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AN EXPERIMENTAL KINETIC STUDY OF BORON NITRIDE CVD FROM BF_3 - NH_3 -Ar MIXTURES

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Abstract - A proper control of the CVD of boron nitride from the B-N-H-F-Ar system, as very thin films in electronic devices or ceramic composite materials, needs a thorough knowledge of the mechanisms of the process. A detailed kinetic study is presented, which provides evidenced a transition from chemical to mass transfer control, as a function of the deposition temperature, total pressure and total flow rate. On the basis of these results, a pressure temperature diagram is proposed, which defines the boundaries of both control domains for a number of compositions of the initial gaseous mixture. For these compositions, the stoichiometry of the boron nitride deposits is given, on the basis of EPMA analysis data. Under conditions of a chemically controlled process, activation energies and apparent reaction orders with respect to NH_3 and BF_3 are reported.

1.- Introduction

Hexagonal boron nitride, prepared as thin films by chemical vapor deposition (CVD), is used in semiconductor devices for its good thermal conductivity, excellent electrical resistivity particularly at high temperature, and inertness to chemical reactants including air [1]. The latter property and the anisotropy of the crystal structure of hex-BN, which are very similar to those of graphite, have also suggested the use of hex-BN as components of ceramic matrix composites (CMC), such as (i) part of the matrix or (ii) interphase between the fiber and the matrix [2-8]. The interphase in a CMC controls the toughness of the material by monitoring the strength of the fiber-matrix bonding. It consists of a uniform coating of the ceramic fibers (less than 1 μm in thickness).

Various precursors have been used for the CVD of BN : (i) a single source species containing boron and nitrogen, such as borazine $\text{B}_3\text{N}_3\text{H}_6$ [9] or β -trichloroborazine $\text{B}_3\text{N}_3\text{H}_3\text{Cl}_3$ [10] ; (ii) a mixture of NH_3 with diborane B_2H_6 [11] or related organoborane species such as $\text{B}(\text{C}_2\text{H}_5)_3$ [12] ; and (iii) a mixture of NH_3 with a boron halide BCl_3 [1, 13-15] and BF_3 [3-5]. In the last chemical system NH_3 - BF_3 , the boron fluoride molecule has a high enough thermal stability to permit the chemical vapor infiltration (CVI) of turbostratic BN whose structure is consistent with its use as interphase in CMC [16].

The purpose of the present contribution is to give a detailed experimental study of the deposition rates of BN in the BF_3 - NH_3 -Ar system in order to derive (i) the conditions of a mass transfer or a chemical reaction controlled kinetic process and (ii) kinetic parameters (i.e. activation energies and reaction orders). The data thus obtained will be able to be introduced in more advanced models, e.g. for describing the CVI process.

2.- Experimental

The deposition experiments on graphite substrates were carried out in a hot wall low pressure CVD reactor heated by radio frequency induction (Fig. 1). The deposition chamber is a vertical cylindrical tube with separated injection nozzles located in a zone hot enough in order to prevent their obstruction by formation of solid complex compounds such as BF_3NH_3 or BF_4NH_4 (which are stable at low temperature). Below these injection nozzles, the isothermal reactional area is large enough to permit a creeping laminar forced flow all around the substrate (i.e. with a very low Reynolds number). The substrate is hung on a microbalance in order to record the mass of the sample and consequently the growth rate. The reactor is equipped with accurate controlling systems for the regulation of temperature, total pressure and gas flow rates. The initial composition of the gas phase is characterised by the ratios $\alpha = P_{\text{NH}_3}/P_{\text{BF}_3}$ and $\beta = P_{\text{Ar}}/(P_{\text{NH}_3} + P_{\text{BF}_3})$. The stoichiometry of the deposit is analysed by using an electron probe X-ray microanalyser (EPMA).

3.- Growth kinetics

3.1.- Influence of temperature

The logarithm of the growth rate R is plotted in Fig. 2 as a function of the reciprocal temperature for various total pressures ranging from $P = 0.5$ to 40 kPa, a total flow rate Q of 119 sccm and an initial composition given by $\alpha = 1.2$ and $\beta = 0.61$. The temperature T is varied from 1125 to 1925 K.

For total pressures $P \leq 10$ kPa, very similar variations are observed with three distinct temperature ranges. In the first one (i.e. for $T < 1300$ K), the growth rate is very low and slightly thermally activated with an activation energy of 100 ± 20 kJ mole⁻¹. The second temperature range (i.e. for $1300 \text{ K} < T < 1600\text{-}1750$ K) corresponds to higher deposition rates with a rather higher activation energy of 290 ± 15 kJmole⁻¹. In the third range (i.e. for $T > 1600\text{-}1750$ K), the growth rate does not depend on the temperature. The only differences between the plots recorded for various total pressures are (i) the level of R which increases with P and (ii) the temperature of the transition from an activated kinetics to a non-activated regime, which increases with P from 1600 to 1750 K. This transition, classically attributed to the change of limiting phenomena in the deposition kinetics (i.e. chemical reactions at low temperatures and mass transfer at high temperatures), was also observed by Matsuda et al. for the $\text{BCl}_3\text{-NH}_3\text{-H}_2$ system between 1600 and 2000 K depending on the total pressure ($0.66 < P < 7.9$ kPa). However, these authors have determined an activation energy of only 134 kJmole⁻¹ [14]. The corresponding value given by Tanji et al. for the $\text{BCl}_3\text{-NH}_3\text{-N}_2$ system and $P = 0.266$ kPa is 210 kJmole⁻¹ [15].

For $P > 10$ kPa, two rate-controlled regimes are also observed but the temperature of the transition is drastically shifted towards relatively low temperatures (about 1350 K) and the growth rate values decrease greatly in the mass transfer rate-limited regime.

3.2.- Influence of total pressure

The variation of the growth rate as a function of the total pressure is shown in Fig. 3 for $P = 0.5\text{-}60$ kPa, $T = 1350$ and 1450 K, $Q = 119$ sccm, $\alpha = 1.2$ and $\beta = 0.61$. Similar behaviour is observed for both temperatures : at low pressure, the deposition rate

increases with P and then it remains rather constant. A transition pressure can be defined which increases from about 10 kPa at 1450 K to about 20 kPa at 1350 K.

As discussed elsewhere, if the kinetic process is controlled by the mass transfer by diffusion and convection in a cylindrical reactor subjected to a creeping laminar flow around the substrate, the growth rate is found to be independent of the total pressure [17]. Conversely, the chemical reaction kinetics are usually highly dependent on the total pressure, due to the reaction orders with respect to the various chemical species involved in the deposition process. As a consequence, the present results exhibit a pressure-induced transition from a chemical (in the low pressure range) to a physical (in the high pressure range) control of the overall kinetic process of BN deposition. Similar results were observed by Matsuda for $\text{BCl}_3\text{-NH}_3\text{-H}_2$ system [14].

3.3.- Influence of total flow rate

As the total flow rate Q influences directly the mass transfer by convection (enhanced by increasing Q) and diffusion (also raised by increasing Q which decreases the boundary layer thickness) and does not affect reaction rates, it is a very convenient parameter to be varied in order to confirm the type of rate-controlling phenomenon for a given pairing of temperature and total pressure.

The growth rate is plotted in Fig. 4 as a function of the total flow rate (which reaches 600 sccm) for various total pressures from 1 to 15 kPa, a temperature of 1450 K and an initial composition given by $\alpha = 1.2$ and $\beta = 0.61$. At a total pressure $P \leq 5$ kPa, the deposition rate does not depend on Q over the large range studied, which means a chemical reaction rate-controlled process, whereas for $P = 15$ kPa, two regimes are observed : (i) for a low total flow rate ($Q < 200$ sccm), R greatly increases with Q and (ii) for $Q > 200$ sccm, R weakly depends on Q . This last result shows that the transition from chemical reaction to a mass transfer controlled kinetics, can be also induced by decreasing the total flow rate. This Q -induced transition was previously reported in the literature for a few other systems [18-21]. It appears from Fig. 4, that for a total flow rate of 119 sccm, the transition induced by the total pressure occurs indeed between 10 and 15 kPa, as already established from Figs. 2 and 3.

The variation of the deposition rate as a function of the total flow rate Q is shown in Fig. 5 for $P = 1$ and 5 kPa, $T = 1700$ K, $\alpha = 1.2$ and $\beta = 0.61$. A decrease of the total pressure below 5 kPa can make the mass transfer the rate-limiting phenomenon again. This feature, which seems characteristic of the high temperature range, is consistent with the shift of the transition temperature observed in the plots of Fig. 2.

3.4- Transition between physical and chemical rate-control

On the basis of the experimental results, the transition from a kinetic process limited by mass transfer to a chemical reaction rate-controlled process, is induced by varying three parameters T , P and Q .

If a Q value of 119 sccm is chosen, the curves giving the growth rate versus T , on the one hand, and P on the other hand, permit one to define various pairings (T , P) corresponding to the transition zone between both limiting phenomena. The pairings (T , P), derived from the $R = f(P)$ and $\text{Log } R = f(1/T)$ curves, are in rather good agreement, as shown in Fig. 6 where these pairings are plotted in a (T , P) diagram for $\beta = 0.61$ and

$\alpha = 1.2$. As a result, by decreasing the total pressure below 10 kPa, it is possible to enlarge the chemical rate-control domain up to almost 1700K. But at very low pressure ($P < 2$ kPa), this domain is again narrowed (Fig. 5). Consequently by increasing the total pressure at $T = 1650$ K, the BN deposition process can be successively controlled kinetically by mass transfer, chemical reaction and mass transfer again. Another set of growth rate measurements carried out for a NH_3 depleted initial gaseous mixture ($\alpha = 0.7$) was used to draw the same type of transition zone, which shows a markedly less important domain with chemical control.

With the purpose of collecting data about the influence of the initial composition of the gaseous mixture, the pressure induced transition was determined for three values of T and α ratio ranging from 0.5 to 5. The transition zone between chemical and physical regimes can be represented in a (P_{NH_3} , P_{BF_3}) diagram, where P_{NH_3} and P_{BF_3} are the initial partial pressures of the reactant species, the temperature and the dilution ratio β being maintained constant (Fig. 7). The narrowing of the pressure range favorable to chemical control as temperature is increased, is confirmed here in terms of reactant partial pressures. Moreover, the transition occurs at a constant pressure for $\alpha > 1$, but at decreasing pressure for $\alpha < 1$. This result means that NH_3 depletion of the initial gaseous mixture is another factor which contributes to decreasing the extent of the domain of the chemically controlled kinetics. The Electron Probe Micro Analysis (EPMA) of the atomic composition of the boron nitride deposited at 1450 K (Table 1), shows that the NH_3 depletion (i.e. $\alpha \leq 1$) yields a slight boron excess ($\text{B/N} = 1.13$), while stoichiometric BN is deposited for $\alpha > 1$.

3.5.-Apparent reaction orders with respect to NH_3 and BF_3

In order to determine the overall kinetic laws which govern the BN deposition process, a knowledge of the apparent reaction orders is needed besides that of the activation energies. These orders can be obtained by varying one partial pressure, with all the others being maintained constant, without going out of the domain (defined in 3.4) where the growth process is rate-controlled by chemical reactions (i.e. at relatively low pressure, low temperature and $\alpha > 1$). A reaction order is directly given by the slope of the curve which represents the variation of the deposition rate versus the partial pressure in a Log-Log plot.

As shown in Fig. 8a, the apparent reaction order with respect to BF_3 is 1 for a temperature of 1450 K and $P_{\text{NH}_3} = 1.5$ and 2 kPa. For the same temperature, the apparent reaction order with respect to NH_3 is approximately 0 at $P_{\text{BF}_3} = 0.5$ and 1 kPa (Fig. 8b). For a lower temperature ($T = 1250$ K), the reaction order becomes 1.5 with respect to BF_3 (Fig. 9a) and remains 0 with respect to NH_3 (Fig. 9b). This result, in conjunction with the lower activation energy observed at low temperature (Fig. 2), suggests the occurrence of two different chemical mechanisms depending on the temperature. Concerning the independence of the growth rate with P_{NH_3} , this behaviour was previously mentioned in several systems where NH_3 is used as nitrogen source (e.g. $\text{BCl}_3\text{-NH}_3\text{-H}_2$ [15] and $\text{Si}(\text{CH}_3)_4\text{-NH}_3\text{-H}_2$ for the deposition of Si_3N_4 [22]).

4.- Conclusion

The present experimental kinetic study of the boron nitride deposition, establishes the influence of the CVD parameters, including the temperature, the total pressure, the total flow rate and the initial composition of the gas phase, on the two main phenomena

which govern the kinetic process. The transition from mass transfer to chemical reaction rate-controlled processes can be induced by all of the mentioned parameters. Moreover, by decreasing the total pressure under specific conditions (i.e. a relatively high temperature of 1650 K), this transition and the reverse one can occur successively. The kinetic parameters determined in this approach, such as the activation energies and the apparent reaction orders with respect to NH_3 and BF_3 , can contribute to the knowledge of the overall kinetic laws which govern the chemical process involved in the deposition of BN from $\text{BF}_3\text{-NH}_3\text{-Ar}$ system.

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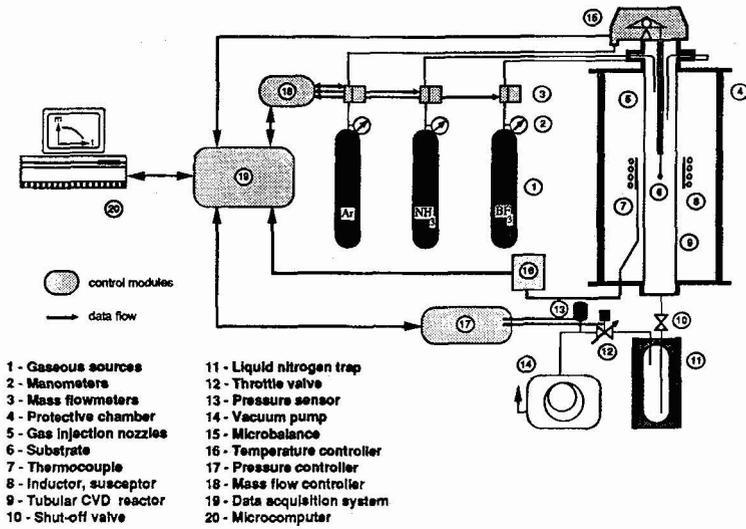


Fig. 1 : Apparatus used for the CVD of BN

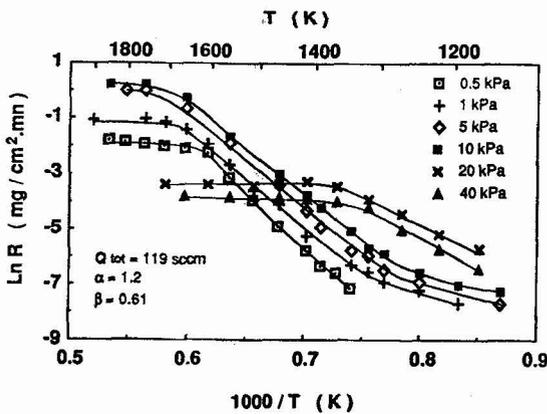


Fig. 2 : Variation of BN growth rate with reciprocal temperature for various total pressures

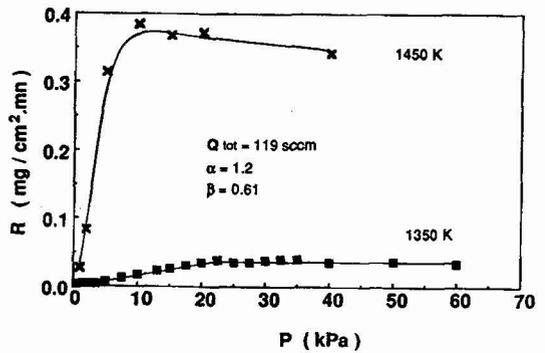


Fig. 3 : Variation of BN growth rate with total pressure at T= 1350 and 1450 K

Table 1 : EPMA derived atomic composition of the deposits for T= 1450 K, P= 2kPa and Q= 119 sccm

α	B (% at.)	N (% at.)	O (% at.)	B/N (at.)
0.5	48.4 ± 0.5	42.1 ± 1.4	9.2 ± 1	1.15 ± 0.05
0.7	47.7 ± 0.6	42.7 ± 0.5	8.4 ± 0.4	1.12 ± 0.03
1	48.0 ± 0.7	42.4 ± 0.5	9 ± 0.2	1.13 ± 0.03
1.2	46.4 ± 0.5	44.0 ± 0.3	8.9 ± 0.3	1.05 ± 0.02
2	45.3 ± 0.5	44.8 ± 0.5	9.3 ± 0.3	1.01 ± 0.02
5	44.4 ± 0.4	43.6 ± 0.7	11.8 ± 0.7	1.02 ± 0.02

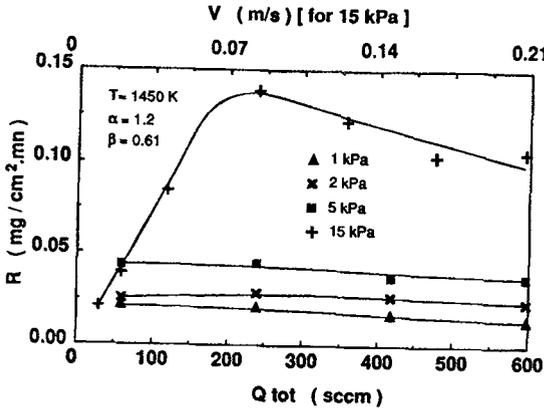


Fig. 4 : Variation of BN growth rate with total flow rate at $T = 1450\text{ K}$ for various total pressures

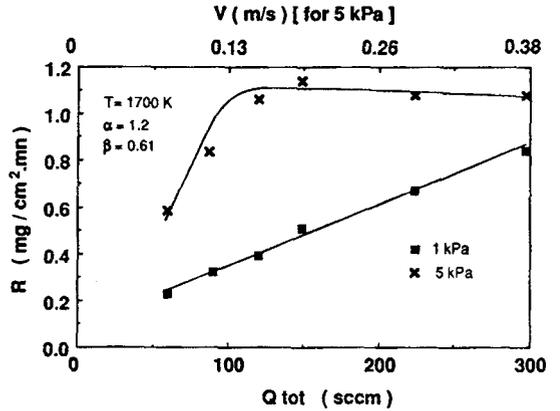


Fig. 5 : Variation of BN growth rate with total flow rate at $T = 1700\text{ K}$ for $P = 1$ and 5 kPa

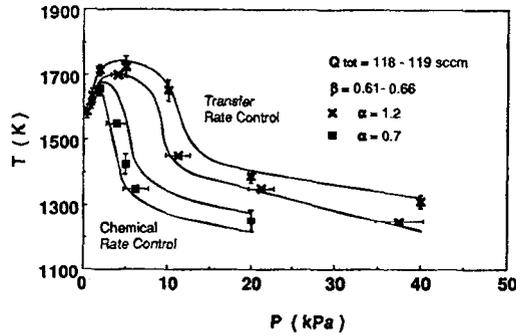


Fig. 6 : P, T ranges of (i) mass transfer control and (ii) chemical reaction control of the BN deposition process

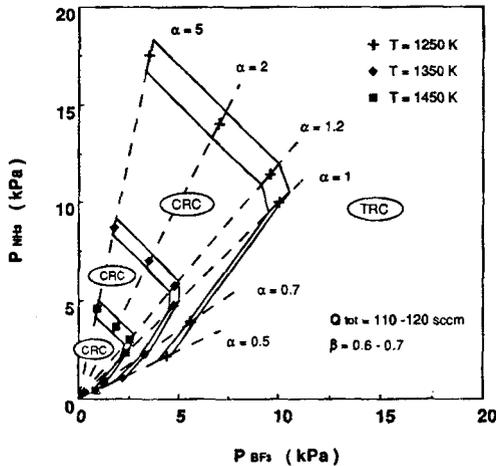


Fig. 7 : Transition zone in terms of P_{BF_3} and P_{NH_3} between transfer rate control (TRC) at high pressures and chemical rate control (CRC) at low pressures of the BN deposition process, for three temperatures and different compositions of the initial gaseous mixture

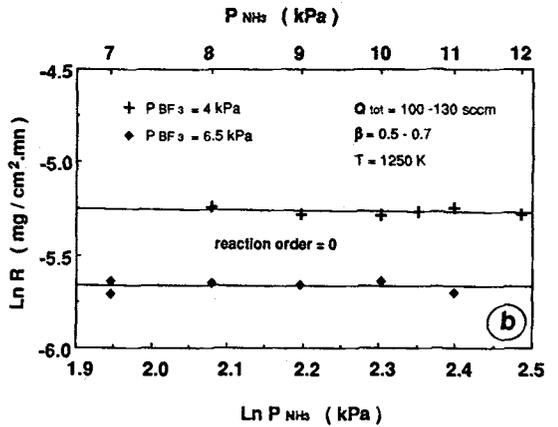
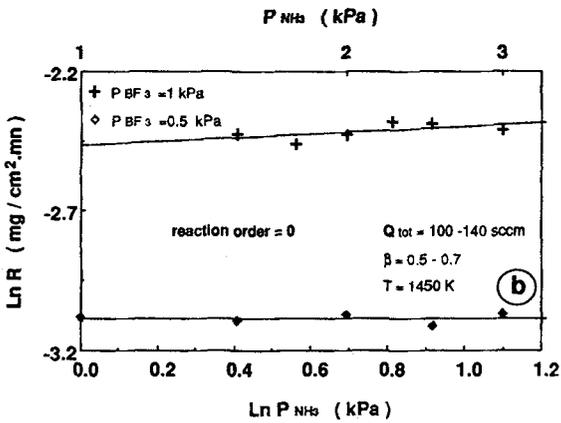
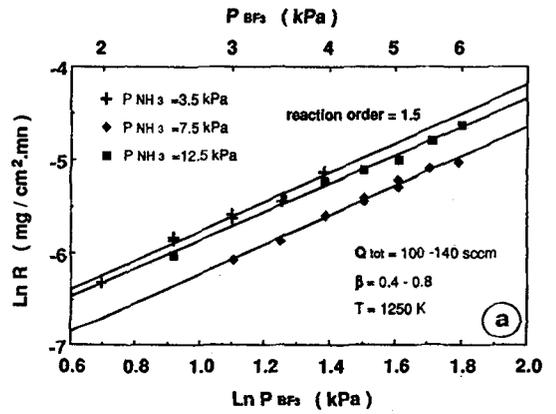
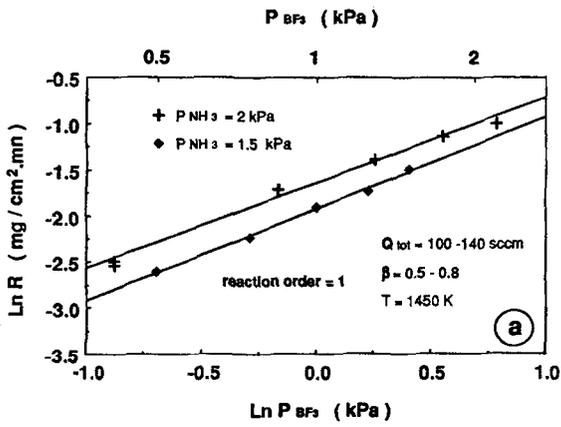


Fig. 8 : Variation of BN growth rate with partial pressure of (a) BF₃ and (b) NH₃ for a temperature of 1450 K

Fig. 9 : Variation of BN growth rate with partial pressure of (a) BF₃ and (b) NH₃ for a temperature of 1250 K