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Boron Nitride Films Prepared by MOCVD

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In this article, the results obtained on films deposited by the metalorganic chemical vapor deposition (MOCVD) method using monomethylhydrazine ($CH_3N_2H_3$, MMH) as a nitrogen source are described. A general atmospheric CVD apparatus with a fused quartz reaction tube and an external heating furnace are used. Experimental conditions are as follows: growth temperature range, 400–1200°C; MMH flow rate range, 0.1–8.0 ml/min; triethylboron (TEB) flow rate, 1.0 ml/min; MMH/TEB range, 0.1–8.0. Boron nitride characteristic spectra are observed in the temperature range 400 to 1100°C. The composition (N/B) of the films deposited at 1000°C increases steeply from N/B = 0.01 at MMH/TEB = 0.1 to 0.69 at 0.2, and then stoichiometric boron nitride deposits over 1.0 of MMH/TEB. The crystal structure of the films is interesting at present, but the crystallinity is inferior to that obtained when ammonia is used as a nitrogen source. It will be influenced considerably by the electronic configuration based on the molecular structure of methylhydrazine. When methylhydrazine is used, we expect to grow the films at a lower deposition temperature. Until now, however, no particular change in the deposition temperature has been recognized. © 2000 Academic Press

1. INTRODUCTION

Numerous studies of boron nitride have reported on its synthesis, properties, and uses. Thin films of boron nitride have recently attracted a lot of attention due to the combination of properties offered by this nonoxide ceramic material, such as low density, optical transparency, hardness, chemical inertness, high electrical resistivity, and high thermal conductivity.

Newer applications of BN films include their use in microelectronic devices, not only as passive layers but also as active dielectric layers, and as wear- and corrosion-protective coatings for cutting tools and optical window.

It has been reported that electron emission occurred from surface hexagonal BN films doped with sulfur atoms at a low electric field, and also at low voltage from C-doped *n*-type boron nitride films synthesized by laser ablation (1, 2). From the viewpoint of practical application of field emitters to vacuum microelectronic devices and field-emission flat-panel displays, it is of great importance to achieve a stable and reliable performance of field emitters. One of the most promising materials for field emitters is diamond film, because negative electron affinity appears at the surface of diamond terminated with hydrogen atoms. Negative electron affinity was observed not only for diamond but also for AlN and BN by ultraviolet photoelectron spectroscopy studies (3–6).

The traditional synthetic routes to hexagonal BN have involved high-temperature syntheses employing inexpensive nitrogen-containing compounds with boron such as borane. Nitridation performed by exposure of a substrate to a reactive nitrogen species such as dimethyl-hydrazine (DMH) plays a key role in the growth of BN.

The availability of the metalorganic chemical vapor deposition (MOCVD) method in the preparation of boron nitride films has been reported previously (7). The fact that the MOCVD temperature of group III nitride is significantly lower than that of stable ammonia is of significant interest. Hydrazine H_2NNH_2 (8) and methyl hydrazine $Me(H)NNH_2$ (MMH) (9), Me_2NNH_2 (DMH) (10, 11) have proved their potentiality for low-temperature CVD of nitrides.

In this paper, we report on the preparation of BN films on Si substrates using triethylboron (TEB), MMH, and H_2 gas mixture sources in the temperature range 700 to 1200°C. The properties of the BN films were analyzed by Fourier transform infrared (FTIR) spectroscopy, electron probe microanalyses (EPMA), and X-ray reflection diffraction (XRD).

2. EXPERIMENTAL

The fused quartz reaction tube has an inside diameter of 25 mm and a length of 600 mm. Substrate was put on the substrate holder (graphite) inclined with a slope of about 20° to the horizontal axis and heated by an external heating furnace. The substrate temperature was measured with thermocouples attached at the rear of the substrate holder.

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TABLE 1
Source Materials

	Triethylboron, $B(C_2H_5)_3$	Monomethylhydrazine, NH_2NHCH_3
Melting point (°C)	− 95.2	− 52.4
Boiling point (°C)	92.5	87.5
Vapor pressure (Torr (0°C))	12.5	10.56

TEB, MMH, and hydrogen (99.999%) were used to grow boron nitride films by CVD. The properties of the source materials are summarized in Table 1.

Silicon wafers (12 × 12 × 0.5 mm, (111) (100)) were used as substrate. TEB and MMH were transported by bubbling hydrogen in the glassware reservoir. The temperature of the TEB and MMH saturator was maintained at 0°C. The flow rates of TEB and MMH were calculated as saturated gases in hydrogen.

The film thickness was measured at the masked parts on the substrate by a microstylus profilometer (DEKTAK II, Slon). Electron probe X-ray microanalyses (EPMA-8705, Shimadzu) were used to analyze the composition of the films. Measurements were carried out at an acceleration voltage of 7 kV, a sample current of 0.1 μA, and a beam diameter of 30 μm by using the lead stearate as a spectral crystal. The composition of the films was determined from the peak height ratio of boron $K\alpha$ and nitrogen $K\alpha$ analyzed by EPMA. Composition N/B was calibrated with bulk boron nitride as a standard sample, but composition C/B was not calibrated.

The crystal structure of the deposited films was studied by X-ray diffraction. The lattice parameters of the films were obtained from the X-ray diffraction angle. Infrared transmission spectra of the films were measured in the wave-number range of 400–4000 cm^{-1} using a Fourier transform infrared spectrometer (FTIR, Digilab, Bio-Rad).

The preparation conditions for the boron nitride films are summarized in Table 2.

TABLE 2
BN Film Preparation Conditions in the TEB–MMH Gas System

TEB flow rate (sccm)	0.5–1.5
TEB flow rate (sccm)	0.2–7.5
MMH/TEB flow rate ratio	0–10
Carrier H_2 (sccm)	400–650
Reaction temperature (°C)	700–1200
Substrate	Si(100) (111)

3. RESULTS AND DISCUSSION

3.1. Deposition Rate

The deposition rate of the films on the silicon substrate at the constant molar ratio MMH/TEB = 1.0 increases from 7.9 Å/min at 700°C to 277 Å/min at 1000°C and then decreases to 82.2 Å/min at 1100°C. At the constant molar ratio MMH/TEB = 10, the deposition rate increases from 0.9 Å/min at 700°C to 38.8 Å/min at 1000°C and then decreases to 10.3 Å/min at 1100°C. For temperatures below 1000°C, the deposition rate increases with temperature. Surface reaction is the rate-limiting step in this region.

Figure 1 shows the relation between the logarithm of the deposition rate and the reciprocal absolute temperature. An activation energy of 30.7 kcal/mol was obtained for the reaction in the temperature range below 1000°C. This value is smaller than 37.4 kcal/mol, obtained for the reaction of TEB with ammonia (1).

Figure 2 shows the deposition rate of thin films deposited at a constant reaction temperature of 1000°C as a function of the flow rate ratio of MMH to TEB. The deposition rate increases steeply up to 468 Å/min at MMH/TEB = 1.9 and then decreases to 38.8 Å/min at MMH/TEB = 10.

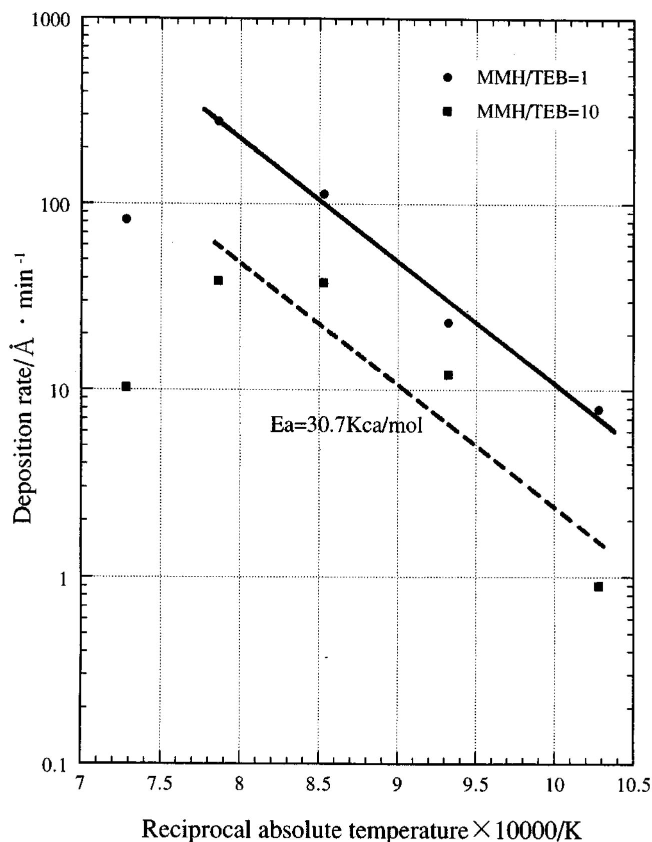

FIG. 1. Logarithm of BN films deposition rate as a function of reciprocal absolute reaction temperature.

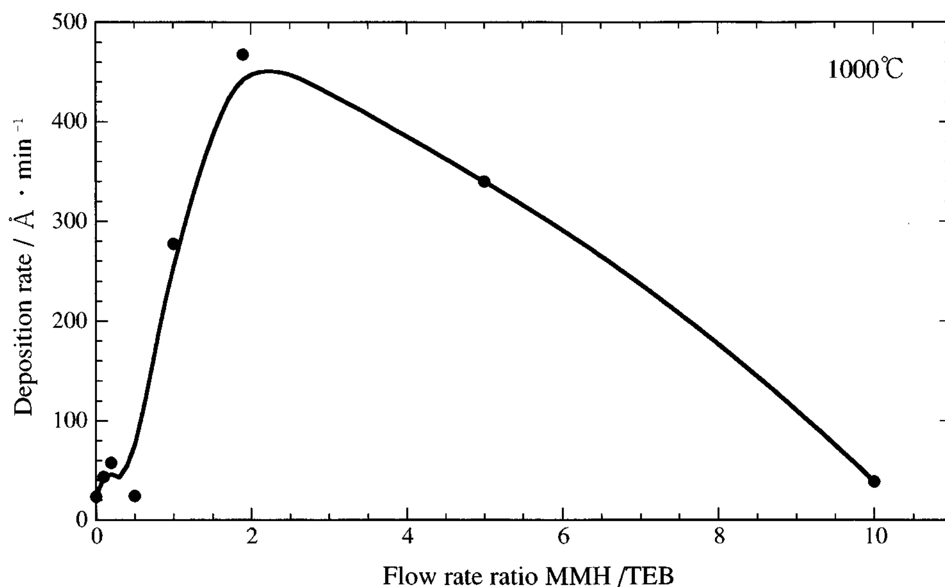

FIG. 2. Deposition rate of BN films as a function of flow rate ratio of MMH to TEB.

Decreases in the deposition rate over MMH/TEB = 1.9 were observed when ammonia was used (1). The decrease is due to the hold-down of the pyrolysis of TEB by an increase in the reducing character with increases in MMH.

3.2. Composition

Figure 3 shows that the composition (N/B) of the films deposited at 1000°C changes from N/B = 0 at MMH/TEB = 0 to about 1.0 at MMH/TEB = 2, and then the composition remains constant for the reactant gas flow rate ratio MMH/TEB > 2. In contrast, the composition C/B decreases from C/B = ∞ at MMH/TEB = 0 to 0 at MMH/TEB = 2.0.

Carbon is the deposition material when only TEB is pyrolyzed; however, the amount of carbon decreases steeply with the increasing introduction of MMH into the system. Deposition of boron and that reacting with nitrogen increase simultaneously, and then the compositions N/B achieve stoichiometry at the flow rate ratio MMH/

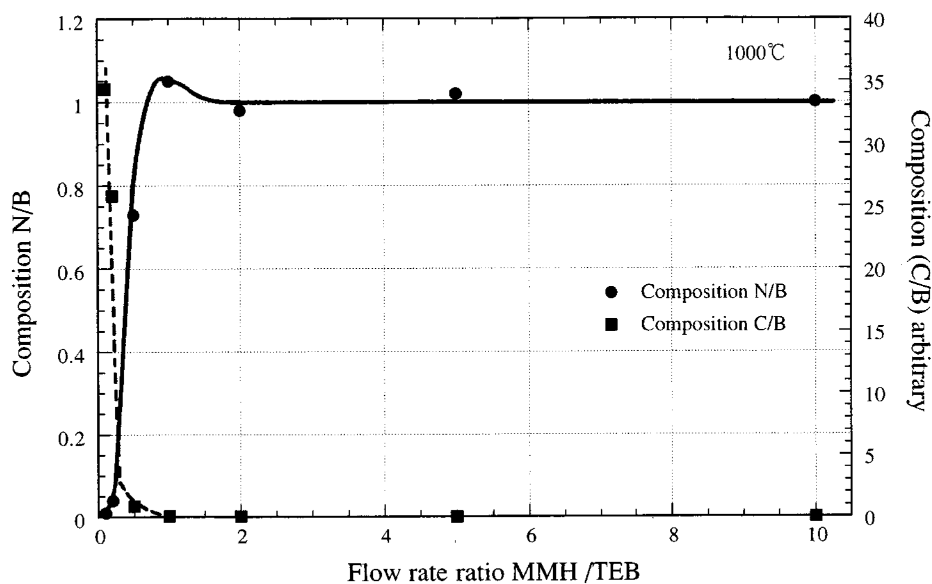

FIG. 3. Composition of BN films deposited at 1000°C as a function of flow rate ratio of MMH to TEB.

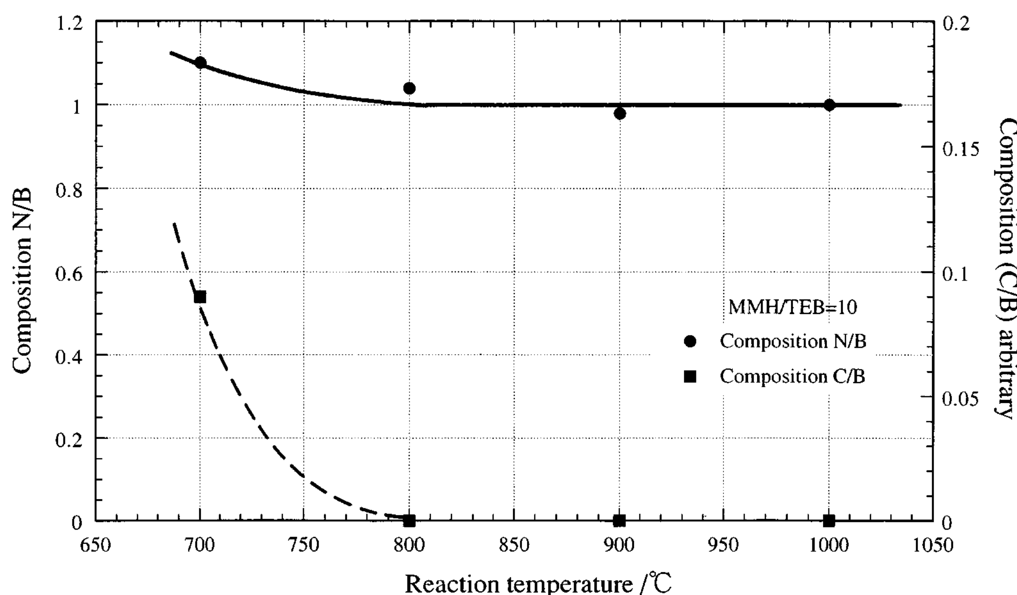

FIG. 4. Composition of BN films deposited at MMH/TEB = 10 as a function of reaction temperature.

TEB = ~ 2.0. Carbon impurities are not detected by EPMA in the films deposited over the ratio 2.0 within the limit of detection.

Figure 4 shows the composition of the films as a function of the reaction temperature at the flow rate ratio MMH/TEB = 10. The deposited films B/N have nearly constant stoichiometric composition 1.0 in the temperature range 700 to 1000°C. The carbon content of the films is also shown in Fig. 4. In deposition at high temperature, the compositions of boron nitride films deposited at MMH/TEB = 10 are stoichiometric. However, a lot of carbon is contained in the films deposited below 800°C, and the nitrogen content increases a little in relation to the quantity of this carbon content. It can been seen from Fig. 4 that at 700°C the carbon contained in the source materials remains in the films deposited, although MMH/TEB = 10.

3.3. *Infrared*

Figure 5 shows the infrared transmission spectra of the films deposited on silicon substrates in the temperature range 700 to 1100°C, at the constant ratio MMH/TEB = 8. It is found from these results that carbon remains in the films deposited at 700°C. Characteristic absorption of hexagonal boron nitride is observed at 1600–1200 cm^{-1} and 800 cm^{-1} in Fig. 5. It is found from this result that hexagonal boron nitride is created at 900°C. This characteristic absorption becomes obvious at 1100°C. A wave profile observed from 1800 to 4000 cm^{-1} is caused by interference of the films.

3.4. *Structure*

The lattice constant of the *c* axis of h-BN films deposited on the silicon substrate is shown in Fig. 6 as a function of the reaction temperature. The lattice constant decreases from 7.38 Å at 800°C to 7.115 Å at 1200°C, which is, however, still much larger than that of bulk BN, 6.66 Å.

3.5. *Pyrolysis Mechanism of Source Gases*

The pyrolysis mechanism of MMH and TEB can be made clear by analyzing the constituents of the exhaust gas. The apparatus used for the analysis was a quadruple mass spectrometer shown in a previous paper (12). The pyrolysis of

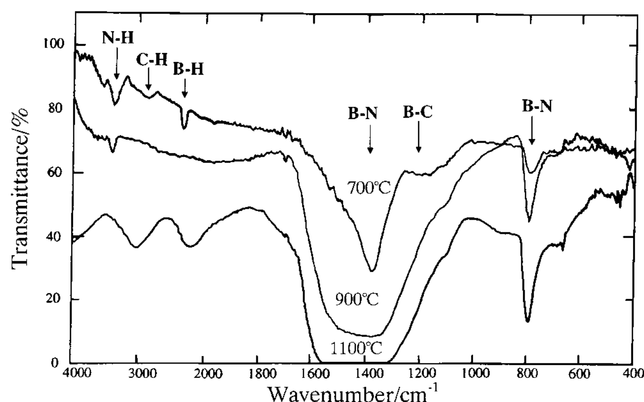

FIG. 5. Infrared spectra of BN films deposited at MMH/TEB = 8 at temperatures of 700, 900, and 1100°C.

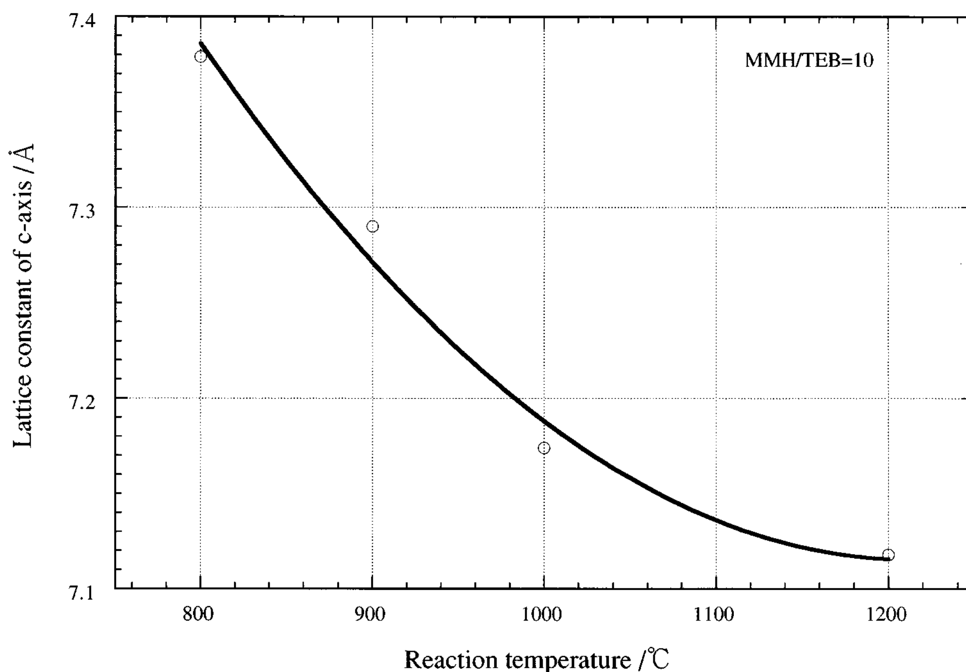

FIG. 6. Lattice constant of c axis of BN films deposited at MMH/TEB = 10 at temperatures of 800, 900, 1000, and 1200°C.

MMH and TEB was studied under a hydrogen atmosphere in the temperature range between room temperature and 1100°C with a step of 20°C. The analyses were carried out by introducing the gases to the mass spectrometer in the range 1×10^{-6} to 5×10^{-6} Torr through a variable leak valve. The condition of mass number m/e was in the range 1 to 150, scanning time was 7 s, and ionization voltage was 25 V.

The results of the mass analysis for pyrolysis of MMH under a hydrogen atmosphere are shown in Fig. 7. Partial pressure of the constituents derived from MMH decreases above 300°C. Remarkable fragments contained in the decomposed gases are shown in the mass spectra in Fig. 7. From these results, we determined pyrolysis of MMH began at about 200°C, and methane and ammonia were generated mainly. The results (Fig. 8) obtained from pyrolyzing TEB have been examined in a similar fashion. Pyrolysis of TEB began at about 300°C, ethane (contained 10% ethylene) was generated mainly, and these hydrocarbons decomposed to methane at high temperature.

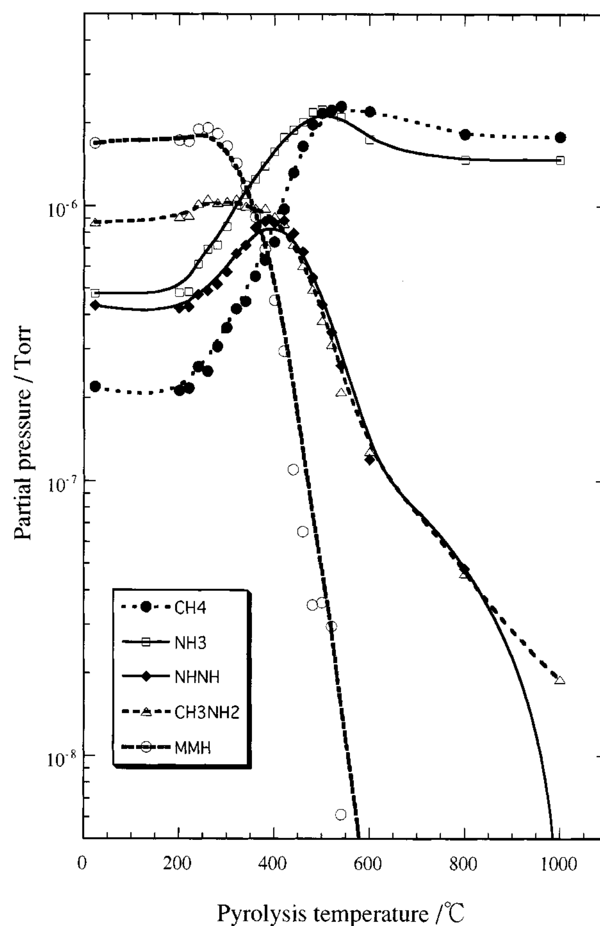

FIG. 7. Partial pressure of pyrolyzed fragments of MMH in H_2 carrier gas as a function of decomposition temperature.

4. CONCLUSION

Boron nitride films could be obtained on silicon substrate by the reaction of TEB with MMH at temperatures above 700°C. The deposition rate depends significantly on the ratio of MMH to TEB and on the reaction temperature. It has been clear that large quantities of carbon remained in the films deposited under the condition that the ratio MMH/TEB < 2. In this study, boron nitride films are

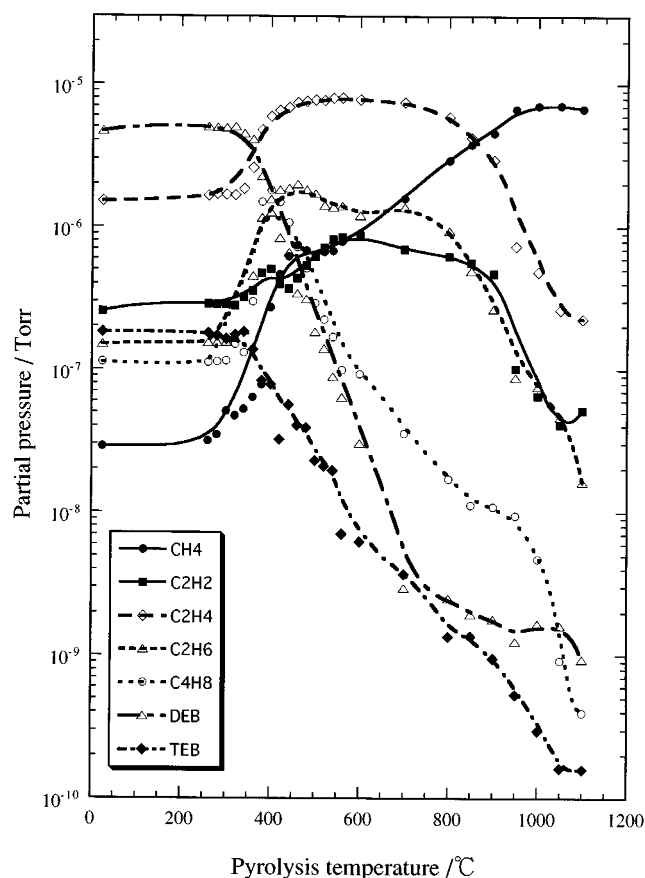

FIG. 8. Partial pressure of pyrolyzed fragments of TEB in H_2 carrier gas as a function of decomposition temperature.

obtained effectively over MMH/TEB = 2 at the temperature of 1000°C.

In comparison with the case of decomposition using MMH, which begin at 200°C, with that using NH_3, stable over 800°C, the reaction of MMH with TEB is expected to take place at fairly low temperature. However, very little boron nitride deposits are generated, even if the beginning reaction temperature is lower.

The *c*-axis lattice constant of boron nitride deposited by this method was considerably large compared with that obtained when ammonia was used (1). Since the interlayer distance along the *c* axis is larger than that of bulk, boron nitride films are suitable for the study of boron nitride intercalation described previously (13).

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