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Synthesis of boron carbonitride (BCN) films by plasma-enhanced chemical vapor deposition using trimethylamine borane as a molecular precursor

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ABSTRACT

Boron carbonitride (BCN) films were deposited on Si substrates by plasma-enhanced chemical vapor deposition (PECVD) using a powdered precursor of trimethylamine borane ($C_3H_{12}NB$). The effect of using different carrier gasses and microwave powers was investigated. Field emission scanning electron microscopy (FE-SEM) revealed that the films have a nanofibrous structure with elongated features 20 nm in diameter and 200 nm in length. Fourier transfer infrared (FT-IR) spectroscopy was used to investigate chemical bonding states present in the deposited films. The FT-IR results suggested that the films have multiple chemical bonding states including C–N, B–N, and B–C bonds, as well as oxygen incorporation in the form of B–O bonds. Mixing the powdered precursor with molecular sieve was found to reduce the oxygen content in the films by removing surface adsorbed water from the precursor.

1. Introduction

Boron carbonitride (BCN) films have recently attracted much attention owing to their promising mechanical, optical, and electronic properties. In the ternary BCN system, there are several industrially important phases such as diamond, graphite, boron carbide (B_4C), boron nitride (BN), and carbon nitride (C_3N_4). Among these covalently bonded materials, diamond, cubic boron nitride (c-BN), and B_4C are the hardest known materials on earth. Graphite and hexagonal boron nitride (h-BN) have layered structures and are also important industrial materials. The former is widely used for electrodes in lithium ion batteries, as a toughening agent in steel, and as a component in high-strength composites, while the later is used in electronic insulators, lubricants, and refractories. Hence, hybridization of boron, carbon, and nitrogen with a controlled composition has been expected to produce new materials with multi-functional properties.

Hybridized BCN films with a variety of compositions have been prepared by chemical vapor deposition (CVD) [1–9], magnetron sputtering [10], ion beam assisted deposition [11], and pulsed laser ablation [12]. Plasma-enhanced chemical vapor deposition (PECVD) has proven to be particularly useful for preparing BCN films. In the CVD processes, molecular precursors such as dimethylamine borane ($C_2H_{10}NB$) [5,6], N,N′,N″-trimethylborazine ($(CH_3)_3N_3B_3H_3$) [7,8], (N-pyrrolidino)diethylborane ($C_8H_{18}BN$) [7], triethylamine borane ($C_6H_{18}NB$) [8], pyridine-borane ($C_5H_5NBH_3$) [9], and triazaborabicyclodecane ($BN_3H_2(CH_2)_6$) [9] have been used as boron, carbon, and nitrogen sources. These liquid molecular precursors are easier to handle than toxic and hazardous gaseous precursors such as B_2H_6 and BCl_3 [1–4]. However, when using such organic precursors, it is difficult to control the compositions of deposited films and prevent the incorporation of oxygen impurities [6,7,9]. The oxygen incorporation has frequently been observed for CVD methods owing to the high reactivity of boron with oxygen [1,2,4].

In this study, we deposited BCN films on Si substrates using a microwave PECVD process with a powdered precursor of trimethylamine borane ($C_3H_{12}NB$; melting point: 94 °C, boiling point: 172 °C). We examined the effects of the deposition conditions, including microwave power and carrier gas, on the film properties. Film composition, chemical bonding state, and morphology were analyzed using X-ray photoelectron spectroscopy (XPS), Fourier transfer infrared spectroscopy (FT-IR), and Field emission scanning electron microscopy (FE-SEM).

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2. Experimental

BCN films were deposited on Si (100) substrates (1 cm^2) by plasma-enhanced chemical vapor deposition (PECVD). A schematic of the microwave PECVD reactor used for the deposition is shown in Fig. 1. The reaction chamber consists of a quartz tube with a length of 420 mm and an inner diameter of 46 mm that is sealed with stainless steel flanges at either end. Silicon substrates were treated with HF, washed with acetone for 10 min under ultrasonic irradiation, and dried using a stream of nitrogen. The deposition time varied between 0.5 and 2 h with microwave powers of 200, 300, and 400 W (2.45 GHz). Substrate temperatures depended on the microwave power applied and ranged between 700 and 900 °C, measured *in situ* with an optical pyrometer (Model IR-U, CHINO).

Trimethylamine borane (TMAB; $C_3H_{12}NB$) powder (97%, Wako Pure Chemical Industries, LTD.) was put in a quartz crucible hung from the ceiling of the reactor and vaporized by plasma heating. The vaporization rate of TMAB was estimated from its weight loss and controlled by varying the distance of the crucible from the plasma. In this study, the distance was set to 20 cm. In some cases, TMAB was mixed with molecular sieve 5A pellets (1.6 mm diameter) (WAKO Pure Chemical Industries, LTD.) in a 1:1 weight ratio. The mixed precursor was put in the crucible to prevent water adsorbed on TMAB from entering the reaction system during deposition. Pellets of molecular sieve were treated at 500 °C prior to use in order to remove adsorbed water and gaseous molecules such as CO_2. N_2 and a gas mixture of CH_4 (10%) and H_2 (90%) were used as carrier gases. The experimental conditions used in this study are summarized in Table 1.

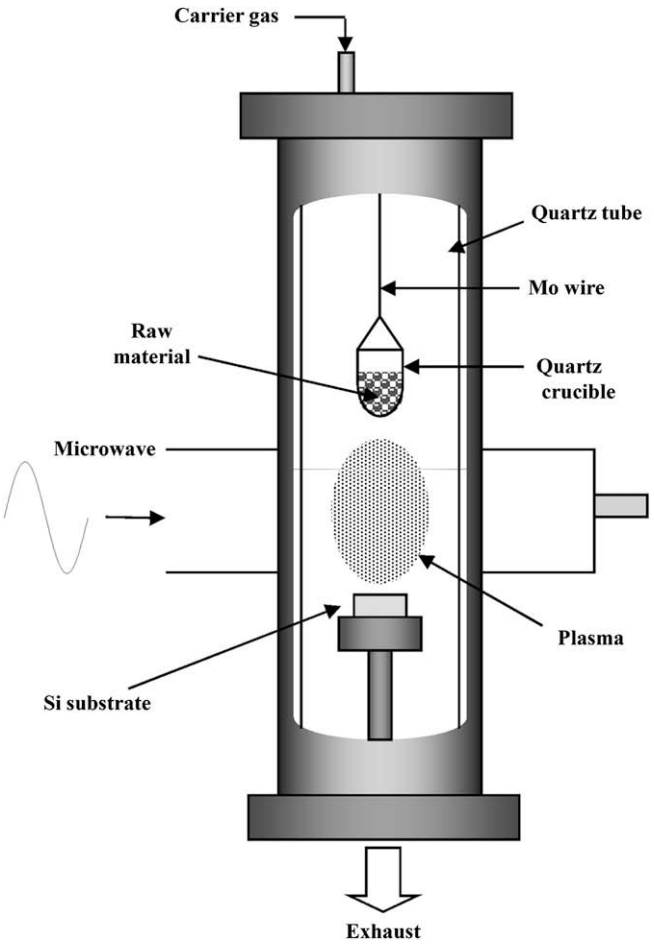

Fig. 1. Schematic of the microwave PECVD reactor used for the deposition of BCN films.

Compositions of the deposited films were analyzed by X-ray photoelectron spectroscopy (XPS; PHI 5800, Physical Electronics). To remove surface contaminates, the films were sputtered with Ar^+ prior to analyses. Fourier transfer infrared (FT-IR) spectra of the deposited films were measured using a spectrometer (Spectrum 2000, Perkin Elmer). A field emission scanning electron microscope (FE-SEM JSM-6700 FSS, JEOL) was used to observe morphologies of the deposited films. Film thicknesses were measured using FE-SEM observations.

3. Results and discussion

Fig. 2 shows the surface FE-SEM images of the BCN films deposited under different conditions. At low magnification, films appear to be uniformly deposited. However, at a higher magnification (see Fig. 2, insets) the fibrous structure of the films is observed. This microstructure differs from the layered structure characteristic of pyrolytic h-BN and graphite. In particular, using N_2 as a carrier gas at 400 W, the film consists of nanofibers 20 nm in diameter and 200 nm in length (shown in Fig. 2 (c)). A similar nanostructure has been observed previously for BN nanotubes prepared by CVD processes [13,14]. From cross-sectional FE-SEM images, the thicknesses of the deposited films were found to range between 0.7 and 5 μm, strongly depending on the deposition conditions (shown in Table 2).

Next, we used FT-IR and XPS to investigate the effects of microwave power on the chemical bonding states and compositions of the deposited films. The deposited films were found to be amorphous under X-ray. Fig. 3 shows a representative wide-scan XPS spectrum of a BCN film deposited at 300 W. The chemical compositions of the deposited films were determined using XPS spectra and the results are summarized in Table 2. Results revealed that the deposited films contain a large amount of oxygen. Fig. 4 (a) shows the FT-IR spectrum of a BCN film deposited from TMAB/N_2 at a microwave power of 200 W. A weak peak near 1100 cm^{-1} can be attributed to B–C bonding [15] and the two intense absorption bands near 1400 and 800 cm^{-1} correspond to B–N stretching and B–N–B bending, respectively [16]. In contrast, as shown in Fig. 4 (b), for a film prepared at 300 W, the B–N band was broadened and absorption bands near 1550 and 1250 cm^{-1}, ascribable to sp^2 C–N and sp^3 C–N bonds, became prominent [17]. In addition, absorption peaks at 650 and 1200 cm^{-1}, corresponding to B–O stretching and B–O–B bending, disappeared [18]. The decrease in oxygen content and the increase in nitrogen content in the film deposited at 300 W, as compared to the film deposited at 200 W (sample A), were confirmed by XPS compositional analyses (Table 2, sample B). This trend was further exaggerated when a film was deposited at a higher microwave power of 400 W; the oxygen content decreased further and the nitrogen content increased (sample C). In addition, the only FT-IR peaks visible were those originating from B–N and sp^3 C–N bonds (Fig. 4 (c)). This suggests that the increased nitrogen

Table 1
Experimental conditions employed for the deposition of BCN films.

No.	Microwave power (W)	Carrier gas	Substrate temperature (°C)	Gas flow rate (sccm)	Reaction pressure (Torr)	Reaction time (h)
1	200	N_2	810	80	20	2
2	300	N_2	850	80	20	1
3	400	N_2	940	80	20	0.5
4	300	CH_4–H_2	700	80	20	1