposition rate is not influenced by the gas-phase mass transport rates.

Further, we have calculated the gas-phase mass transport\_rates and compared them with the measured deposition rates. For a gas-phase transport rate-limited process, the deposition rate can be calculated by

$$J = -D \frac{C}{\Delta x}$$
[9]

where, D is the gas-phase diffusivity, C is the concentration of the gaseous species in the bulk stream, and  $\Delta x$  is the diffusion distance (boundary-layer thickness under laminar flow conditions). Note that the diffusivity term varies inversely with  ${\rm pressure}^{26\text{-}28}$  and the concentration term varies directly with pressure; and hence the D.C term is independent of pressure and is independent of gas velocity also. The dependence of J on these parameters, if any, comes through the diffusion distance ( $\Delta x$ ). In our experiments, the maximum sample boundary-layer thickness can be one-half the radius of the tube used. The i.d. of the quartz tube used is 2.5 cm which gives a maximum diffusion distance of 0.625 cm. At a temperature of 950°C, the calculated deposition rate of BN is 15 mg/cm<sup>2</sup> min for an NH<sub>3</sub>/BCl<sub>3</sub> ratio of 1.5. This calculation was performed using a diffusivity of 310 cm/s calculated at 3.5 Torr using the diffusivity equation provided in Ref. 26-28. For comparison, the observed deposition rate under these conditions  $(950^{\circ}C, 3.5 \text{ Torr}, \text{ and } \text{NH}_3/\text{BCl}_3 = 1.5) \text{ is } 0.123 \text{ mg/cm}^2 \text{ min},$ which is two orders of magnitude lower than the calculated rate. This analysis confirms that the deposition process is not under a mass transport control and indicates an interfacial reaction control.

Let us further consider the prospect of an interface reaction control. In this case, a change in gas velocity should not influence the rate of deposition. However, a change in pressure would influence the reactant concentration at the sample surface and hence the rate of deposition. Results presented in Fig. 6 and 7, satisfy these prerequisites indicating that the deposition process is limited by an interface reaction. The data presented in Fig. 8 through 10 indicate that in the temperature range of 850 to 1050°C the interface reaction proceeds at a rate independent of the substrate chemistry with an activation energy of about  $35 \pm$ 3 kcal/mol. This value compares favorably with the activation energies reported by Matsuda et al.<sup>16</sup> and Lee et al.<sup>19</sup> Matsuda et al.<sup>16</sup> reported an activation energy of 32 kcal/ mol for BN deposited using BCl<sub>3</sub>-NH<sub>3</sub>-H<sub>2</sub> gas mixtures in the temperature range 1200 to 1400°C at pressures 5 and 10 Torr. Lee *et al.*<sup>19</sup> reported an activation energy of 39 kcal/mol for the deposits obtained using BCl<sub>3</sub>-NH<sub>3</sub>-Ar mixtures in the temperature range 800 to 1000°C at a pressure of 40 Torr.<sup>19</sup> Tanji et al. <sup>17</sup> reported an activation energy of 50 kcal/mol for BN deposited with BCl<sub>3</sub>-NH<sub>3</sub>-N<sub>2</sub> gas mixtures between 900 and 1250°C at a pressure of 2 Torr. We believe the high activation energy reported by Tanji et al. is due partly to the limited number of data points (two) used to obtain their value.<sup>1'</sup>

Having established that the BN deposition is interfacial reaction controlled (IRC), let us now try to identify the rate-limiting step of the interface reaction. A cursory look





at the data in Table I shows that the reaction rate is dependent on the partial pressure of BCl<sub>3</sub> with little or no dependence on the partial pressures of  $NH_3$ ,  $H_2$ , and  $N_2$ . Figure 14 shows a plot of the deposition rate constants measured at 950°C as a function of the BCl<sub>3</sub> partial pressure along with the data of Lee et al.<sup>19</sup> measured at 900°C. In this log-log plot the data of Lee *et al.* conform to a slope of  $1.02 \pm 0.09$ and agree with their conclusion of a first-order dependency between the deposition rate constant and the BCl<sub>3</sub> concentration. Lee et al.<sup>19</sup> conducted all their experiments at NH<sub>3</sub>/ BCl<sub>3</sub> ratios of five or less. Most of our experiments, except for three, were conducted at ratios of four or less. The deposition rate constants measured in the three experiments with NH<sub>3</sub>/BCl<sub>3</sub> ratios of 10 or 20 (closed circles) lie somewhat differently than the others (Fig. 14), possibly indicating a change in mechanism at high NH<sub>3</sub>/BCl<sub>3</sub> ratios. Further work is needed to establish this hypothesis. Our data measured with NH<sub>3</sub>/BCl<sub>3</sub> ratios of four or less show a slope of  $0.8 \pm 0.06$ . We believe that this slope (0.8) can be taken as a representation of first-order dependency for our data taken over the range of BCl<sub>3</sub> partial pressures, between 0.09 and 1.4 Torr, used. Considerable scatter in the slope is understandable especially if the oxygen contamination seen in our BN deposits comes from the oxygen sensitive BCl<sub>3</sub> precursor.

To evaluate the dependence of K on  $NH_3$  partial pressure, the deposition rate constants normalized to unit BCl<sub>3</sub> partial pressure are plotted in Fig. 15 as a function of  $NH_3$ partial pressure. The data of Lee et al. 19 also normalized for unit BCl<sub>3</sub> partial pressure are included in Fig. 15. Again the data measured with  $NH_3/BCl_3 \ge 10$  are higher than the rest and therefore excluded from further analysis. In the log-log plot of Fig. 15, our data taken with  $NH_3/BCl_3 \le 4$  as well as the data of Lee et al.<sup>19</sup> suggest that the normalized deposition rate constant is independent of NH<sub>3</sub> partial pressure. The independence of K from partial pressure of  $NH_3$  has been suggested by other investigators.<sup>9,17-19</sup> The deposition rate constant's first order dependence on BCl3 partial pressure and its independence from NH<sub>3</sub> partial pressure agrees well with the linear dependence of K on the total pressure observed in this and in other studies.<sup>16-19</sup> Based on this analysis the deposition rate constant given in Eq. 8 may be rewritten as

$$K(\mu m/s) = 12.3 \pm 1.3 \times 10^{3} (p_{BCl_{3}}) \exp\left(\frac{-35 \pm 3 \text{ kcal/mol}}{RT}\right)$$
[10]

where  $p_{BCl_3}$  is the partial pressure of BCl<sub>3</sub> in Torr.

Our results indicated that no deposition was seen when  $NH_3$  was replaced completely by corresponding amounts of  $N_2$  and  $H_2$ , suggesting that  $NH_3$  participates in the surface reaction as a gas molecule either in unadsorbed or readily adsorbed form, but not as a dissociated, or adsorbed and dissociated species. The first-order dependence of K on the partial pressure of BCl<sub>3</sub> (Fig. 14) suggests that the surface



Partial Pressure of NH<sub>3</sub> (torr)

Fig. 15. Rate of BN deposition normalized for unit partial pressure of BCl<sub>3</sub> as a function of NH<sub>3</sub> partial pressure at 950°C. Also shown are data of Lee *et al.*<sup>19</sup> measured at 900°C.

reaction involves either adsorbed  $BCl_3$  molecule or adsorbed and dissociated  $BCl_3$ . The surface chemical reactions can then be written as<sup>3</sup>

$$NH_3(g) = NH_3(ad)$$
 [R.1]

$$BCl_3(g) = BCl_3(ad)$$
 [R.2a]

$$BCl_3(ad) = B(ad) + 3Cl(ad)$$
 [R.2b]

 $NH_3(g/ad) + BCl_3(ad) = BN(s) + 3HCl(ad)$  [R.3a]

$$NH_3(g/ad) + B(ad) = BN(s) + 3H(ad)$$
 [R.3b]

3H(ad) + 3Cl(ad) = 3HCl(ad) [R.4b]

$$3HCl(ad) = 3HCl(g)$$
 [R.5]

Note that the reactions may proceed in either path "a" or path "b" between R.2 and R.4. The following discussion is valid for either path. If R.1 is to be the rate-limiting step, the deposition rate should be influenced by NH<sub>3</sub> partial pressure but not by BCl<sub>3</sub> partial pressure. If either of R.2(a/b) is to be the rate-limiting step the reverse is expected to be true, *i.e.*, the rate should be dependent on  $BCl_3$ partial pressure and independent of NH<sub>3</sub> partial pressure. If any one of the other reactions, R.3 through R.5, is to be the rate-limiting step, then the deposition rate should depend on both BCl<sub>3</sub> and NH<sub>3</sub> partial pressures and thereby result in a more complex than linear dependence on the total pressure. Based on the data plotted in Fig. 14 and 15, reaction R.2 may be the rate-limiting step in deposition of BN from BCl<sub>3</sub> and NH<sub>3</sub> gas mixtures. Generally, an adsorption reaction such as R.2a is expected to have a low activation energy. The high activation energy (35 kcal/mol) observed in the present work suggests that either the dissociation (R.2b) or the dissociative adsorption (R.2a + R.2b) of BCl<sub>3</sub> molecule is the likely rate-limiting step. Reaction R.2 can go through intermediate compounds, such as BCl<sub>2</sub>, and so the specific compound that participates in adsorption may be different from BCl<sub>3</sub>. However, the dependence of the deposition rate constant on the partial pressure of BCl<sub>3</sub> remains the same.

#### Conclusions

1. The rates of BN deposition from  $BCl_3-NH_3-(N_2/H_2/Ar)$  mixtures are measured, in the temperature range 850 to 1050°C, between the pressures 1.1 and 3.5 Torr, under conditions where the deposition process is controlled by an interfacial reaction.

2. The deposition rate constant is independent of substrate chemistry and shows an activation energy of  $35 \pm 3$  kcal/mol.

3. The BN deposition rate constant is independent of  $NH_3$  partial pressure and shows a first-order dependence on the  $BCl_3$  partial pressure suggesting either the dissocia-

tion or the dissociative adsorption of BCl<sub>3</sub> as the rate-limiting step of the interfacial reaction.

## Acknowledgment

The authors acknowledge the help of W. A. Morrison and C. M. Montanaro with some of the experimental work.

Manuscript received April 13, 1992; revised manuscript received Aug. 18, 1992.

General Electric Corporate Research and Development assisted in meeting the publication costs of this article.

#### REFERENCES

- 1. W. Schmolla and H. L. Hartnagel, Solid-State Electron., 26, 931 (1983).
- H. P. R. Frederiske, A. H. Kahn, A. L. Dragoo, and W. R. Hosler, J. Am. Ceram. Soc., 68, 131 (1985).
- 3. S. S. Dana and J. R. Maldonado, J. Vac. Sci. Technol., B4, 235 (1986).
- 4. O. Dugne, S. Prouhet, A. Guette, R. Naslain, and J. Sevely, in Dev. Science and Technology of Composite Materials, Third European Conference on Composite Materials, p. 129 (1989).
- 5. R. N. Singh and M. K. Brun, Adv. Ceramic Mat., 3, 235 (1988).
- M. K. Brun and R. N. Singh, *ibid.*, 3, 506 (1988).
   B. Bender, D. Shadwell, C. Bulik, L. Incorvati, and D. Lewis III, Am. Ceram. Soc. Bull., 65, 363 (1986)
- 8. G. Clerc and P. Gerlach, in Proceedings of the Fifth International Conference on Chemical Vapor Deposition, J. M. Blocher, Jr., H. E. Hintermann, and L. H. Hall, Editors, p. 177, The Electrochemical Society, Softbound Proceedings Series, Princeton, NJ (1975). 9. G. Malé and D. Salanoubat, in Proceedings Seventh
- International Conference on Chemical Vapor Deposition, 1979, T. O. Sedgwick and H. Lydtin, Editors, PV 79-3 p. 391, The Electrochemical Society Softbound Proceedings Series, Princeton, NJ (1979).
- 10. T. Takahashi, H. Itoh and A. Takeuchi, J. Crystal Growth, 47, 245 (1979).
- 11. T. Takahashi, H. Itoh and M. Kuroda, ibid., 53, 418 (1981).

- 12. M. Sano and M. Aoki, Thin Solid Films, 83, 247 (1981). 13. S. Motojima, Y. Tamura, and K. Sugiyama, ibid., 88, 269 (1982)
- 14. H. Hannache, R. Naslain and C. Bernard, J. Less-Com*mon Metals*, **95**, 221 (1983). 15. T. Matsuda, N. Uno, H. Nakae, and T. Hirai, *J. Mat.*
- Sci., 21, 649 (1986).
- 16. T. Matsuda, H. Nakae and T. Hirai, ibid., 23, 509 (1988).
- 17. H. Tanji, K. Monden, and M. Ide, in Proceedings of the Tenth International Conference on Chemical Vapor Deposition, G. W. Cullen, Editor, PV 87-8, p. 562, The Electrochemical Society, Softbound Proceed-ings Series, Pennington, NJ (1987).
- W. J. Lackey, G. B. Freeman, J. A. Hanigofsky, J. R. Thompson, G. J. Gerard, W. Y. Lee, P. K. Agrawal, D. J. Twait, T. S. Moss III, and A. J. Green, Ultrafine Ministry Computing Description 2010 Microstructure Composites Prepared by Chemical Vapor Deposition, Georgia Tech Final Report A-4699-3 prepared for Office of Naval Research (1989).
- 19. W. Y. Lee, W. J. Lackey, and P. K. Agrawal, J. Am. Ceram. Soc., 74, 2642 (1991).
- 20. N. Patibandla and K. L. Luthra, Submitted to J. Am.
- Ceram. Soc. (1992).
  21. JANAF Thermochemical Tables, 3rd ed., American Chemical Society and American Institute of Physics for National Institute of Standards Technology (formerly National Bureau of Standards) (1985)
- 22. K. L. Luthra and H. S. Spacil, This Journal, 129, 649 (1982).
- 23. R. Naslain, O. Dugne, and A. Guette, J. Am. Ceram. Soc., 74, 2482 (1991).
- C. D. Wagner, W. M. Riggs, L. E. Davis, J. F. Moulder, and G. E. Muilenberg (Editor), Published by Physical Electronics Div., Perkin-Elmer Corp., Eden Prairie, MN (1979).
- 25. W. A. Bryant, J. Mat. Sci., 12, 1285 (1977).
- 26. D. E. Rosner, Transport Processes in Chemically React-
- D. D. B. Bohel, Indisport Processes in Chemically Reacting Flow Systems, Butterworths, London (1986).
   R. B. Bird, W. E. Stewart, and E. N. Lightfoot, Transport Phenomena, John Wiley, New York (1960).
   Chemical Engineers' Handbook, pp. 3-246, R. H. Perry and C. H. Chilton, Editors, McGraw-Hill, 5th ed., New York. New York.

# Low-Temperature Growth of 3C-SiC on Si Substrate by Chemical Vapor Deposition Using Hexamethyldisilane as a **Source Material**

# Koji Takahashi, Shigehiro Nishino, and Junji Saraie

Department of Electronics and Information Science, Faculty of Engineering and Design, Kyoto Institute of Technology, Matsugasaki, Sakyo-ku, Kyoto 606, Japan

#### ABSTRACT

Crystal growth of 3C-SiC on Si(100), (111) substrate was carried out by atmospheric pressure chemical vapor deposition using hexamethyldisilane ( $Si_2(CH_3)_6$ :HMDS) and  $H_2$  gas mixtures. Temperature dependence of growth rate and crystal substrate subst tallinity of SiC films were examined. The growth process was characterized by a mass spectrometric study of the decomposition of HMDS and H<sub>2</sub> mixtures. Using HMDS as a source material, low temperature epitaxy was realized at a substrate temperature of 1100°C. With and without a carbonized buffer layer, single-crystal 3C-SiC was grown on Si(111) substrate at the growth rates as high as 700 Å/min. With Si(100) as a substrate, single crystals were grown only with a buffer layer.

Cubic silicon carbide (3C-SiC) is an eminently suitable semiconductor material for high temperature, high power, and high frequency electronic devices, because of its wide bandgap (2.2 eV), high electron mobility (1000 cm<sup>2</sup>/Vs)<sup>1</sup>, high saturated electron drift velocity (calculated as  $2.7 \times$  $10^7$  cm/s at  $2 \times 10^5$  V/cm),<sup>2</sup> and thermal stability. In the last decade, techniques for heteroepitaxial growth of 3C-SiC on Si by chemical vapor deposition (CVD) have been established.<sup>3</sup> The temperature for single-crystal growth being approximately 1350°C is so high for the combination of SiC and Si system that slip lines and dislocations are induced in the substrate and the epilayer. From the point of view of device fabrication with heteroepitaxially grown 3C-SiC on Si, low temperature epitaxy is desired.

Recently, several researchers have reported low-temperature epitaxy of 3C-SiC on Si substrates via low pressure chemical vapor deposition (CVD),<sup>4</sup> gas source molecular beam epitaxy,<sup>5,6</sup> etc. However, from the standpoint of prac-