Preparation and Properties of Boron Nitride Films by Metal Organic Chemical Vapor Deposition

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ABSTRACT

Boron nitride films have been deposited by a metal organic chemical vapor deposition (MO-CVD). The reaction between ammonia and triethylboron ($B(C_2H_5)_3$) is carried out in the temperature range of 750°-1200°C with the molar ratio of $NH_3/B(C_2H_5)_3 = 0\text{-}200$. Colorless and transparent films are obtained at temperatures of 950°-1100°C with the molar ratio of 20-70. The composition of the films, N/B, is found to vary from 0.46 to 1.0. For a fixed $NH_3/B(C_2H_5)_3$, the deposition rate increases with temperature up to 1000°C and then decreases. The deposition rate shows an Arrhenius-type behavior in the temperature range of 750°-1000°C. X-ray diffraction studies indicate that the crystal structure of the films is hexagonal. The energy of the direct allowed transition, obtained from optical measurements, is estimated to be 5.90 eV.

Several papers have been published describing the preparation of boron nitride films, the physical and chemical properties, and the potential applications of those films. Boron nitride films have been prepared by chemical vapor deposition (CVD) using borontrichloride or diborane as source materials (1-3). Recently in the preparation of compound semiconductors, CVD using metalorganic compounds has been developed, and its achievements have become of major interest lately. This method, called MOCVD, has been developed with reference to the deposition of GaAs by Manasevit (4) in 1968, and a number of related papers have been reported mainly for the growth of III-V compound semiconductors (5-7).

In a previous paper (8), we reported on the amorphous boron nitride films deposited by the molecular flow chemical vapor deposition (MFCVD), by which we could control the composition easily. In this paper, we report the preparation and properties of boron nitride films deposited using triethylboron and ammonia by MOCVD.

Experiments

Triethylboron (TEB, Arfa Products, 98%); ammonia (99.9%), hydrogen (99.999%), and argon (99.995%) were used to grow boron nitride films by CVD. Sapphire (12 × 12 × 0.6 mm^3) and silicon (12 × 12 × 0.25 mm^3) were used as substrates.

The schematic diagram of the apparatus for the deposition of boron nitride is shown in Fig. 1. The fused quartz reaction tube has an inside diameter of 25 mm and is 600 mm long. Substrates were put on the substrate holder (sintered boron nitride) with slope of 20° against the horizon and heated by external heating furnace. The substrate temperature was determined by a thermocouple attached at the rear of substrate holder.

Triethylboron was transported by bubbling hydrogen through the TEB. The temperature of the TEB saturator was controlled between 0° and 25°C. TEB is a colorless clear liquid, and is moisture and air sensitive and pyrohoric. The vapor pressure at 0°C is 12.5 torr (9). The flow of TEB was determined from the loss of TEB in the saturator. The preparation conditions of boron nitride films are summarized in Table I.

The crystal structures of the deposited films were studied by x-ray diffraction. Optical transmission and reflection spectra of films deposited on sapphire were measured over the wavelength range 190-2500 nm using a spectrophotometer, MPS-50 (Shimadzu). In the transmission and the reflection measurements, an uncoated sapphire and an evaporated aluminum film were used as the references, respectively. Infrared transmission and reflection spectra of the films on Si were also measured in the wavelength range of 2.5-50 μm using an infrared spectrophotometer, DS-701G (Jasco). In the infrared, an uncoated Si and an evaporated aluminum film were used as the references for the transmission and reflection measurements, respectively.

Table I. Experimental conditions

Growth temperature	750°-1200°C
Gases flow rate	ml/min
$(C_2H_5)_3B$	0-2.8
NH_3	15-250
H_2	48-120
Total	60-300
$(C_2H_5)_3B$ saturator temp.	0-25°C

An electron probe x-ray microanalyzer (EPMA) was used to analyze the composition of the films. Because the films had high resistivities, berylium was deposited on the sample surfaces to avoid charging. The measurement conditions have been described elsewhere (4). The peak wavelengths of the fluorescence x-ray from the boron and nitrogen were 68.5 and 32Å, respectively. The wavelength of the boron $K\alpha_2$ is shifted by the nitrogen in the boron nitride. The composition of the films was estimated from the x-ray fluorescence intensity of boron and nitrogen. The compositions were corrected using measurements from a standard boron nitride sample.

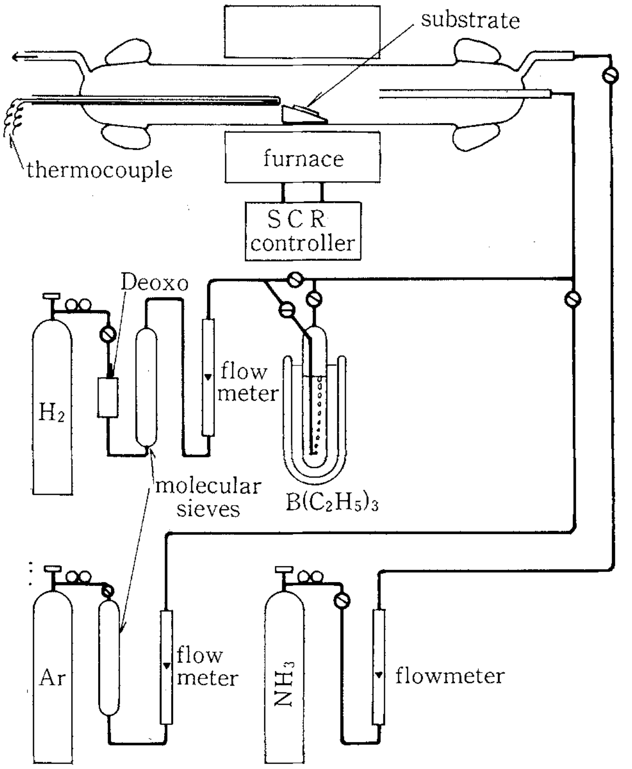

Fig. 1. Schematic diagram of the apparatus used for the deposition of boron nitride films by metal organic chemical vapor deposition.

Results and Discussion

Influence of the gas flow rate on the appearances of the films.—The changes of the color and the surface roughness of the films deposited for different flow rates of triethylboron and ammonia are shown in Fig. 2. The stoichiometric boron nitride is colorless and transparent because of its wide bandgap. However, some of the deposited boron nitride films are colored due to nonstoichiometry of the films. It was found that the color of the deposited films depends on the reactant molar ratio $NH_3/B(C_2H_5)_3$, and that the surfaces become rough with increasing flow rate. The black colored films with smooth surfaces were obtained when the films were deposited only with triethylboron or with a small amount of ammonia. X-ray diffraction analysis shows that the black colored films are amorphous. It is found from EPMA analysis that the black film is carbon containing boron. At the deposition temperature of 1000°C, the colorless and transparent films were obtained when the flow rates of ammonia and TEB were in the ranges between 25 and 70 ml/min and 0.25 and 1.0 ml/min, respectively. The color of the transparent films changed from colorless to dark brown by increasing the ratio of TEB to ammonia. Colorless and brown films were found to be hexagonal boron nitride by x-ray diffraction analysis.

For TEB flow rates below 1.0 ml/min, the colorless films change from transparent to opaque at ammonia flow rates of 80 ml/min. The brown-colored films deposited with the TEB flow rates above 1.0 ml/min also change from transparent to opaque at ammonia flow rates of 120 ml/min. These results suggest that the opaque films deposition is caused by gas phase reaction and/or that uniform growth is inhibited by numerous nucleation sites that increase with increasing source gas supply to substrate surface are caused by the increasing flow rate. This is consistent with the fact that the deposition rate increases with increasing flow rate.

Crystal structure.—The deposited films were found to be hexagonal boron nitride by x-ray diffraction analysis. In most cases, only the (002) diffraction peak was observed, which indicates that the c-axis is preferentially oriented perpendicular to the substrate surface. However, for the opaque films with rough surfaces, diffraction peaks other than the (002) peak were observed. Since these films were deposited at high deposition rates, it is thought that the numerous nucleations occur on the substrate surface and several orientations grow as the deposition takes place.

The diffraction pattern of the films deposited at various temperatures shows that the peak shifts to higher angles and the full width at half maximum (FWHM) decreases with increasing deposition temperature. These dependencies indicate that the crystalline size of the films deposited at high temperature is larger than that at low temperatures, and that the amount of the boron nitride deposited depends strongly on the temperature.

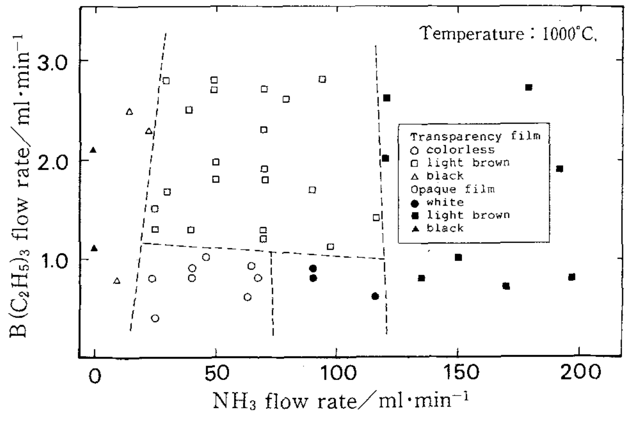

Fig. 2. Relation between the flow rate of triethylboron and ammonia and the appearance of the film deposited at 1000°C.

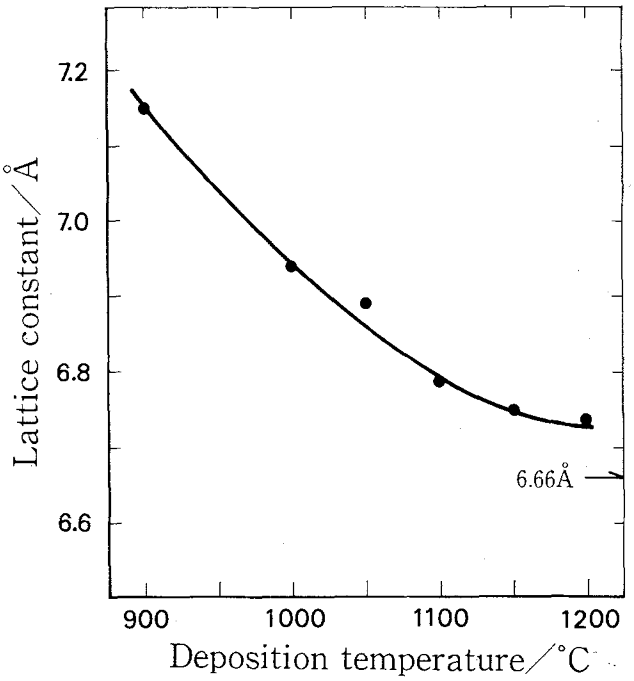

Fig. 3. Lattice constant c_0 of boron nitride films deposited at various temperatures.

Figure 3 shows the deposition temperature dependences of the lattice constant, c_0, of the deposited films. The lattice constant decreases from 7.15Å at 900°C to 6.73Å at 1200°C. For bulk boron nitride, c_0 is reported to be 6.66Å (JCPDS). The lattice constant of the boron nitride films deposited at 1200°C is larger than the value in JCPDS. From the extrapolation in Fig. 3, a deposition temperature of about 1500°C is necessary to deposit films having a lattice constant equal to that of bulk BN.

Figure 4 shows the temperature dependence of the crystallite size calculated from the FWHM of the diffrac-

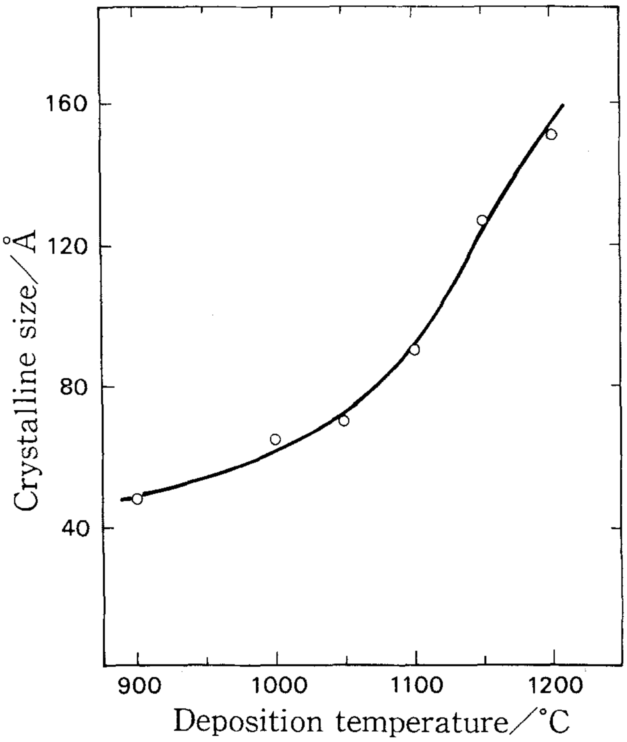

Fig. 4. Temperature dependence of the crystalline size of the boron nitride films.

tion peak corresponding to the (002) plane by using the Scherrer-Laue equation. The crystalline size of 47Å at 900°C increases gently to 65Å at 1150°C and then increases steeply to 150Å at 1200°C. This crystalline size shows on c-axis direction, not a-axis, thus indicating regularity of piled up to c-axis direction. Since the distance of deposited boron nitride layer to layer is about 3.4Å, it is estimated that the boron nitride deposited at 900° and 1200°C is systematically piled up 14 and 45 layers, respectively.

Deposition rate of the films.—The deposition rate of the films is estimated from the x-ray diffraction peak area, because the diffraction peak intensity is proportional to the thickness of the film at constant diffraction condition. The relation between the diffraction peak intensity and the thickness of the films was obtained in advance. When the total flow rate is increased by addition of argon at a constant molar ratio of 50 and a temperature of 1000°C, the deposition rate increases steeply with increasing total flow rate because the amount of reactant species arriving at a substrate surface increases with increasing total flow rate. The reactant species arriving at the substrate surface are decreased by the dissipation of the reactants at the reactor wall.

The deposition rates of the films on the sapphire substrate at the constant molar ratio $NH_3/B(C_2H_5)_3$ = 30 increases from 0.025 μm/h at 750°C to 0.96 μm/h at 1000°C and then decreases steeply to 0.235 μm/h at 1100°C. At temperatures below 1000°C, the deposition rate increases with temperature because of surface reactions. At temperatures above 1000°C, the deposition rate decreases with temperature because of homogeneous reaction and the dissipation of the reactants at the reactor wall. White powder precipitated on the wall increases steeply above 1000°C.

Figure 5 shows the relation between the logarithm of the deposition rate and the reciprocal absolute temperature. We obtain an activation energy of 37.4 kcal/mol for the reaction in the temperature range below 1000°C. This value is larger than that of 20.4-25.6 (10) and 32.6 kcal/mol (11) obtained for the reaction of diborane with ammonia.

Composition of the films.—It is shown in Fig. 6 that the composition of the films deposited at 1000°C changes from N/B = 0.45 at $NH_3/B(C_2H_5)_3$ = 5 to 1.0 at 35, and then the composition is constant for the reactant gas molar ratio $NH_3/B(C_2H_5)_3$ > 35. Stoichiometric boron nitride deposits over this point.

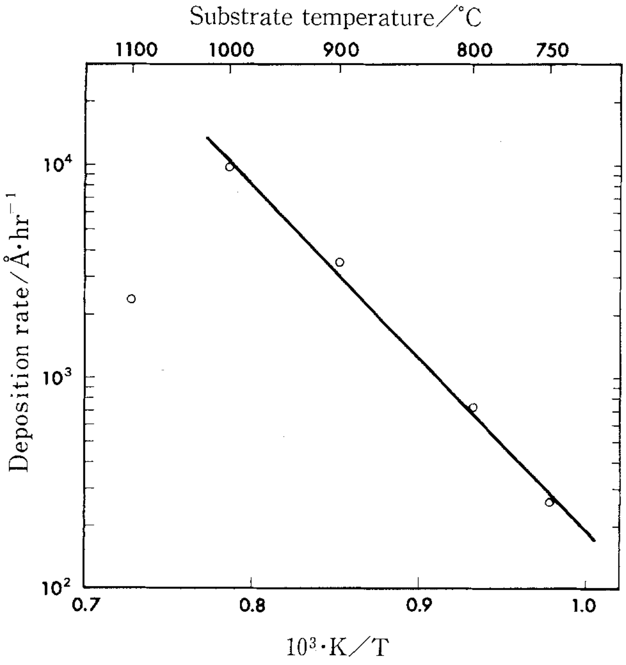

Fig. 5. Logarithm of the deposition rate as a function of reciprocal absolute reaction temperature.

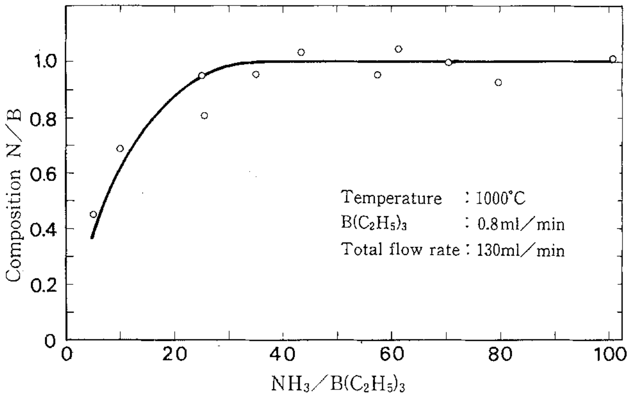

Fig. 6. Molar ratio NH_3/TEB dependence of the composition of the films deposited.

Coloration of the films depends on the molar ratio of the reactants. It is found from the results of the composition analysis that the coloration is caused by an excess of boron in the film.

Figure 7 shows the composition of the films deposited as a function of the growth temperature at the molar ratios 10 and 30. In the case of the molar ratio $NH_3/B(C_2H_5)_3$ = 10, the composition of the deposited films increases from 0.46 at 800°C to 0.75 at 950°C and then decreases slightly to 0.73 at 1200°C. The composition is less than 1.0 even at 1000°C, which is believed to be due to the small ammonia ratio.

While in the case of the molar ratio 30, the relation between the composition and the growth temperature have the same tendency as that with the ratio 10. However, the films deposited in the temperature range from 950° to 1000°C have the stoichiometric composition.

The increase of the composition with temperature below 950°C is based on the fact that the reaction of boron and nitrogen is accelerated. The decrease in composition above 1000°C can be explained because the deposition rate of boron decomposed from TEB exceeds the rate of combination with nitrogen or the effective ammonia is decreased by decomposition at the reactor wall.

Optical properties.—Figure 8 shows the transmission spectra in the wavelength range of 0.18-1.0 μm for the films deposited on sapphire substrates at various compositions. The spectrum varies from (a) to (d), corresponding to the composition 0.4, 0.6, 0.8, and 1.0 of the films, respectively.

The adsorption coefficient, α, near the absorption edge for the direct allowed transition can be described as a function of photon energy, $h\nu$

$$\alpha h\nu \propto (h\nu - E_g)^{1/2}$$

where E_g is the optical bandgap energy. The variation of the square of absorption coefficients multiplied by pho-

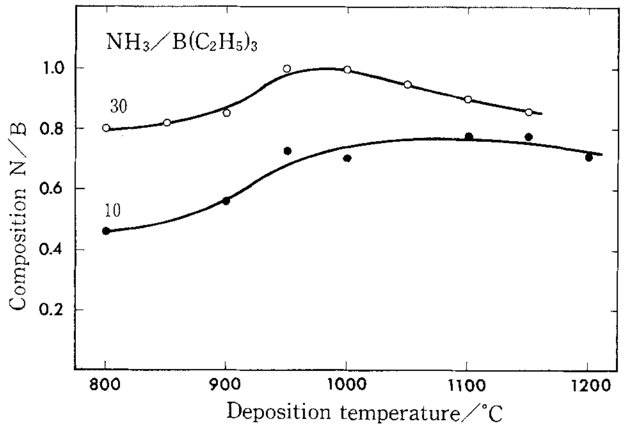

Fig. 7. Composition of the boron nitride films deposited at the molar ratios 10 and 30 as a function of the deposition temperature.

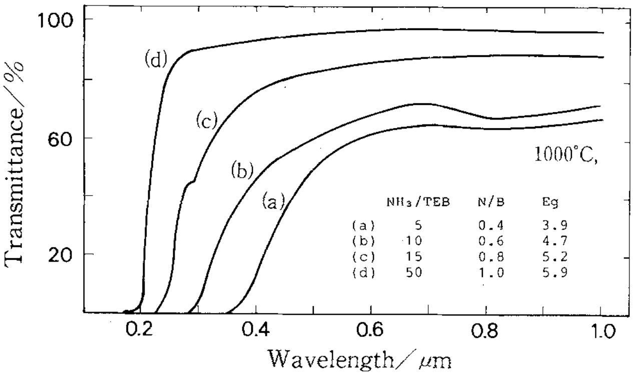

Fig. 8. Transmission spectra of the boron nitride films deposited at various conditions. (a) to (b) corresponding to the composition 0.4, 0.6, 0.8, and 1.0, respectively.

ton energy, $(\alpha h\nu)^2$, of the boron nitride films deposited at $NH_3/B(C_2H_5)_3$ = 20 and 1000°C with incident photon energy is shown in Fig. 9. The figure shows that the boron nitride is a semiconductor having a direct energy bandgap. The energy gap, E_g, is estimated to be 5.90 eV by extrapolation of the linear part to the horizontal axis in the figure. This value is in good agreement with the value reported recently by Nakamura (8).

Infrared transmission and reflection spectra of a film 5 μm thick are shown in Fig. 10. The figure shows that the reststrahlen band lies in the frequency range between 1600 and 1300 cm^{-1}. This band corresponds to in plane vibration of boron nitride (12). The absorption at 780 cm^{-1} corresponds to an out of plane vibration (12). The oscillations of the spectra in Fig. 10 are due to interference effect in the film.

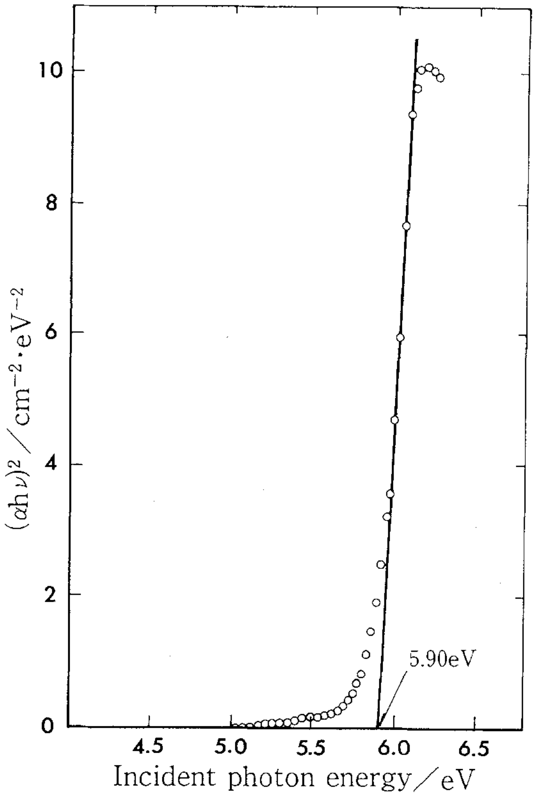

Fig. 9. Absorption edge fitted to direct allowed transition

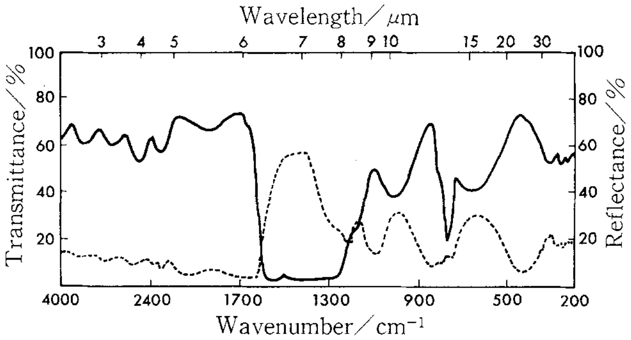

Fig. 10. Infrared transmission and reflection spectra of boron nitride films deposited on Si.

Conclusion

It is shown that MOCVD is a useful method for the deposition of boron nitride films. Colorless and transparent films were obtained by MOCVD at temperatures between 950° and 1100°C and at $NH_3/B(C_2H_5)_3$ ratios between 20 and 70. Growth rates show an Arrhenius-type behavior in the temperature range (750°-1000°C), and the activation energy was 37.4 kcal/mol. The maximum growth rate was 0.96 μm/h at 1000°C.

From the x-ray diffraction analysis, it is found that the crystal structure of the deposited films is hexagonal and the lattice constant of the film deposited at 1200°C is 6.73Å. The composition, N/B, of the films changes from 0.46 to 1.0. No carbon impurities in the film were detected by EPMA. The optical bandgap of the films having stoichiometric composition was estimated to be 5.90 eV.
eV.

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