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Preparation of SiBN films deposited by MOCVD

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Abstract

SiBN films were prepared by the MOCVD method using triethylsilane and triethylboron as source materials. The SiBN films were a mixture of boron nitride and silicon nitride determined by IR spectra. The relationship between the ratio of mixture and the preparation condition is clarified. The ratio of silicon nitride to boron nitride in the films was proportional to the ratio of triethylsilane to triethylboron under a large excess of ammonia flow condition. The reaction temperature also influenced the ratio of boron nitride and silicon nitride in the films. The deposition rate of the film increased up to 800°C with a maximum at 1000°C, and decreased up to 1300°C with small value. The crystallinity of SiBN films was very poor because the crystal growth was obstructed.
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1. Introduction

SiBN composite is expected to be useful for large thermal shock resistance material [1]. Bulk SiBN has been studied [2], but research papers on SiBN thin films are few. Boron nitride films have been prepared by MOCVD using triethylboron (TEB) as boron source [3]. Silicon was added into boron nitride films to improve the properties of boron nitride. The films deposited in an entire range of composition from boron nitride to silicon nitride. This concept led to investigations of a new composite, including additional elements to design multicomponent materials with attractive properties.

In the case of deposition of a mixture of BN and SiN, it is necessary to clarify the relationship between preparation conditions and the ratios of BN to SiN in the films.

We have prepared the films by the MOCVD method using TEB and triethylsilane (TES) as source materials to characterize them.

2. Experiment

SiBN films were prepared by MOCVD using the reaction of TEB $((C_2H_5)_3B)$, and TES $((C_2H_5)_3SiH)$,

with ammonia. The chemical properties of two source materials are summarized in Table 1. The apparatus for deposition of SiBN films constructed from a fused quartz reaction tube has an inside diameter of 46 and is 500 mm long. High-resistivity silicon ($12 \times 12 \times 0.5$ mm^3, >1000 Ω cm, (100)) and magnesium oxide ($5 \times 5 \times 0.5$ mm^3) were used as substrates for deposition and EPMA sample, respectively. Substrates were placed on the graphite susceptor with a slope of 30° from horizon and heated by a RF induction furnace with a 400 kHz, 15 kW generator. Chemical bonding characteristics, crystal structure and composition of the films deposited were analyzed by FT-IR, XRD and EPMA, respectively. Experimental conditions for the preparation of SiBN films are summarized in Table 2.

3. Results and discussion

Fig. 1 shows the XRD pattern of the films deposited at TEB flow rate 3 mL/min, NH$_3$ = 78 mL/min, reaction temperature 1300°C and reaction time 180 min.

Diffraction peaks at $2\theta = 26.16$ ($d = 3.4036$ Å) and $2\theta = 63.65$ ($d = 1.7069$ Å) correspond to the (002) plane and (004) planes of hexagonal boron nitride crystal, respectively, indicating the growth direction of the c-axis.

Fig. 2 shows the XRD pattern of the films deposited at TEB flow rate 3 mL/min, TES = 3 mL/min,

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$NH_3 = 78$ mL/min, reaction temperature 1200°C and reaction time 180 min. Diffraction peaks at $2\theta = 26.20$ ($d = 3.3985$ Å) and $2\theta = 34.0$ ($d = 2.6346$ Å) correspond to the (002) plane of hexagonal boron nitride and the (101), (210) planes of hexagonal silicon nitride crystal (βSi_3N_4), respectively. The peak at $2\theta = 33.0$ ($d = 2.71$ Å) corresponds to diffraction from Si substrate. The results of XRD for SiBN films of the mixture show a broad diffraction pattern (Fig. 2) with low crystallinity.

Table 1
Properties of source materials

	Triethylsilicon (TES)	Triethylboron (TEB)
Molecular formula	$(C_2H_5)_3SiH$	$(C_2H_5)_3B$
Molecular weight	116.3	98
Melting point (°C)		−92.9
Boiling point (°C)	109	95
Density (g/cm^3)	0.751	0.6961
Vapor pressure (Torr)	7.5	12.5

Table 2
Experimental conditions for the preparation of SiBN films

TES flow rate (mL/min)	0.3–6.0
TEB flow rate (mL/min)	0.5–5.0
NH$_3$ flow rate (mL/min)	78
TES/TEB	0.1–10.0
Reaction temperature (°C)	700–1300

Fig. 3 shows the temperature dependency of the deposition rate of the films deposited at TES and TEB flow rate 3 mL/min, $NH_3 = 150$ mL/min for the reaction temperature range from 700°C to 1200°C. The deposition rate steeply increases from 700°C to 900°C and has a maximum at 900°C. The deposition rate decreases from 900°C to 1200°C. The increase of deposition rate in the range from 700°C to 900°C would be caused by the rate-limited reaction and the steep decrease of deposition rate above 900°C is caused by the decrease of residence time and sticking probability of the source gases onto the substrate surface.

Fig. 4 shows the deposition rate of the films as a function of the flow rate of TES at a constant flow rate of TEB 3 mL/min, NH_3 150 mL/min, and a temperature of 1000°C. The deposition rate of the films increases from 0.05 to 0.09 mm with a flow rate of TES from 1 to 5 mL/min.

Fig. 5 shows the deposition rate of the films as a function of the flow rate of TEB at a constant flow rate of TES 1 mL/min, NH_3 150 mL/min, and a temperature of 1000°C.

The deposition rate of the films increases from 0.25 to 1.15 mm with the flow rate of TES from 1 to 5 mL/min. Figs. 5 and 6 show a similar tendency, i.e., the deposition rate increased in proportion to the increasing source gasses.

Fig. 6 shows the deposition rate of the films as a function of the flow rate of NH_3 (in the range from 10 to
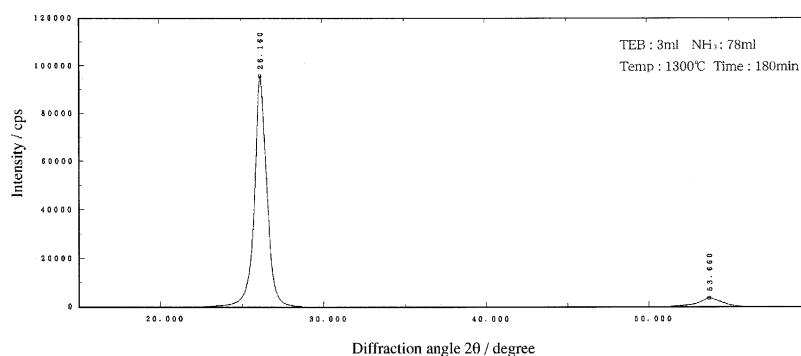

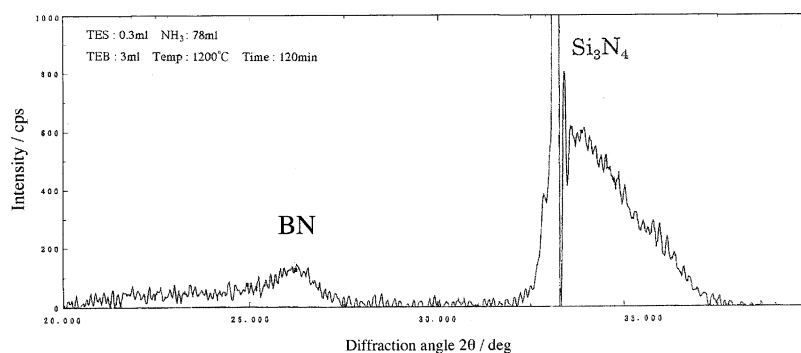Fig. 1. X-ray diffraction pattern of deposited boron nitride film.

Fig. 2. X-ray diffraction pattern of deposited silicon boron nitride film.

200 mL/min) at a constant flow rate of TES and TEB of 3 mL/min, respectively, and a temperature of 1000°C. The decrease of deposition rate with increasing ammonia flow rate would be caused by the inhibition of decomposition for TEB and TES.

Fig. 7 shows the transmission IR spectrum of the films deposited at TES flow rate 1.0 mL/min, TEB flow rate 0.5 mL/min, NH_3 78 mL/min, and a temperature of 1200°C in a time of 120 min. Absorption at 1380 and
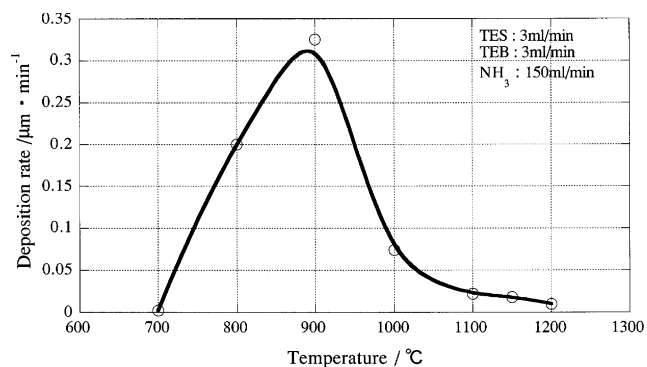
900 cm^{-1} in the spectrum corresponds to the B–N bond [3] and Si–N bond [4] respectively.

Fig. 8 shows the reflection IR spectrum (diffuse reflection spectroscopy by the Kubelka–Munk method) of the films deposited at TES flow rate 3.0 mL/min,

Fig. 3. Deposition rate of silicon boron nitride films as a function of deposition temperature.
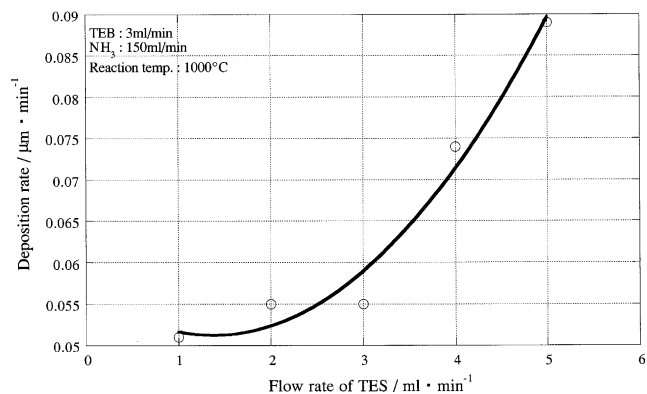

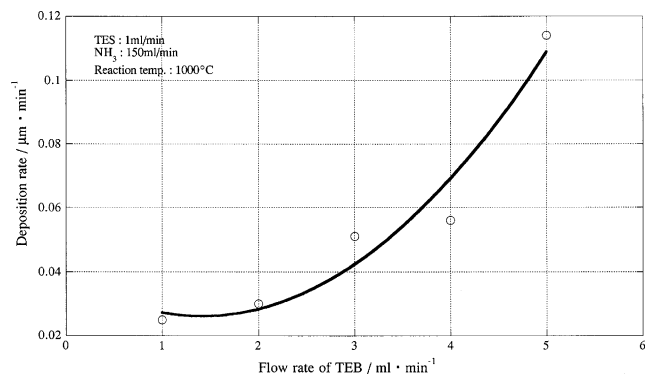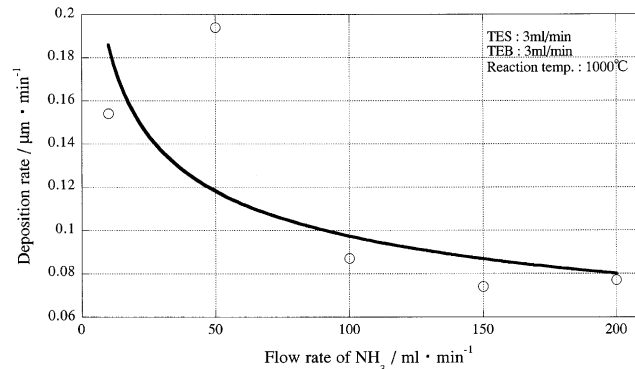Fig. 4. Deposition rate of silicon boron nitride films as a function of TES flow rate.

Fig. 5. Deposition rate of silicon boron nitride films as a function of TEB flow rate.

Fig. 6. Deposition rate of silicon boron nitride films as a function of NH_3 flow rate.
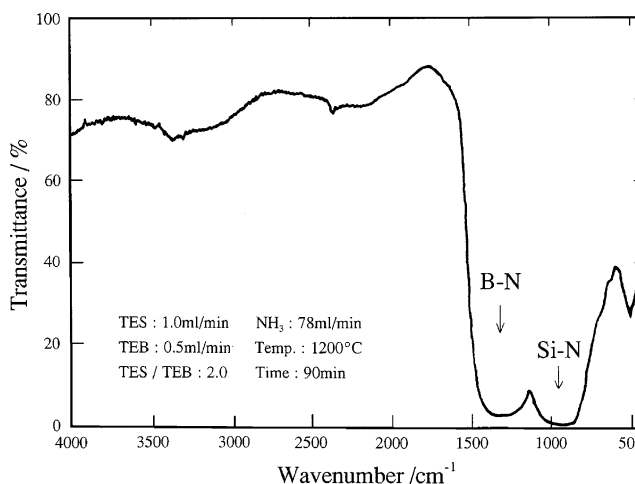

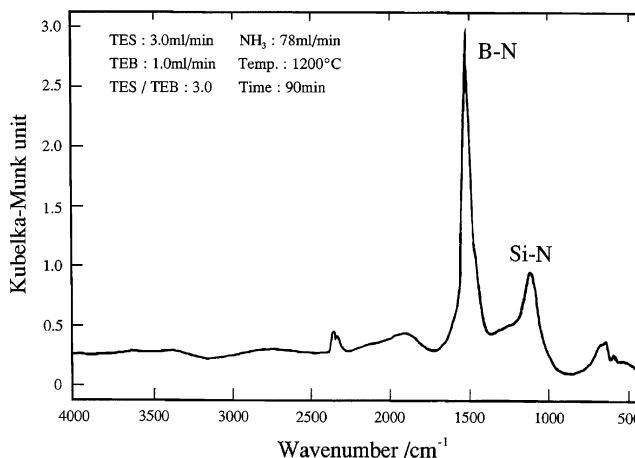Fig. 7. FT-IR transmission spectrum of silicon boron nitride film.

Fig. 8. FT-IR diffuse reflection spectrum of silicon boron nitride film.

TEB 1.0 mL/min, NH_3 78 mL/min, and a temperature of 1200°C in a time of 90 min.

Reflection peaks at 1510 and 1150 cm^{-1} in the spectrum correspond to the B–N bond and Si–N bond, respectively. The absorption peak of the B–N bond shifts to 1510 from 1580 cm^{-1} and that of Si–N bond shifts to 1150 from 1250 cm^{-1} in comparison with BN and Si_3N_4 only. This shows that the mixing of BN and Si_3N_4 weakens the strength of Si–N and B–N bonds.

The absorbance intensity ratio of I_{BN} to I_{SiN} on the films deposited by a constant flow rate of TES = 3 mL/min, TEB = 3 mL/min and NH_3 = 150 mL/min is shown in Fig. 9 as a function of reaction temperature in the range from 800°C to 1200°C. The reaction temperature produces an increase in the ratio of BN in the films.

Fig. 10 shows the absorbance ratio of I_{BN} to I_{SiN} corresponding to B–N and Si–N bond on the films deposited by a constant flow rate of TES = 1 mL/min and a reaction temperature of 1000°C as a function of flow rate of TEB in the range from 1 to 5 mL/min.

It is seen from the figure that the B–N bond in the films is increased by increasing TEB flow rate, and fixing a constant ratio of the B–N/Si–N bond for a TEB flow rate of more than 3 mL/min. This tendency is seen in a case of increasing TEB flow rate at a constant TES flow rate. Deposition of BN or SiN is obstructed with each other at a large flow rate ratio of TES/TEB or TEB/ TES, respectively. The ratio of the Si–N bond to B–N bond is not affected so much by increasing NH_3 flow rate at a constant TES and TEB flow rate and reaction temperature.

The composition of films deposited at constant reaction temperature 1200°C and NH_3 150 ml/min analyzed by EPMA are shown in Fig. 11 as a function of TES flow rate ratio to TEB flow rate, which is not corrected by the SiBN standard sample. The composition of films is shown as a relative value with characterized X-ray intensities of Si, B and N. Silicon and nitrogen increase and boron decreases with an increasing ratio of TES to TEB. However, Si, B and N become constant over a certain value of flow rate ratio. This tendency is also observed in the case of 1000°C. It
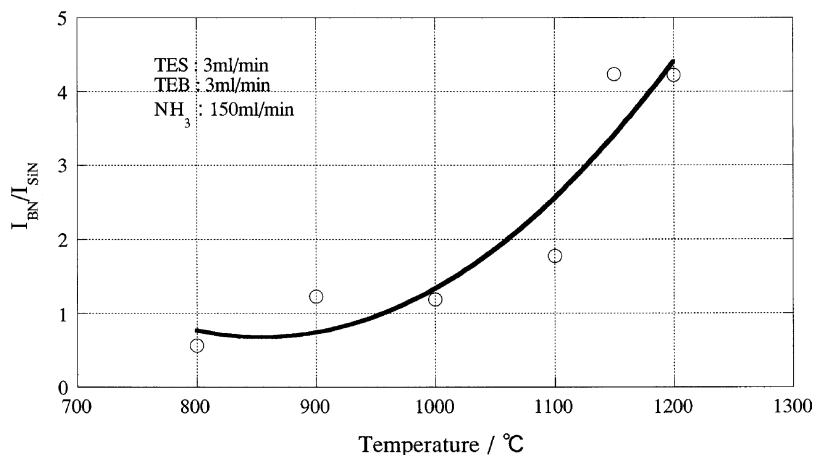

Fig. 9. Absorbance intensity ratio of I_{BN} to I_{SiN} on films deposited as a function of reaction temperature.
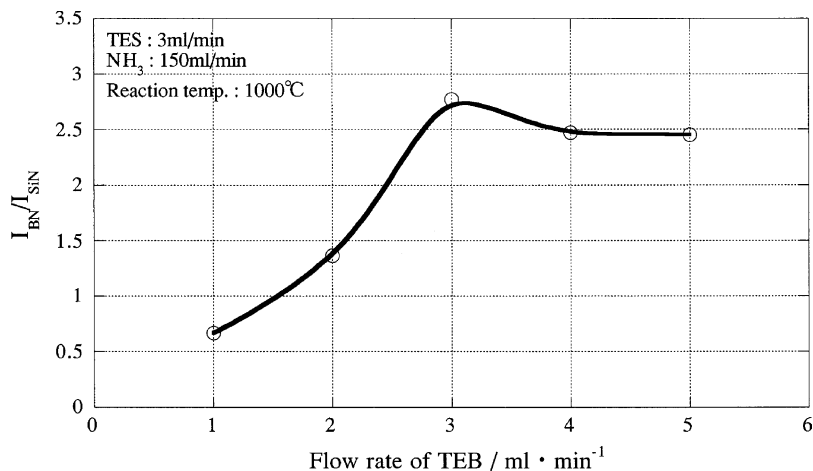

Fig. 10. Absorbance intensity ratio of I_{BN} to I_{SiN} on films deposited as a function of TEB flow rate.
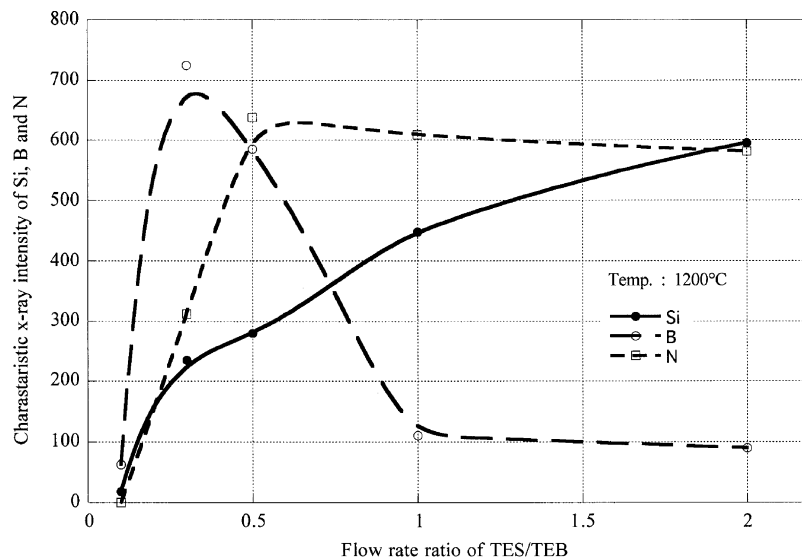
Fig. 11. Characteristic X ray of silicon, boron and nitrogen included in the films deposited as a function of source gas flow rate ratio of TES/TEB.

is found from these results that increasing the source materials increases the respective nitride in films. However, at a flow rate ratio over 1.0, the ratio of two nitrides in the films becomes constant, although the reaction mechanism is not clear, and a large supply of source gases disturbs the deposition of film.

From the XRD results, it is obvious that two nitride simultaneous depositions have large influences on the crystal growth of silicon nitride and boron nitride. This phenomenon also affects the deposition of films; either nitride in the films deposits abundantly by increasing one of the two sources and the amount of other nitride deposition decreases.

with ammonia flow rate. The deposited films were a mixture of boron nitride and silicon nitride from the IR spectra. From the results of EPMA, in the relationship of the quantities of boron, silicon and nitrogen including films to the flow rate ratio of TES/TEB, the silicon and nitrogen were increased and the boron was decreased with increasing TES flow rate. SiBN films that are a mixture of boron nitride and silicon nitride and had very poor crystallinity were prepared. This result will lead to investigations of new preceramic polymer films, including additional elements to design novel multicomponent composites with attractive properties.

4. Conclusion

Crystalline boron nitride film was obtained by the reaction of TEB with ammonia. However, the crystallinity of the boron nitride and silicon nitride mixture film was very poor. The deposition rate of the films increases with increasing TES and TEB flow rate, and decreases

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