

# Formation of thick cubic boron nitride films in noble gases

Tetsutaro OHORI,<sup>†</sup> Hiroki ASAMI, Jun SHIRAHATA, Tsuneo SUZUKI, Tadachika NAKAYAMA,  
Hisayuki SUEMATSU and Koichi NIIHARA

Extreme Energy-Density Research Institute, Nagaoka University of Technology, 1603-1, Kamitomioka, Nagaoka 940-2188

**A radio frequency magnetron sputtering method, specifically tailored for the deposition of thick, adherent cubic boron nitride (c-BN) thin films on silicon substrates, was developed. The surface morphology of the boron nitride thin films was changed by altering the noble gases (Kr, Ar, Ne, and He) in the chamber present during the sputtering. The sample prepared in the gas with He showed especially good adhesion. This method enabled us to grow a 1.7- $\mu\text{m}$ -thick c-BN thin film on a Si(100) substrate in only rare gases at a low temperature for the first time. Fourier transform infrared spectroscopy (FT-IR) indicated that the fraction of sp<sup>3</sup>-bonded BN in the thick films was above 60%.**

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## 1. Introduction

Cubic boron nitride (c-BN) thin films are known to exhibit high hardness, but they have not yet been produced with sufficient substrate adhesion for use in industrial applications. Their poor adhesion strength can be attributed in part to the growth of an amorphous, sp<sup>2</sup>-bonded boron nitride layer initially on the substrate, and also to the existence of a large residual compressive stress in the c-BN films.<sup>1)</sup> These features cause the thin films to peel off the substrates. Using various coating techniques, the thickness of the c-BN thin films formed that avoid this peeling-off has been limited to the range of 100–300 nm.<sup>2)</sup> At present, only eight research groups have reported preparation of c-BN thin films with micrometer-scale thickness. Among the groups, three groups produced thick c-BN films. Matsumoto and Zhang succeeded in the preparation of 20- $\mu\text{m}$ -thick c-BN thin films by DC jet plasma chemical vapor deposition (CVD),<sup>3)</sup> however, very high temperatures up to 1000°C and harmful boride gases were required. These conditions did not allow them to use substrates with transformation temperatures below 1000°C, including tool steel. Physical vapor deposition, which is a low temperature process to prepare c-BN thin films, was used in two studies. Bewilogua et al. were able to grow 2- $\mu\text{m}$  thin films using a B<sub>4</sub>C target with an inserted inter-layer by a sputtering technique.<sup>4)</sup> Ulrich et al. reported deposition of 2- to 3- $\mu\text{m}$ -thick c-BN thin films using additional O<sub>2</sub> gas.<sup>5)</sup> In these studies, additional elements were needed to improve adhesion strength and/or reduce internal stress. To the best of the authors' knowledge, no reports on low temperature deposition of thick c-BN films in noble gases have been reported thus far. The development of new deposition methods for the preparation of thick c-BN thin films remains a major challenge.

Ar has been commonly used as a sputtering gas because of its low cost and sputtering efficiency. Studies using other noble gases for preparation of c-BN thin films are limited in number. Kester et al. reported c-BN thin films prepared using Ar, Kr, and

Xe gases by ion beam assisted deposition.<sup>6)</sup> Although the use of He was reported by Andoh et al. using dual-ion vapor deposition (D-IVD)<sup>7)</sup> and Jensen et al. with radio-frequency sputtering,<sup>8)</sup> the effects of these gases were not well-described. It is therefore necessary to understand the effects of noble gases on c-BN deposition. In the present study, the effect of noble gas (Kr, Ar, Ne, and He) addition during sputtering has been investigated and is reported.

## 2. Experimental setup

The growth of the boron nitride thin films was carried out using radio-frequency magnetron sputtering as described previously.<sup>9)</sup> A sintered rectangular plate of hexagonal boron nitride with a size of 88 × 200 × 5 mm<sup>3</sup> and purity above 99.0% was used as a large-size target for deposition of the BN thin films. A single-crystal Si(100) wafer was cut into pieces with size of 25 × 25 mm<sup>2</sup> for use as substrates. Six substrates were placed in a line on a substrate holder. The substrate temperature was maintained at about 450°C, and the base pressure was kept below 1 × 10<sup>-3</sup> Pa using a rotary pump as well as a turbo-molecular pump. Deposition was conducted in a mixture of Ar gas and a noble gas. Since these gases have higher ionization potentials than that of Ar, the mixture was mandatory to maintain discharge. The noble gases were controlled to a flow rate between 45 to 50 sccm by a mass flowmeter. Typical processing parameters for the BN thin film preparation are listed in Table 1.

In the present study, the chemical bonding character of the deposited thin films was investigated by Fourier transform infrared spectroscopy (FT-IR: JASCO Co., FT/IR-4200). The raw absorption data were typically recorded for 50 scans from 4000 to 500 cm<sup>-1</sup> with a resolution of 4 cm<sup>-1</sup>, and were measured by transmission through both BN thin films and their substrates. The absorption spectra were obtained by subtracting the Si substrate background intensity from the original data and within one day after the deposition. The absorption band around 1080 cm<sup>-1</sup> was due to sp<sup>3</sup>-bonded boron nitride (c-BN),<sup>10)</sup> and those at 1380 and 780 cm<sup>-1</sup> were due to in-plane and out-of-plane vibration modes of sp<sup>2</sup>-bonded boron nitride (h-BN) respectively.<sup>11)</sup> sp<sup>3</sup> and sp<sup>2</sup> intensities of the FT-IR spectra are described as I<sub>sp3</sub> and I<sub>sp2</sub>,

<sup>†</sup> Corresponding author: T. Ohori; E-mail: t\_ohori@etigo.nagaokaut.ac.jp

Table 1. Experimental Conditions

	Pre-sputter process	Deposition process		
Target material	—	h-BN (over 99.0%)		
Process time [h]	0.33	8, 40		
Cathode power [W]	—	1000		
Substrate bias voltage [V]	-650	-100		
Ar gas flow rate [sccm]	400	50		
Noble gas flow rate [sccm]	—	Kr	Ar	Ne He
		50	50	45 45
Working pressure in deposition process [Pa]	0.04	0.08	0.09	0.08 0.10
Substrate temperature [°C]	~450			

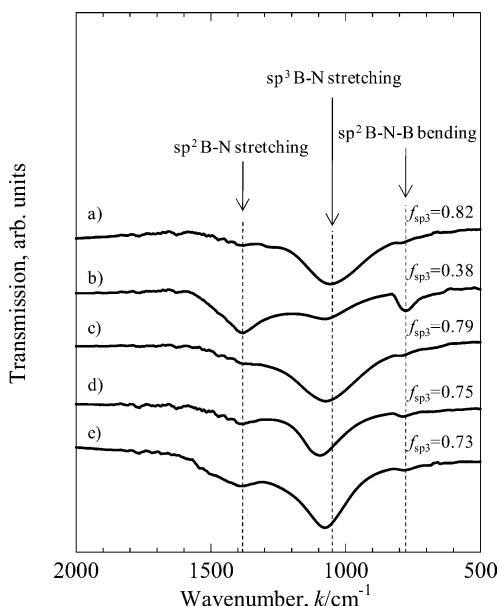


Fig. 1. FT-IR spectra of BN thin films deposited in various noble gases, (a) Ar, 50 sccm, 8 h (about 400 nm) deposition, (b) 50 sccm Ar + 50 sccm Kr, (c) 100 sccm Ar, (d) 50 sccm Ar + 45 sccm Ne, (e) 50 sccm Ar + 45 sccm He.

respectively. These were normalized using FT-IR intensities of the absorbance at approximately 1050–1100 and 1380  $\text{cm}^{-1}$ , and the  $\text{sp}^3$  fraction ( $f_{\text{sp}^3}$ ) was defined as  $f_{\text{sp}^3} = I_{\text{sp}^3}/(I_{\text{sp}^3} + I_{\text{sp}^2})$ . Microstructural observations of the film surface and cross-sections were carried out with a scanning electron microscope (SEM: JEOL Ltd., JSM6700F).

### 3. Results and discussion

FT-IR spectra of the BN thin films deposited in the presence of the various noble gases are shown in Fig. 1. The Ar gas flow rate was kept at 50 sccm. As shown in the top spectrum (Fig. 1(a)), an Ar gas flow rate of 50 sccm was sufficient to form  $\text{sp}^3$ -bonded BN. The noble gases were then added to the 50 sccm Ar gas flow. FT-IR spectra of the deposited thin films with additional noble gases are shown in Figs. 1(b)–(e). Plan-view SEM images of the thin films deposited in the noble gases are shown in Figs. 2(a)–(e). The samples presented in Figs. 1 and 2 are identical BN samples with thicknesses of about 400 nm. The sur-

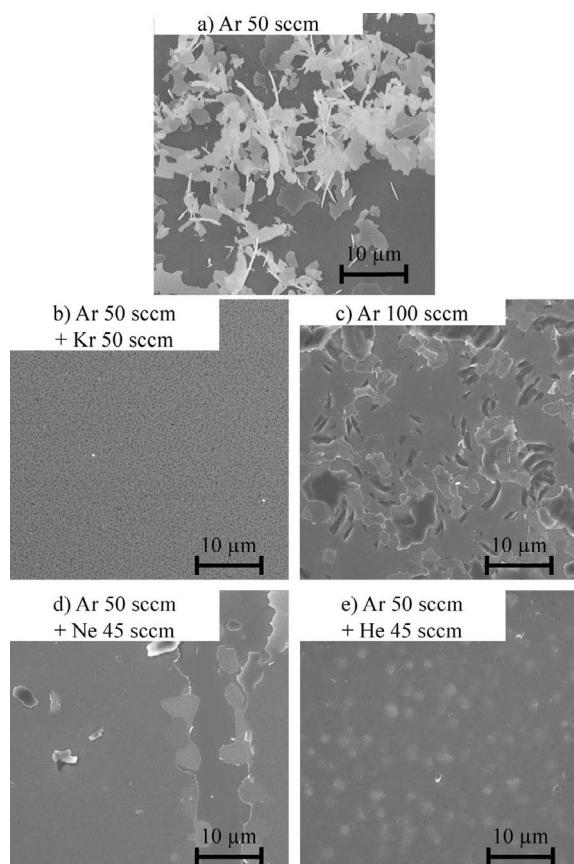


Fig. 2. Surface SEM images of BN thin films deposited in various noble gases. (a) Ar, 50 sccm, 8 h (about 400 nm) deposition, (b) 50 sccm Ar + 50 sccm Kr, (c) 100 sccm Ar, (d) 50 sccm Ar + 45 sccm Ne, (e) 50 sccm Ar + 45 sccm He.

faces of the BN thin films grown with Ar and Kr gas were smooth and the films did not peel off (Fig. 2(b)). However, the  $\text{sp}^3$  fraction was relatively low,  $f_{\text{sp}^3} = 38\%$ . It is well known that a sufficiently high ion energy is necessary for the formation of the  $\text{sp}^3$ -bonded BN phase.<sup>6,12)</sup> It has been reported that a higher energy was required for the transition of  $\text{sp}^2$  to  $\text{sp}^3$  in the case of Kr.<sup>6)</sup> The  $\text{sp}^3$  fraction of the thin films prepared with Ar gas in the present study at only 100 sccm was about 79%, and the degree of peeling off of the films (Fig. 2(c)) was the same as that for the thin films prepared with an Ar flow rate of 50 sccm. The sample made with Ar and Ne gas showed some peeling off, as seen in Fig. 2(d). The  $\text{sp}^3$  fraction was almost the same as that in the sample made only with Ar gas. The sample made using Ar and He did not show any peeling off, and the  $\text{sp}^3$  fraction in this case was 73%. These results show that the  $\text{sp}^3$  fraction and peeling off area decreased with decreasing atomic weight of the additional gases.

The sample made using Ar and He gas had no peeling off, as shown in Fig. 2(e). This preparation method using He gas was thus expected to enable the preparation of thick c-BN films. A cross-sectional SEM image of a 1.7- $\mu\text{m}$ -thick  $\text{sp}^3$ -bonded BN layer made with Ar and additional He gas of 45 sccm, deposited for 40 h is shown in Fig. 3. The formation of the  $\text{sp}^3$ -bonded phase of the BN thin films is evident in the FT-IR spectra, as shown in Fig. 4. The intensity of the peak around 1070  $\text{cm}^{-1}$  due to the  $\text{sp}^3$ -bonded BN was high. The oscillation from 2000 to 4000  $\text{cm}^{-1}$  was caused by interference depending on the c-BN

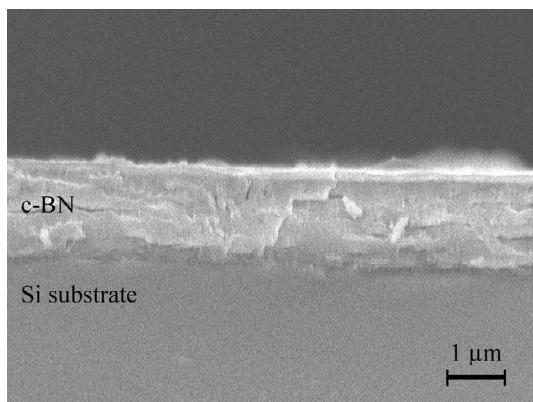


Fig. 3. Cross-sectional SEM image of a thick BN film deposited for 40 h in Ar and He gas.

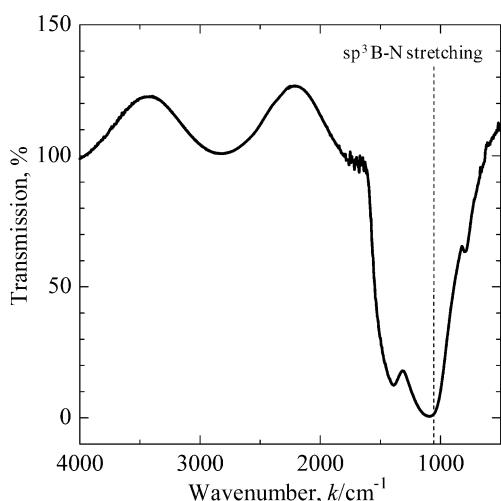


Fig. 4. FT-IR spectrum of BN film shown in Fig. 3.

film thickness.<sup>13)</sup>

There have been two prior successful reports on the preparation of c-BN thin films over 2  $\mu\text{m}$  deposited by sputtering methods, wherein adhesion was improved by adding an intermediate layer and a compositional gradient.<sup>4,5)</sup> In contrast, the present method can deposit c-BN thin films without an intermediate layer or a compositional gradient. He and other noble atoms used in the present study cannot directly improve the adhesion, as they are chemically inert. It was thus seen that the possibility of depositing thick c-BN thin films depends on a decrease in the residual stress. It is likely that the decreasing residual stress has a connection with the sputtering conditions used. One possible mechanism for synthesizing the cubic phase and decreasing residual stress, based on a thermal spike model by Weissmantel et al.<sup>14)</sup> and Mirkarimi et al.,<sup>15)</sup> is as follows. He is lighter than B and N atoms and with the bias voltage of -100 V, He ions

formed by sputtering are accelerated to 100 eV ( $\text{He}^+$ ) and 200 eV ( $\text{He}^{2+}$ ) incident to the BN thin film formed. Since the kinetic energies of He ions are comparable to the displacement energy of the diamond structure (~80 eV)<sup>16)</sup> and He ions are lighter than B and N atoms, displacement of atoms is not likely to occur. On the other hand, He ions can locally heat the atoms. This local heating can diffuse the atoms leading to decreased residual stress. However, the local heating volume is sufficiently small to prevent formation of h-BN seeds. This is the likely scenario of why a decrease in stress and preservation of c-BN in the thin film occurs simultaneously in the presence of He gas.

#### 4. Conclusions

Growth of c-BN films using magnetron sputtering in the presence of noble gases was achieved. Thick BN films deposited in an Ar + He gas flow had significantly reduced stress. This processing method achieved the preparation of high-quality cubic boron nitride thin films with a thickness of 1.7  $\mu\text{m}$ .

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