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Reaction of Diborane and Ammonia Gas Mixtures in a Chemical Vapor Deposition Hot-Wall Reactor

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Boron nitride has been deposited by chemical vapor deposition from diborane and ammonia gas mixtures, in the form of either films or powders depending on the pressure in the reactor. IR analysis of the boron nitride deposits has been used to obtain the composition of the films. In the temperature range studied, 600–850 °C, the effect of the deposition temperature on the reaction kinetics has been interpreted by assuming a change in the relative concentration of activated species arising from diborane and ammonia molecules. This change modifies the reaction path followed in the boron nitride synthesis through the formation of different intermediate compounds: aminodiborane in the low-temperature range (<700 °C) and borazine at the higher temperatures (≥775 °C). The presence of either of these intermediate compounds determines the deposition rate and the final composition of the boron nitride films.

Introduction

Diborane and ammonia gas mixtures are widely used in the synthesis of boron nitride films by chemical vapor deposition (CVD) or plasma assisted chemical vapor deposition (PACVD).[1–3] The material, in either the hexagonal or amorphous structure, has outstanding properties, such as chemical inertness, high melting point, and thermal conductivity, large bandgap etc., which make it a unique candidate in many technological applications, mostly in modern electronic devices and in ceramic materials.[4] Compared with diamond films, for instance, although lower in hardness, cubic BN films present higher oxidation resistance and surface adhesion with some metals, making this material a very useful coating in cutting tools.[5a] In addition, boron nitride powders are also used as additive in the conforming of ceramic pieces due to its low thermal coefficient and bulk modulus.[5b]

One of the most important aspects of the CVD techniques in ceramic coating applications is the conforming coverage which allows the homogeneous coating of pieces with complex shapes. Other unique advantage of CVD over other methods is the relative ease of creating new materials of a wide range of accurate controllable stoichiometric compositions and layer structures that are difficult or impossible to attain by other techniques. Nevertheless, the materials deposited by CVD techniques at low temperatures may present some foreign atoms incorporated in their network from the reacting gases. But, when diborane and ammonia are used as molecular precursors for boron nitride deposition, only hydrogen atoms, as –NH and –BH groups, are present in the deposits. This is an advantage related to the material resulting from boron halides or organic compounds where halogen atoms or oxygenated groups are commonly found in the final product. However, the ability of diborane to form different compounds when reacting with ammonia makes the $B_2H_6 + NH_3$ reaction very complex, as has been already pointed out in numerous papers.[3,6]

In this work we have studied the deposition mechanism of boron nitride in a hot-wall reactor by CVD from diborane and ammonia gas mixtures. The influence of the temperature and gas flow ratio on the material characteristics and deposition rate can be interpreted as due to different mechanism dominating during the reaction. To elucidate the reaction paths between diborane and ammonia, we have investigated the effect of the temperature on the formation of the intermediate compounds which may be present during the deposition process.

Experimental Section

Boron nitride was deposited by CVD from diborane and ammonia gas mixtures. Diborane (5 vol %) diluted in hydrogen was used to prevent the decomposition of the diborane molecules at room temperature. This gas mixture was introduced into the reactor through an independent inlet in the high-temperature zone of the reactor. The reactor consisted of a quartz tube 100 cm long and 12 cm in diameter, heated by an external furnace up to 850 °C. The gas supply ($B_2H_6/H_2/NH_3$ in the ratio 40:760:730) was automatically controlled during the experiments by mass flow controllers, being 1530 seem for the total gas flow. The pressure was kept constant at 4.0 kPa and the temperature was varied from 600 to 850 °C. As a safety precaution, the resultant gases at the exhaust were passed through a series of stainless steel bubblers, filled with sodium hypochlorite and water, in order to complete the consumption of not-reacted diborane molecules before the byproducts reached the atmosphere.[2]

Infrared spectroscopy (IR) has been used for the characterization of the boron nitride deposits. Changes in the film composition were followed by IR observations, fitting the experimental spectra to a sum of Gaussian curves,[7] centered at the maxima of the negative second derivative. This method, already described in a previous work, consists in using Fourier transform techniques along with a Blackman D4 filter.[8] To avoid nonreal features which may appear in the negative second derivative as a consequence of low signal-to-noise ratios, the original IR spectra have been used to corroborate the observed peaks. Using as a reference the peak at 610 cm^{-1}, corresponding to the silicon substrate, the resulting band positions were very close in all the spectra. Finally, the contribution of the different bands to the measured spectra were calculated by means of nonlinear regression methods. Thickness and refractive index measurements were also made by ellipsometry using a L116B Gaertner ellipsometer.

Experimental Results

It is well-known that in CVD processes the surface reaction on the substrate occurs in parallel with the gas-phase reaction.[9] In the last case (homogeneous reaction), the material is obtained in the form of fine microparticles which can be harvested by adequate means. In this work, we used a graphite felt to collect the boron nitride powder in the hot zone of the reactor. which yields the purer deposits. The details of the filter used for the collection of the material has been presented elsewhere.[10]

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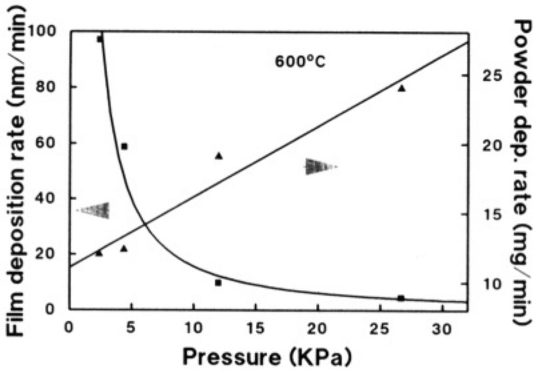


Figure 1. Variation of the CVD boron nitride deposition rate (film and powder) with pressure at 600 °C.

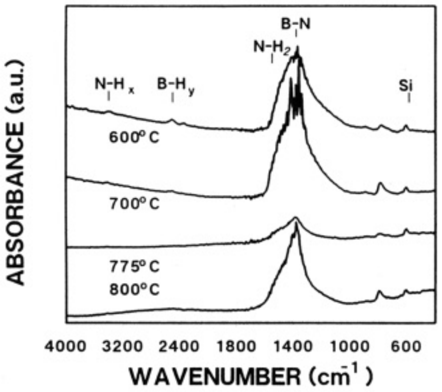


Figure 2. IR spectra of boron nitride films deposited at different temperatures.

Simultaneously, boron nitride films have also been deposited on silicon substrates, located in the high-temperature zone of the reactor. When the pressure inside the chamber increases, the homogeneous reaction is favored and in contrast the surface reaction rate is inhibited, since both reactions are competitive. As an example, Figure 1 shows the deposition rates for the film and powder deposits when the pressure varies in the 2.4–27 kPa range. As can be observed, the increase in the pressure produces a sharp reduction in the film deposition rate and a corresponding increase in the rate of boron nitride powders formation. It should be noted that the deposition rate for the powder can be only roughly estimated since a part of its escapes to the vacuum system.[10] Due to this difficulty, the reaction mechanism of BN formation from diborane and ammonia, both in the gas phase and on the surface, has been followed through the study of the nitride films deposited under conditions which also produce powders. Previous work has shown that boron nitride powders have similar compositions to those of the films, exhibiting in both cases a similar trend between the temperature and the impurities incorporated in the material from the reacting gases.[11]

Figure 2 shows the IR spectra of boron nitride films deposited from diborane and ammonia gas mixtures at different temperatures in the 600–850 °C range. One can observe a broad band at ≈1380 cm^{-1}, attributed to the B–N stretching vibration[12] and also other bands corresponding to $-NH_x$ and $-BH_y$ groups.[13] In Table I, the peak position as well as the assignation of the bonds present in boron nitride films are given, along with the peak corresponding to the Si–O vibration, which can be also present in the IR spectrum of oxidized samples deposited on silicon substrate. This band could also be associated with the cubic structure of boron nitride,[12] but at the experimental conditions used in this work, the presence of highly crystalline BN films can be disregarded.[5a]

The IR spectrum of films deposited at 600 °C (Figure 2) contains the broad B–N band at ≈1380 cm^{-1}, and two small peaks at ≈3300 and ≈2500 cm^{-1} attributed to the stretching vibrations of N–H and B–H bonds, respectively. The intensity of these two peaks diminishes when the deposition temperature increases. At the temperature of 775 °C the band intensity associated with the B–N bond clearly becomes lower and narrower than in the samples deposited at a lower temperature. At still higher temperatures the B–N band increases again.

TABLE I: IR Peak Position in Boron Nitride Films Deposited by CVD from Diborane and Ammonia

assignation	position peak, cm^{-1}	ref
B–N	hex 1380	12
	cubic 1070	12
N–H	3300	13
	1500	13
B–H	2500	13
B–O	1440	18
	1300	
Si–O[a]	1100	23

[a] IR peak due to silicon substrate oxidation.

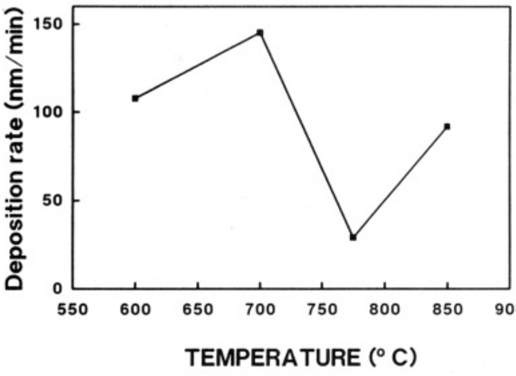


Figure 3. Deposition rate of CVD boron nitride films vs temperature.

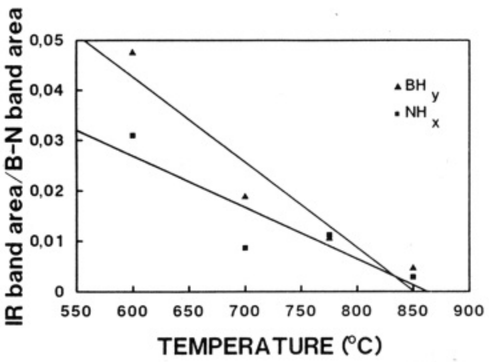


Figure 4. Variation of hydrogen content in boron nitride films with the temperature.

The influence of the deposition temperature on the B–N band intensity correlates well with the variation in the deposition rate (determined by ellipsometry), as depicted in Figure 3. Both curves can be explained in terms of the changes induced in the mechanism of the B_2H_6 and NH_3 reaction giving different intermediate compounds when the temperature increases, as we shall discuss below. The change observed in the band width of the spectra in Figure 2 has been attributed to the lower impurity content in the deposits, as well as to a higher reordering of the atoms in the network when the temperature increases.[10]

Figure 4 shows the variation in the hydrogen content in the films, as determined from the IR band area of the $-NH_x$ and $-BH_y$ stretching modes. As expected, a strong decrease in the hydrogen content in the films is observed when the deposition temperature increases from 600 up to 850 °C, which can be associated with the breakdown of the hydrogenated bondings in the NH_x and BH_y radicals in the films as a consequence of the thermal energy supplied to the reaction (N–H = 75 kcal mol^{-1} and B–H = 79 kcal mol^{-1}).[14] This tendency is generally displayed in the CVD synthesis of materials.[15]

TABLE II: Contributions to the Total IR Band at ≈1400 $\mathrm{cm^{-1}}$ in Boron Nitride Films

T (°C)	1520 $\mathrm{cm^{-1}}$ N–H	1416 $\mathrm{cm^{-1}}$ B–O	1372 $\mathrm{cm^{-1}}$ B–N	1268 $\mathrm{cm^{-1}}$ B–O	1100 $\mathrm{cm^{-1}}$ Si–O	A_t[a] (au)
600	100.1	81.5	144.1	65.2	35.1	426.1
700	125.2	125.3	188	80.3	35.2	553.8
775	32.3	2.5	58.9	10.0	3.3	107.4
850	100.3	25	188.1	30.1	17.5	360.8

[a] A_t = total band area.

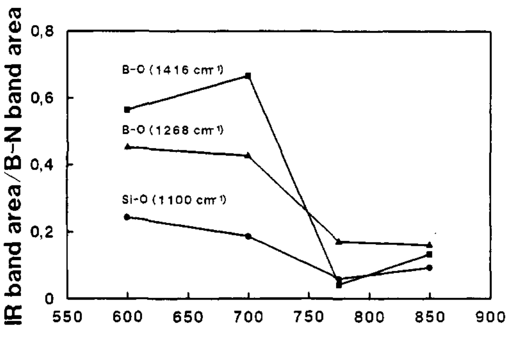


Figure 5. Effect of the temperature in the B–O and Si–O content in boron nitride films.

The complex shape of the main band in the spectra (at ≈1380 $\mathrm{cm^{-1}}$) has been resolved by fitting the experimental spectra to a sum of Gaussian curves, as stated above. Table II gives the different contributions to the total IR band. In addition to the B–N band at 1372 $\mathrm{cm^{-1}}$, the other IR peaks included in the broad band are (a) the band at 1520 $\mathrm{cm^{-1}}$, associated with $-\mathrm{NH_2}$ groups,[13,16] (b) two bands attributed to the B–O vibration at 1416 and 1268 $\mathrm{cm^{-1}}$,[17] and finally (c) the peak at 1100 $\mathrm{cm^{-1}}$, which can be related to either the Si–O vibration or that of the boron nitride network with a cubic structure. The band located at 1520 $\mathrm{cm^{-1}}$ corresponds to the in-plane bending vibration, being very weak for the –NH group but strong for $-\mathrm{NH_2}$ groups as it occurs in our samples. As can be observed in Table II, the intensity of this band, normalized to the B–N band at 1372 $\mathrm{cm^{-1}}$, diminishes with the increase in the temperature similarly to the $-\mathrm{NH}_x$ band at 3300 $\mathrm{cm^{-1}}$. Therefore, the band at 1520 $\mathrm{cm^{-1}}$ can be assigned to the $-\mathrm{NH}_x$ groups, being likely associated with the presence of $-\mathrm{NH_2}$ groups in the deposited boron nitride films.[13,16]

When the temperature increases, a decrease in the relatively intensity of the both B–O bands with respect to the B–N band is also apparent in the table. This can be better appreciated in Figure 5, which shows the variation of the B–O and Si–O bands intensity, normalized to the B–N band, with the temperature. As can be observed, the B–O and Si–O contents in the films stay nearly constant at temperatures lower than 775 °C, with an abrupt decrease at $T \geq 775$ °C. The presence of B–O bonds in the film is attributed to the oxidation of boron atoms, which may be present in excess over the 1:1 stoichiometric ratio of the BN films.[6] Although we used high $[\mathrm{NH_3}]/[\mathrm{B_2H_6}]$ ratios (=18) in our experiments, which supposedly give rise to nearly stoichiometric boron nitride films,[6] at low temperatures ammonia is not totally dissociated and the concentration of activated boron species in the reactor is high. It is also expected that there would be a less compact structure for the films deposited in the low-temperature range, due to the hydrogenated radicals incorporated in their network. The open structure of these low-temperature BN films would then favor the penetration of oxygen into the films,[18] resulting in a simultaneous oxidation of the film and the underlying silicon substrate. The oxidation of the substrate would explain the presence of the IR Si–O peak at 1100 $\mathrm{cm^{-1}}$.

In the high-temperature range ($T \geq 775$ °C), the contribution of B-N band (at 1372 $\mathrm{cm^{-1}}$) to the total IR band is nearly twice this contribution at lower temperatures. This increase in the percentage contribution of the B–N band is accompanied by a strong reduction in the deposition rate (see Figure 3). This implies that purer BN deposits are obtained in this temperature range, although the absolute formation rate of B–N bonds may be lower. The increase in the deposition rate from 775 to 850 °C observed in the high-temperature side can be considered to be due to the increase in the thermal activation of the reaction path for pure BN films.

Discussion

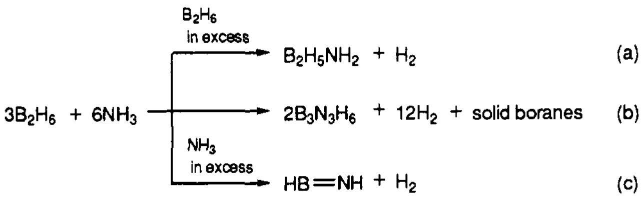
Before discussing the reaction mechanisms between diborane and ammonia it is pertinent to examine the chemical behavior of the reactants. As is known, the diborane molecule decomposes spontaneously forming boranes and hydrogen mixtures, even at temperatures below 0 °C.[19] In gas mixtures with 5% diborane in hydrogen, the decomposition reaction is retarded by the effect of the high hydrogen concentration according to the chemical equilibrium

$$\mathrm{B_2H_6} \rightleftarrows \text{boranes} + \mathrm{H_2}$$

However, at about 100 °C, the diborane molecules polymerize and, apart from some pentaborane molecules ($\mathrm{B_5H_9}$, $\mathrm{B_5H_{11}}$), tetraborane ($\mathrm{B_4H_{10}}$) is predominantly formed.[19] In the range 175–250 °C, a high percentage of nonvolatile boranes[19] exists in the final product. Therefore, to avoid the presence of other species different from the diborane molecule in the reactor, the diborane gas should be diluted and fed as quick as possible into the reaction zone.

Adding ammonia to diborane at room temperature results in the adduct compound $\mathrm{H_3B{\cdot}NH_3}$ (white solid), which sublimates just above room temperature.[20] Aminoborane ($\mathrm{H_2B{-}NH_2}$) is produced by heating the adduct compound and at $T > 200$ °C the adduct rearranges to the ring compound $\mathrm{B_3N_3H_6}$ (borazine). Continued heating produces a progressive loss of hydrogen until boron nitride is finally obtained.[6]

The final product of the reaction depends also on the ratio between the activated $\mathrm{B_2H_6}$ and $\mathrm{NH_3}$ molecules present in the reactor.[19] In the 150–300 °C temperature range, the mechanism of the reaction between diborane and ammonia can be described by the equations



When the $\mathrm{B_2H_6}/\mathrm{NH_3}$ molecular ratio in the reactants is 1:2, borazine ($\mathrm{B_3N_3H_6}$) with N/B = 1 is obtained along with hydrogen and solid boranes (reaction b, above). If there exists a diborane excess in the mixture, the final product is aminodiborane ($\mathrm{B_2H_5}$-$\mathrm{NH_2}$) with a ratio N/B = 0.5 (reaction a). And finally, if ammonia is in excess, borimide (HB=NH) is obtained (reaction c).[19] It is important to note that both borazine and borimide have the same B:N ratio as the boron nitride molecule. The intermediate compound may or may not be molecular precursor for boron nitride deposition depending on the ratio N/B in the molecule and also on the angle between B–N bonds in its structure.[21]

Furthermore, in the 600–850 °C temperature range it is expected that the diborane molecules are fully dissociated whereas ammonia remains only partially dissociated.[22] Therefore, the ratio of diborane to ammonia-active species will decrease as the temperature in the reactor increases. This in turn will affect the formation of either the intermediate compounds (aminodiborane, borazine, or borimide) which may be present during the reaction.

At low temperatures (600–700 °C), we will have aminodiborane whose B:N ratio is 2 (reaction a, above) which after decomposition will give boron rich films. This would explain the high percentage of B–O bonds detected in these films. However when the temperature increases ($T \geq 775$ °C), borazine is obtained as the intermediate compound (reaction b), as we have detected in some zones of the reactor. In this case, near stoichiometric boron nitride films are finally deposited.[11]

From the above, it follows that the intermediate compounds derived during the boron nitride synthesis from diborane and ammonia is strongly controlled by both the temperature and the reactant gas concentration. Adams[13] observed a decrease in the deposition rate for films obtained from borazine, as compared with those deposited from diborane and ammonia. In his work, aminodiborane is probably the intermediate compound formed ffrom the diborane and ammonia molecules, since in this case the $[NH_3]/[B_2H_6]$ gas ratio is low (in the 0.5–4.5 range) and the resulting final product is a boron-rich film (B_6NH_x). In a similar way, the decrease in the deposition rate observed in our work when the temperature increases in the 600–850 °C range, can be explained by a change in the formation mechanism of boron nitride, depending on the intermediate compound. As stated above, at low temperatures the intermediate is aminodiborane, while at temperatures ≥775 °C borazine is formed. This change in the mechanism would explain the differences in the activation energies obtained in each range: 35 kcal mol^{-1} for $T \geq 775$ °C and 5 kcal mol^{-1} for $T \leq 700$ °C. The former corresponds well to a reaction controlled by a surface reaction as it is typical in many of the CVD processes.[9] However, the low activation energy at low temperatures is less understandable. This is an indication of the complex reaction paths follows in this temperature range.

Conclusions

Boron nitride films and powders have been obtained by CVD from diborane and ammonia gas mixtures in the 600–850 °C temperature range in a hot-wall reactor. Both deposition processes (film and powder) are controlled by the pressure inside the chamber. The composition of the boron nitride films, deposited with $[NH_3]/[B_2H_6] = 18$, depends on the temperature during the deposition process. We have observed a change in the reaction mechanism within the above range at a temperature of 775 °C. At lower temperatures, aminodiborane is probably the intermediate compound, giving as a result rich boron films with high hydrogen content and favoring the film and substrate oxidation. However, at 775 °C, borazine is formed as an intermediate compound and the final boron nitride is purer with a more compact structure, thus preventing the oxidation of the film. For temperatures higher than 775 °C, the increase in the temperature produces the thermal activation of the reaction increasing the deposition rate and reducing the hydrogen content in the films.

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