# A STUDY OF DEPOSITION RATE AND CHARACTERIZATION
# OF BN THIN FILMS PREPARED BY CVD

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**Abstract** – Triethylboron (TEB) and ammonia were employed as precursors in preparation of boron nitride thin films on Si(100) substrate by CVD. Operating parameters such as reactor pressure and feed rates of gases were varied to investigate their effects on deposition rate and film characteristics. Total gas pressure in the reactor was varied from near atmospheric to near 1 torr. Deposition temperature was in the range of 850-1,100 °C. Deposition rate increased with increase of partial pressure of TEB, but decreased with increase of total pressure in the reactor. Deposited films were examined with SEM, FTIR, XPS, AES and XRD. Films were BN of turbostratic structure and their texture and carbon content varied with deposition conditions.

Key words : CVD, BN, Thin Film, Deposition Rate, Film Characteristics, Reaction Pressure

## INTRODUCTION

Boron nitride (BN) is a man-made material with outstanding properties such as optical transparency, chemical inertness, hardness, high electrical resistivity, high thermal conductivity, and low dielectric loss [Kempfer, 1990]. Recently, many investigators have studied BN thin films prepared by various physical vapor deposition (PVD) and chemical vapor deposition (CVD) methods [e.g., Arya and D'Amico, 1988; Kester et al., 1994; Kuhr et al., 1995; Ichiki et al., 1996].

In CVD various physical and chemical parameters are involved in the formation of thin films. It is not easy, if not impossible, to measure profiles of temperature and gas flow in the reactor as well as concentration of all the chemical species involved in the deposition. This is despite the fact that, CVD being an often-preferred method in preparation of industrially much important III-V thin films such as GaAs and GaN, extensive efforts have been made to elucidate the kinetics and mechanisms in the MOCVD of those materials. However, due to intrinsic difficulties and complexities associated with MOCVD much more work is needed. In III nitrides such as GaN and AlN, ammonia is often used as a precursor for nitrogen, which combines readily with alkyls, standard MO precursors in these cases, to form adducts. Epitaxy of GaN is possible by atmospheric pressure MOCVD, but epitaxy of AlN requires reduced pressure MOCVD due to parasitic reactions [Chen et al., 1996].

Compared to MOCVD of GaN and AlN thin films, little work has been reported on CVD of BN with alkyl boron. Most investigators have employed halogen compounds or diborane as a precursor in their study of CVD BN thin films. In this

study we investigated effects of deposition conditions on the deposition rate and characteristics of BN thin films using triethyl boron (TEB) as a precursor. Nakamura reported results of CVD using the same precursor but pressure was fixed at atmospheric pressure [Nakamura, 1986]. Here we present experimental results including effects of reactor pressure on BN film deposition.

## EXPERIMENTS

Fig. 1 shows a schematic diagram of the CVD system used in this study. The reactor was made of a quartz tube and a substrate was put upon a graphite substrate holder. The reactor was heated by a three-zone electrical heater, and a K-type thermocouple was inserted into the substrate holder. The reactor was jacketed with a large diameter quartz tube and air was supplied in the annulus for the cooling of the reactor wall, thereby reducing deposition on the inner wall of the reactor. Hydrogen was used as a carrier gas to transport triethylboron (TEB) into the reactor. The feed rate of TEB was controlled by adjusting the bubbler temperature and the carrier gas flow rate through it. The TEB inlet tube was positioned along the axis of the reactor, and the distance between the tip of the inlet tube and the substrate could be varied. Ammonia and argon were fed into the reactor through a separate line to avoid formation of adducts in the gas feed line. All the gases were fed into the reactor through mass flow controllers, and traps to remove moisture and oxygen were installed in the gas lines from cylinders. Working pressure of the reactor could be regulated through a control loop consisting of a throttling valve in the gas exhaust and vacuum pump. Exhaust gases from the reactor were passed through a scrubbing unit before discharge.

Single crystal silicon (100) wafers were cut into 10×10× 0.53 mm chips and used as substrates for deposition of BN.

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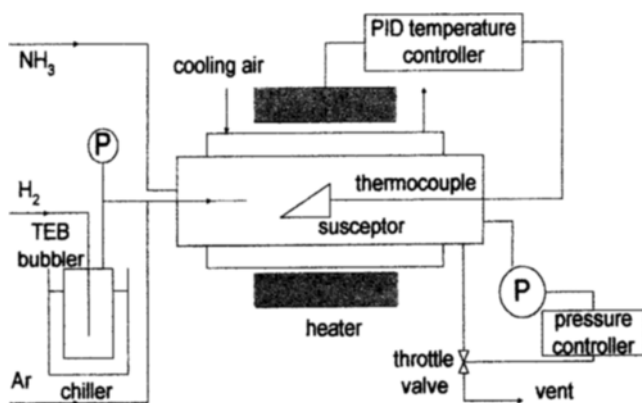E-mail : pdk93@kistmail.kist.re.kr

Fig. 1. Schematic diagram of CVD system for the deposition of BN thin films.

Table 1. Deposition conditions for CVD of BN thin film

| Deposition temperature | 850-1,100 °C |
|---|---|
| Reactor pressure | 1-740 torr |
| Feed rate of TEB | 0.06-1.5 ml/min |
| Feed rate of $NH_3$ | 10-300 ml/min |
| Feed rate of Ar | 0-700 ml/min |
| Feed rate of $H_2$ | 9-50 ml/min |

Substrate was put in boiling solution of $H_2SO_4/H_2O_2/H_2O$ for ten minutes to remove organic material and then cleaned of oxides with $HF/H_2O$ solution. After drying with nitrogen gas it was placed into the reactor and baked at 600 °C for ten minutes under vacuum. Then argon was introduced to adjust reactor pressure to the desired value and reactor temperature was raised at the rate of 6.7 °C/min to the deposition temperature. Deposition was carried out by feeding reactant gases. Conditions for the deposition are summarized in Table 1.

Substrates were weighed before and after deposition to measure the mass of deposited films. Deposited films were examined with FTIR, XPS, SEM, AES, and XRD.

## RESULTS AND DISCUSSION

It was found that deposition rate is highest for a certain value of the distance between the inlet of TEB and substrate. This distance for maximum deposition rate varied with deposition pressure. When the distance is short, gases do not have enough time for a good mixing before reaching the substrate. Then the probability of forming adducts is low, and thus the deposition rate of BN is low. On the other hand, adducts formed in the reactor have a high probability of moving toward the reactor wall instead of deposition on the substrate when the distance from the TEB inlet to the substrate is large (i.e., surface area of reactor wall is much larger than substrate). In the former case gases continue to mix downstream of the substrate and a solid phase can be formed there. It was confirmed that a sizable number of particles were found there when the reactor was opened at the end of the deposition experiment. In the latter case deposition of films on the reactor wall between the tip of the TEB inlet tube and the substrate should occur. This was also confirmed, as there was significant deposition in that region

of the reactor wall.

The deposition rate increased with an increase of the total gas flow rate, but not significantly within the experimental ranges of the study. To investigate the effect of partial pressures of individual gases on the deposition rate, the feed rate of each gas was varied while flow rate of argon was adjusted to maintain total gas feed rate constant. It was found that the effects of hydrogen and ammonia partial pressures were insignificant. This is as expected because the feed rate of ammonia was much in excess, as is usual with CVD of III-V compounds. The ratio of ammonia to TEB feed rate was 20 or larger in this study. When the total gas feed rate was constant, the deposition rate increased with an increase of the TEB feed rate. At a constant reactor pressure of 740 torr, the deposition rate was proportional to the 0.7 power of TEB inlet partial pressure.

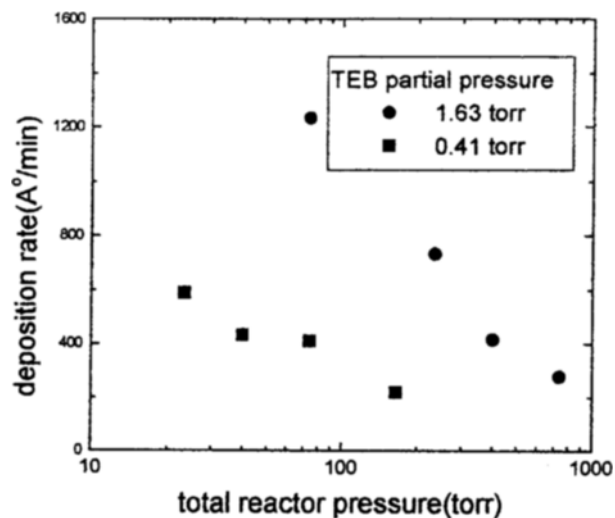However, the effects of total reactor pressure turned out to



Fig. 2. Effects of reaction pressure on the deposition rate at constant TEB partial pressure (total gas flow rate, 91 sccm; $NH_3$/TEB ratio, 40; substrate temperature, 1,000 °C).
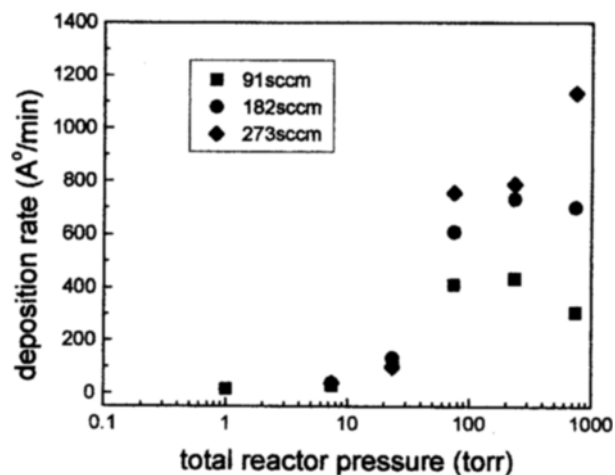


Fig. 3. Effects of reaction pressure on the deposition rate at 1,000 °C at various total gas flow rates (mole fraction: TEB, $5.5 \times 10^{-3}$; $NH_3$, $2.2 \times 10^{-1}$).

be very significant. Fig. 2 shows the variation of deposition rate with total reactor pressure at constant TEB partial pressure. Flow rate of argon was adjusted to control partial pressures of reactant gases and total gas flow rates. Deposition rate increased dramatically with decrease of total reactor pressure. With reduced pressure in the reactor the molecular diffusivities of gases increase, thereby increasing the transport rate of film forming materials toward the substrate surface. Notice that mole fraction of TEB in the gas increased with a decrease of total pressure as the partial pressure (i.e., the flow rate) of TEB was kept constant.

If we vary total reactor pressure while keeping molar fraction of TEB constant, the partial pressure of TEB is proportional to the total pressure. Effects of total reactor pressure in this case are shown in Fig. 3. Here for each of the total gas flow rates 91, 182, and 273 sccm, the ratio of flow rates of all the gases were kept constant while the total pressure of the reactor was varied, thereby keeping the mole fraction of the gases constant. From near atmospheric pressure to about 70 torr, the deposition rate either decreased or increased slightly depending on the total gas flow rate. In this regime the de-

position rate was insensitive to the partial pressure of TEB, though it was a little higher at a larger total gas flow rate. At a reactor pressure of 740 torr, powders of fine particles were observed downstream of the substrate in the reactor. Although we do not know the exact location of powder formation, it depletes reactants that can reach the substrate surface, thereby obstructing formation of thin film. Thus, the deposition rate does not increase with reactor pressure despite the increase in partial pressure of the reactant gases in the feed. However, the deposition rate decreased dramatically as reactor pressure decreased further below 70 torr, showing dependency of deposition rate on partial pressure of TEB. Below 20 torr of the reactor pressure, the deposition rate becomes very small, and below 1 torr deposition hardly occurs. When the deposition rate was very small deposition on the reactor wall near the tip of TEB inlet tube was significant. As the reactor pressure decreases, diffusion becomes active, but residence time of gases in the reactor decreases and the rate of adduct formation decreases as well. Note that concentrations of both TEB and ammonia in the reactor decrease with a decrease of reactor pressure.
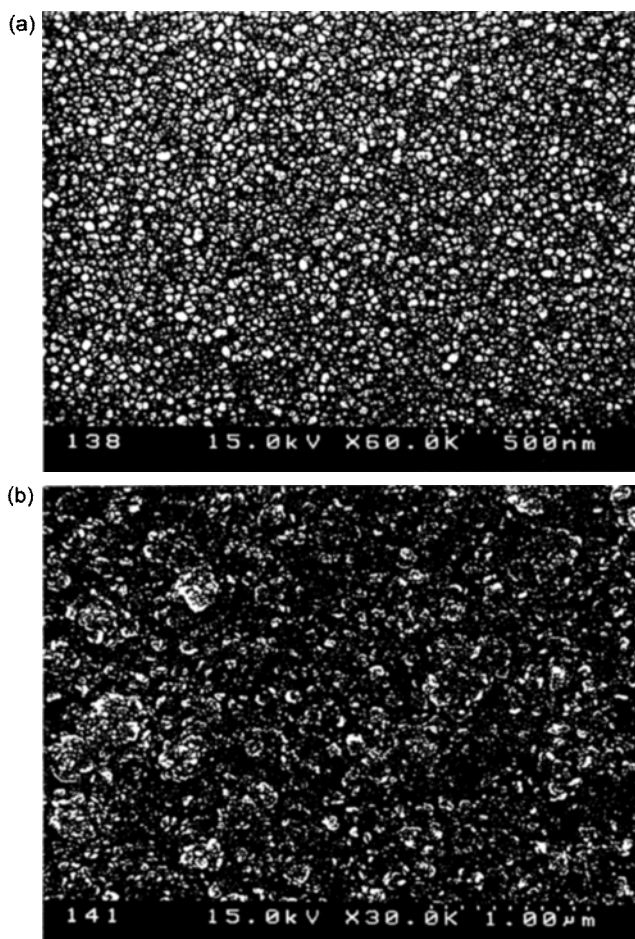


Fig. 4. SEM images of the surface of BN thin films deposited at different reactor pressures.
(a) 7.4 torr, (b) 234 torr (gas flow rates: TEB, 1 sccm; NH₃, 40 sccm; total gas flow rate, 182 sccm; substrate temperature, 1,000 °C)
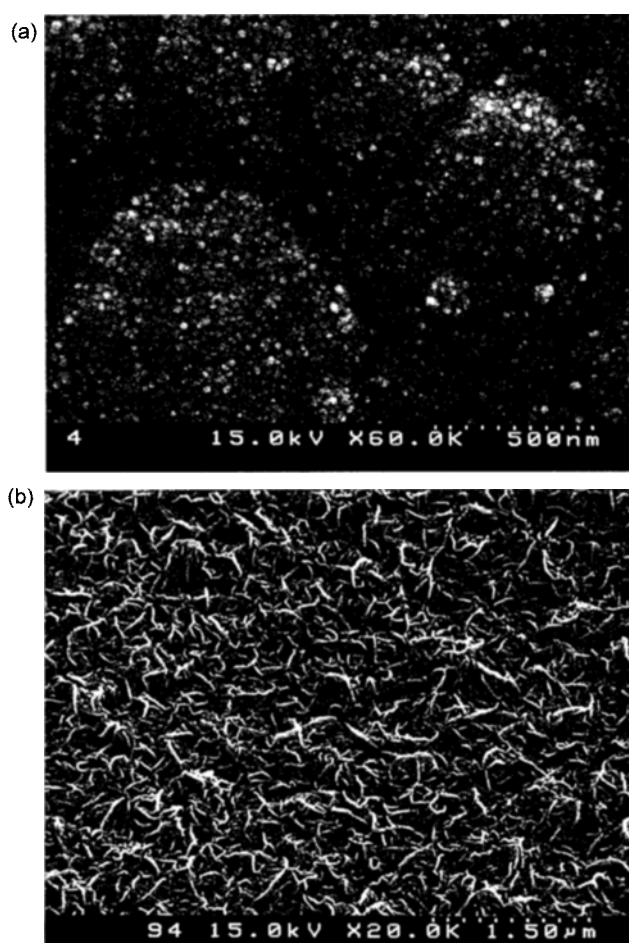


Fig. 5. SEM images of the surface of BN thin films deposited at different NH₃/TEB ratio.
(a) 20, (b) 180 (gas flow rates: TEB. 0.84 sccm; H₂, 50 sccm; total gas flow rate, 310.34 sccm; substrate temperature, 1,000 °C; reactor pressure; 740 torr)

Deposition rate increased with an increase of deposition temperature up to 1,050 °C, but decreased with a further increase in temperature. This is not unusual in CVD. Activation energy for the temperature range of 850 to 1,050 °C was 313 kJ/mol at the deposition pressure of 740 torr.

SEM photographs of the surfaces of deposited BN thin films show pebble-like structure. Fig. 4 shows films deposited at low pressure having more surface uniformity compared to those deposited at atmospheric pressure. But Fig. 5 shows that the morphology of the film depends also on the ratio of ammonia to TEB feed rate: for ammonia to TEB ratio of equal to or more than 180, flaky types of films were deposited. The density of the flaky films was 1.8 g/cm³ compared to 2.1 g/cm³ of pebble-like films. The density of the film was determined from the film thickness measured by cross-sectional SEM photography and weight change of substrate from deposition. Measured density of the film was in the range of 1.88-2.15 g/cm³. This was comparable to the results of 1.99-2.20 g/cm³ from CVD with $BCl_3$-$NH_3$ at 1,850-2,200 °C.

Figs. 6 and 7 show typical FTIR spectra of deposited BN thin film. B-N stretching mode showed up at wave number of 1,380-1,400 cm⁻¹ resulting from in-plane vibration. It is construed that the film is of h-BN structure with sp² orbital. B-N-B bending mode, which showed up at wave number 790-800 cm⁻¹, is the result of out-of-plane vibration. In this study B-N-B bending was not found when the deposition rate was lower than 960 mg/m²hr. This suggests that deposition rate influences B-N-B bonding in deposition. And at conditions of similar deposition rate, deposition temperature also influences
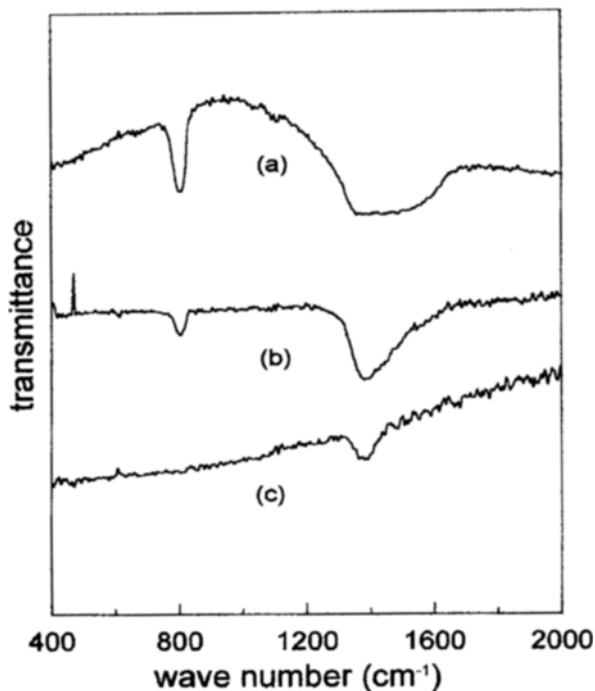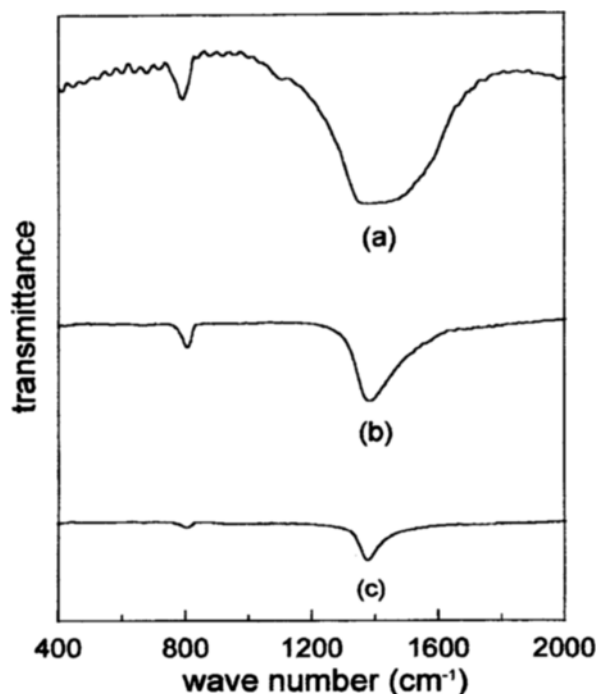


Fig. 7. FTIR transmission spectra of BN films deposited at different reactor pressure.
(a) 7.4 torr, (b) 23.4 torr, (c) 740 torr (gas flow rate: TEB, 0.5 sccm; NH₃, 20 sccm; total gas flow rate, 91 sccm; substrate temperature, 1,000 °C)

B-N-B bonding.

The trial of RBS for the determination of film composition was not successful as a silicon substrate was used in this study. A wide scan of XPS spectra shows peaks for B, N, C and O (Fig. 8). AES also confirms deposited films are made of boron and nitrogen (Fig. 9). A depth profile shows constant B/N composition across film thickness. Values of N/B ratio in film were in the range of 0.83-1.06. This indicates that deposited films are nearly stoichiometric BN. From AES and narrow scan of XPS (Fig. 10) of the film deposited at total reactor pressure of 740
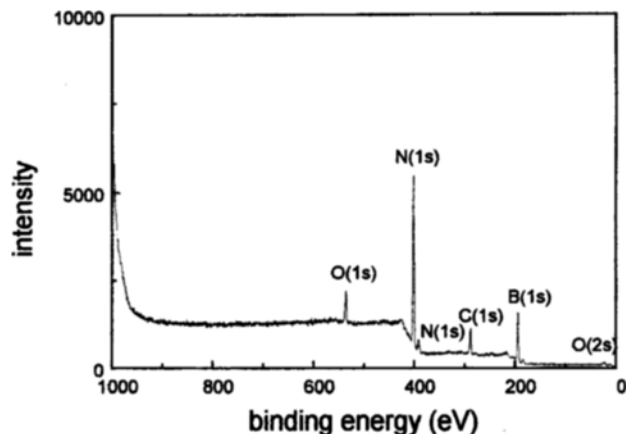


Fig. 6. FTIR transmission spectra of BN films deposited at different substrate temperature.
(a) 1,100, (b) 1,050, (c) 1,000 °C (gas flow rates: TEB, 0.08 sccm; NH₃, 200 sccm; H₂, 12 sccm; Ar, 188 sccm; reactor pressure, 740 torr)



Fig. 8. Wide scan of XPS spectra of deposited BN film.
(gas flow rate: TEB, 0.5 sccm; NH₃, 20 sccm; H₂, 30 sccm; Ar, 40.5 sccm; substrate temperature, 1,000 °C; reactor pressure, 740 torr)
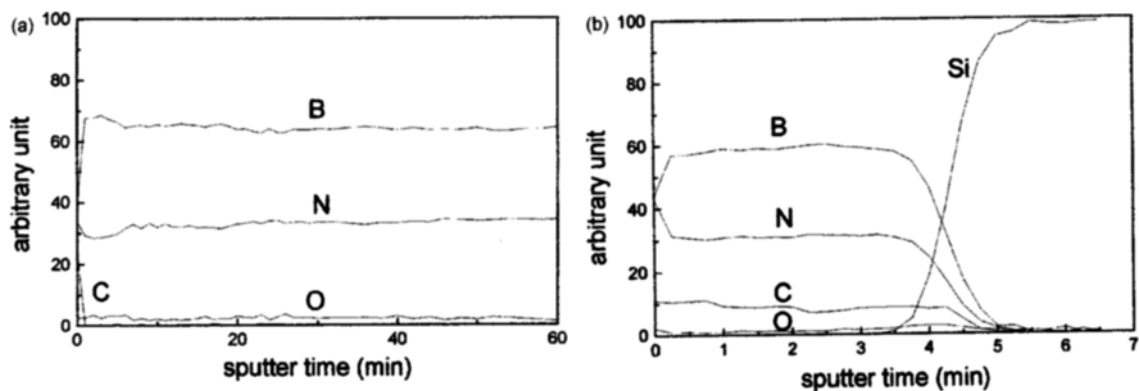
**Fig. 9. AES depth profile of BN films deposited at different reactor pressure.**
(a) 740 torr, (b) 7.4 torr (sputtering condition: 4 kV Ar beam (235 A° SiO₂/min); gas flow rate: TEB, 0.5 sccm; NH₃, 20 sccm; total gas flow rate, 91 sccm; substrate temperature, 1,000 °C)
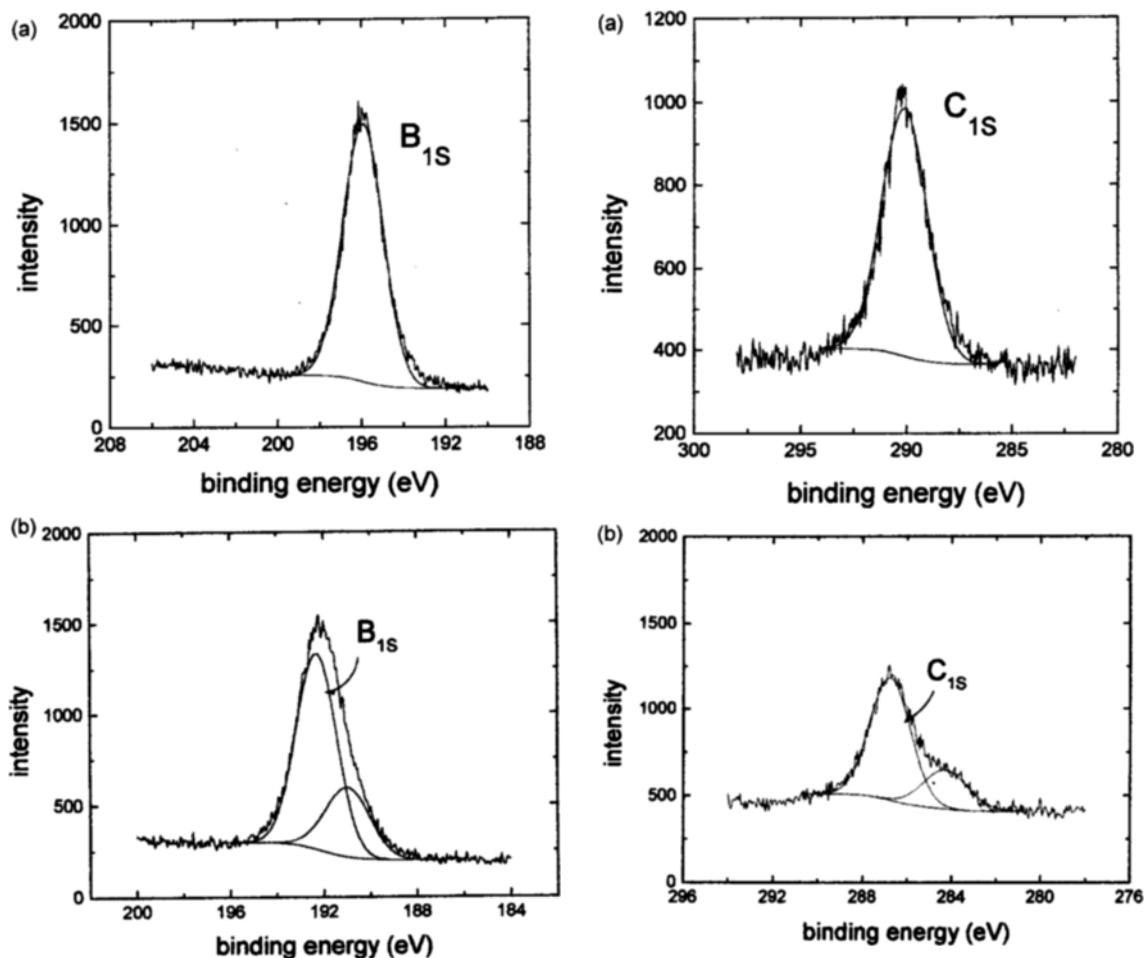


**Fig. 10. Narrow scan of XPS spectra of BN films deposited at different reactor pressure.**
(a) 740 torr, (b) 7.4 torr (gas flow rate: TEB. 0.5 sccm; NH₃, 20 sccm: total gas flow rate, 91 sccm; substrate temperature, 1,000 °C)

torr, no bonding other than B-N could be found between B and N. Carbon was concentrated near the film surface, suggesting that it came from contamination after deposition. But at low total reactor pressure formation of carbide could not be excluded. The B₁ₛ peak, shown in Fig. 10(b), could be resolved into a peak at a binding energy corresponding to BN and another

corresponding to a compound with lower binding energy for boron. Although additional work is needed to identify this boron, carbon may be present as $BC_xN_y$. It is construed that carbon found near the film surface comes from contamination after deposition, and carbon exists in carbide form in deposited films.
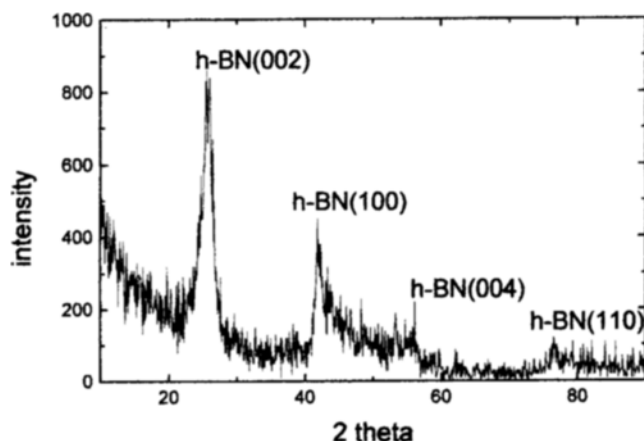
**Fig. 11. XRD pattern of deposited BN film.**
(gas flow rate: TEB, 0.84 sccm; NH₃, 151.2 sccm; H₂,
50 sccm; Ar, 108.3 sccm; substrate temperature, 1,000 °C;
reactor pressure, 740 torr)

XRD shows (002), (004), (001), (110) planes of h-BN. Peaks
are shifted toward lower angles and broadened (Fig. 11), thus
indicating that the film is of turbostratic structure (t-BN) hav-
ing irregular stacking of hexagonal network layers of B and
N in the c-axis.

## CONCLUSIONS

Thin films of BN were deposited by flowing TEB, ammo-
nia, hydrogen and argon through a CVD reactor. Deposition
parameters such as pressure, temperature, and flow rate of each
gas were varied to investigate their effects on deposition rate
and film characteristics. It was found that the deposition rate
increased with the partial pressure of TEB to the power of 0.7
at total reactor pressure of 740 torr. Partial pressures of other
gases showed negligible effects on deposition rate within the
experimental ranges of this study. At 740 torr activation ener-
gy was estimated to be 313 kJ/mol for temperatures from 850
to 1,050 °C.

The effect of total pressure in the reactor on the deposition
rate was significant. When total pressure was varied while par-
tial pressures of TEB and ammonia were kept constant, the
deposition rate increased with decrease in total pressure. In-
crease of gas diffusivity with decrease of pressure might be a
cause of deposition rate increase. When total pressure in the
reactor was varied, while feed rates of all the gases were
kept constant, two distinct regimes were observed. From at-
mospheric pressure to about 70 torr the deposition rate did not
vary much. As pressure decreased, the mass transfer of de-
positing material increased due to increased diffusivity. On
the other hand, partial pressures of reactants decreased in pro-
portion to the total pressure. Thus, these two effects canceled
each other out, resulting in insignificant effects of total pres-
sure in this regime. For total reactor pressure less than 70 torr,
the deposition rate decreased dramatically with decrease of total
pressure. Decrease of depositing species outweighs increase
in transport rate, resulting in rapid decrease in deposition rate
with decrease of total pressure.

SEM shows that the morphology and the density of deposit-
ed thin films were influenced by deposition conditions. XPS
and AES confirms deposited films were nearly stoichiometric
BN. FTIR shows h-BN. Broad XRD peaks suggest films are
of turbostratic structure.

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