Rapid communication

The effects of dc bias voltage on the crystal size and crystal quality of cBN films

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Abstract. For the deposition of cubic boron nitride thin films in Ar $-N_2-BF_3-H_2$ system by dc jet plasma chemical vapor deposition, the role of dc substrate bias ranging from -70 Vto -150 V was investigated. A critical bias voltage was observed for the formation of cBN phase. The cBN content in the film increased with bias voltage and reached a maximum at the bias voltage of -85 V. Increasing the bias voltage further caused a decrease in cBN content and peeling of the films from the substrate. By combining the results of infrared spectroscopy, Raman spectroscopy and X-ray diffraction, the bias voltage was also found to strongly affect the crystal size, crystal quality and residual stress of the deposited films. A bias voltage a little higher than the critical value was demonstrated to be favorable for the deposition of a high-quality cBN film with large crystal size and low residual stress.

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Due to its unique properties, i.e., its hardness being second only to diamond, high thermal conductivity, chemical inertness, high refractive index and wide band gap in connection with *p*- and *n*-type dopability, cubic boron nitride (cBN) is an extremely promising material for applications in optical, electronic and mechanical techniques. During recent years, much effort has been put into improving the preparation of cBN films; different kinds of deposition methods including both physical vapor deposition (PVD) [1-7] and chemical vapor deposition [8-12] were developed. For all these methods, the production of energetic ions and the ion-bombardment of the substrate was found to play an important role in the formation of the cubic phase of boron nitride. By involving low-energy ion bombardment during film growth, the deposited cBN films generally exhibited high compressive stress, which was believed necessary in order to obtain the cubic phase [13-15]. This stress results in a restricted maximum film thickness (several hundred nanometers) while leading to the destruction of the cBN samples when the film was too thick. Litvinov et al. [16, 17] observed narrowing and downshifting of the characteristic infrared (IR) absorption of the cBN phase by reducing the bias voltage in a two-step process of ion-assisted sputtering, which suggested an improvement in film crystal quality as well as a decrease of stress with decreasing ion energy. A "thick" film (~ 2500 Å) with high cBN content was obtained by this method. It is, however, difficult to evaluate the crystal quality and stress of the thick cBN films (near or thicker than 1 μ m) by using only the IR technique. Therefore a combined study by means of IR spectroscopy, Raman spectroscopy and X-ray diffraction (XRD) were performed in this work to investigate the dependence of crystal size, crystal quality and stress of the cBN films on the negative substrate biases applied during the depositions.

The cBN films studied in this paper were deposited by dc jet plasma CVD which is well known as a successful method for the high-rate deposition of CVD diamond. In Ar, N₂ and BCl₃ gas systems, Bern et al. reported the deposition of cBN films in arc jet flows in low pressure (0.1 - 1 Torr) [18, 19]. In this report, the deposition of cBN films was performed in an $Ar-N_2-BF_3-H_2$ gas mixture where argon was used as a plasma gas, and nitrogen, boron fluoride and hydrogen were used as reactant gases. The experimental setup has been shown elsewhere [20]. (001) Silicon wafers of size $14 \times 14 \times$ 0.5 mm³ were used as substrates. Silicon substrate were prescratched with $5-10 \,\mu\text{m}$ diamond powders and then chemically cleaned with acetone, deionized water and ethanol, in succession, in an ultrasonic bath before deposition. The substrate was put on a water-cooled Mo/Cu substrate holder that can be dc biased. During deposition, an hBN cover was used to expose only the silicon substrate to the plasma and thus to concentrate the ion-bombardment on the substrates and to avoid the contamination of the samples from the substrate holder. The details of the experimental conditions are listed in Table 1. The substrate temperature was measured from the backside with a sapphire rod sensor and a glass fiber transmitting system (Optonico OT-100). After deposition, the phase composition, structure and crystal quality of the films were investigated by Fourier-transform infrared spectroscopy, glancing-angle XRD, scanning electron microscopy (SEM) and macro-Raman spectroscopy.

Figure 1 shows the IR spectra of the samples deposited under different substrate biases ranging from -70 V to -150 V. For the substrate bias voltage of -70 V (curve (a)),

Table 1. Experimental parameters for the deposition of cBN films by dc jet plasma CVD

Ar (slm)	20	
N_2 (slm)	1.5	
BF ₃ (sccm)	3	
H ₂ (sccm)	5	
Substrate tempreture (°C)	980	
Pressure (Torr)	50	
Bias voltage (V)	-70150	
Duration (min)	10	



Fig. 1. IR spectra of the films deposited under the substrate bias voltage of (a) -70, (b) -80, (c) -85, (d) -100 and (e) -150 V, respectively

only two intensive absorption bands at about 1380 and $780 \,\mathrm{cm}^{-1}$ were observed, which can be assigned to in-plane and out-of-plane TO modes of hBN, respectively. Increasing the substrate bias voltage to -80 V (curve (b)), an absorption band at about $1080 \,\mathrm{cm}^{-1}$ appeared, which can be assigned to the presence of cubic phase of boron nitride. The deviation of this absorption to the higher wave number from that of HPHT single-crystal cBN ($\sim 1065 \text{ cm}^{-1}$) is believed to be due to the compressive stress caused by ion bombardment. The cBN absorption dramatically increased with a small increase of the bias voltage and reached a maximum at $V_{\rm b} = -85$ V. The corresponding IR spectrum (curve (c)) shows a top-cut absorption band from about 1000 to 1200 cm^{-1} . The film thickness was observed to be $3.4 \,\mu m$ with SEM. In this case, it is not feasible to evaluate accurately the cBN content in the film by using the normal definition $(I_{1065}/(I_{1065}+I_{1370}))$, where I_{1065} and I_{1370} are IR absorption-integrated intensities of cBN and hBN TO modes at 1065 and 1370 cm⁻¹, respectively). Meanwhile, it is also difficult to evaluate the residual stress and crystal quality from the peak position and linewidth of such top-cut absorption band. Increasing the bias voltage further leads to the peeling of the films from the substrates just after the deposition. Meanwhile, the cBN content decreased and the cBN characteristic absorption became broad from the IR investigations (curve (d) and (e) for bias voltage of -100 and -150 V, respectively).

Figure 2 shows glancing-angle XRD patterns of the sample deposited under substrate biases ranging from -80 to -150 V. The incident X-ray angle α was set at 0.05° and the diffraction pattern was taken by 2θ continuous mode with a step width of 0.02°. For the sample deposited under -80 V, diffraction appeared for both cBN and hBN. When the the voltage was increased to -85 V, the diffraction for the cBN phase intensively increased. In agreement with the IR observations, the cBN diffraction became weak and broad at higher bias voltage of -100 and -150 V. The crystal size can be obtained from the diffraction patterns by using the well-known Sherrer's equation:

$$L_{hkl} = \frac{K\lambda}{\sqrt{(B^2 - b^2)\cos\theta}} \tag{1}$$

where K = 1, $\lambda = 1.5418$ Å, *B* and *b* are the half-maximum width of the diffraction peak and instrument, respectively. Furthermore, the strain ε_{ψ} was calculated from lattice distortion $(d_0 - d)/d_0$, as listed in Table 2. Assuming a biaxial stress and neglecting shear components in the film, the stress can be roughly estimated by using Hooke's law:

$$\sigma = \varepsilon_{\psi} E / (1 - \gamma), \tag{2}$$

where E = 833 GPa and $\gamma = 0.112$ [15]. To ensure the precision, we used the strongest 111 peak for the calculation of crystal size, and both 111 and the second strongest peak 220 for the calculation of stress. The calculated crystal sizes and stresses of the samples deposited under different substrate biases are summarized in Table 3. The tendency of the increase of stress and the decrease of crystal size with increasing bias voltage can be clearly seen. The small crystal size and high residual stress at higher bias voltages may be due to the excessive damage caused by ion bombardment. It should be noticed that the compressive stress of the sample deposited under -85 V is only 1.4 - 2.1 GPa, which is remarkably lower than that reported before. The effective decrease of stress allowed us to increase the film thickness. Figure 3 shows the SEM cross-sectional morphology of a cBN film deposited for 3 h under the substrate bias of -85 V. A columnar growth of



Fig. 2. XRD patterns of the films deposited under the substrate bias of (a) -80, (b) -85, (c) -100 and (d) -150 V, respectively

Table 2. The measured lattice spacing (*d*) of each cBN reflection of the sample deposited under different substrate bias compared with JCPDS-35-1365. The strain (ε_{ψ}) calculated from the lattice distortion for each reflection is also presented

	JCPDS 35-1365		Sample A ($V_{\rm b} = -80 \rm V)$	Sample B ($(V_{\rm b} = -85 \text{ V})$	Sample C (V	$V_{\rm b} = -100 \rm V$	Sample D ($V_{\rm b} = -150 \rm V$)
hkl	d_0 (Å)	I/I_0	d (Å)	I/I_0	d (Å)	ε_{ψ}	d (Å)	ε_ψ	d (Å)	ε_{ψ}
111	2.0872	100	2.0924	-0.0025	2.0920	-0.0023	2.0978	-0.0051	2.0983	-0.0053
200	1.8081	5	1.8111	-0.0017	1.8146	-0.0036	1.8149	-0.0038	1.8153	-0.0040
220	1.2786	24	1.2790	-0.0003	1.2805	0.0015	1.2832	-0.0036	1.2862	-0.0060
311	1.0900	8	1.0911	-0.0010	1.0914	-0.0012	1.0929	-0.00265	1.0893	0.0007

Table 3. Calculated stresses and crystal sizes for the samples deposited under different bias voltage. The crystal size was obtained from the strongest reflection 111, and the stress was obtained from 111 and the second strongest reflection 220

	Stress (GPa)	Crystal size L ₁₁₁ (Å)
Sample A ($V_{\rm b} = -80$ V)	0.3~2.3	129
Sample B ($V_b = -85$ V) Sample C ($V_b = -100$ V)	$1.4 \sim 2.1$ $3.4 \sim 5.0$	158 94
Sample D ($V_{\rm b} = -150$ V)	$5.0 \sim 5.6$	71



Fig. 3. SEM cross-sectional morphology of a film deposited for 3 h under the substrate bias of -85 V. XRD, IR and Raman measurements were used to identify it as a cBN film with a high cubic content

the film can be clearly seen. The film thickness was measured to be about $25 \,\mu$ m. The film shows good stability and no peeling was observed even after deposition for over nine months.

In this work, the effects of substrate bias voltage on the film quality were also investigated by macro-Raman spectroscopy. The laser spot size is about 200 μ m so that an overall contribution of phase composition and crystal quality could be obtained. Figure 4 shows Raman spectra of the samples deposited under different bias voltage. For the bias voltage of -80 V, a silicon vibration band from 900 to 1000 cm^{-1} and a peak at about 1367 cm^{-1} were observed. The latter is due to the hBN phonon mode ($2E_{2g}$), as marked in the figure. With an increase in the bias voltage to -85 V, two clear peaks located at about 1051.9 and 1302.4 cm⁻¹ appeared, which can be assigned to scattering by the TO and LO phonon modes of cBN. The TO and LO phonon modes of cBN shifted to a lower wave number by



Fig. 4. Raman spectra of the films deposited under the substrate bias of (a) -80, (b) -85, (c) -100 and (d) -150 V, respectively

about 4 and 2 cm^{-1} with respect to that of single-crystal cBN by HPHT (1056 and 1304 cm^{-1}) [21]. The shift of the TO and LO modes to the lower wave number has been reported to be due to the small grain size [21] The full-width at half maximum (FWHW) of TO and LO phonon modes is measured to be about 28.1 and 25.4 cm^{-1} , respectively. At a bias voltage of -100 V, the intensity of the hBN peak increased, and both cBN TO and LO modes became broad and moved more towards the lower wave number. Finally, when the bias voltage increased to -150 V, only weak and broad LO mode could be observed. It is known that, as the crystal quality is reduced or defects increase, the selection rules that allow only the near-zone-center phonons to be observed break down, leading to broadening and shifting of the peaks. Therefore, it can be concluded that highquality cBN films were deposited under a bias voltage of -85 V. As the bias voltage increased, the crystal size decreased and the defects in the films increased, demonstrating a decrease in the film quality. The Raman results show a good agreement with those obtained from IR and XRD measurements.

In conclusion, by combining XRD, IR and Raman spectroscopy, the effects of substrate bias voltage on the quality of the deposited cBN films, i.e., phase composition, residual stress, crystal size and quality, were systematically studied. It was found that the quality of the boron nitride films depended strongly on the bias voltage. A critical value for the formation of cubic phase was observed, which was found to be about -80 V in our experimental conditions. A bias voltage a little higher than this critical value is favorable for the deposition of cBN films with high cubic content, large crystal size and low stress. At this optimized bias voltage, the deposition of cBN films with a thickness over 25 μ m was demonstrated to be possible. Too high bias voltage led to the peeling of the films from the substrates and had negative effects on the film quality.

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