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Impact of low-energy ions on plasma deposition of cubic boron nitride

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ABSTRACT

Plasma deposition of cubic boron nitride (cBN) films under low-energy (a few eV to ~40 eV) ion impact with the chemistry of fluorine is studied in terms of ion energy, ion flux, and ion to boron flux ratio onto the substrate. The ion energy and the ion to boron flux ratio are determined from the sheath potential and the ratio of incident ion flux to net deposited boron flux, respectively. For negative substrate biases where a mixture of turbostratic and amorphous BN phases only or no deposit is formed, both the ion energy and the ion to boron flux ratio are high. For positive substrate biases where cBN phase is formed, the ion energy and the ion to boron flux ratio are in the range of a few eV to 35 eV and 100 to 130, respectively. The results indicate that the impact of positive ions with high ion to boron flux ratios makes a substantial contribution to the formation of cBN phase, while that of negative ions and electrons makes only a minor contribution.

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1. Introduction

Cubic boron nitride (cBN) has outstanding physical and chemical properties similar to diamond such as high hardness, high thermal conductivity, large band gap, and high breakdown field. Among the potential advantages of cBN over diamond is that cBN is chemically inert against ferrous materials and resistant to oxidation even at high temperatures up to ~1000 °C. cBN can be synthesized in the form of films from vapor phase. In the last two decades, research on cBN film synthesis has been put on a variety of physical vapor deposition (PVD) processes such as sputtering, ion beam deposition, ion beam assisted deposition, ion plating, and laser ablation rather than plasma-enhanced chemical vapor deposition (CVD) [1–3]. This is because dynamic effects of ion bombardment are necessary to deposit cBN films. The deposition conditions have often been characterized by total momentum transferred by bombarding ions per depositing boron atom [4]. The threshold energy of ion impact for cBN film deposition has been shown to decrease with increasing ion to depositing boron flux ratio [5]. An increase of ion to boron flux ratio was also shown to extend the temperature range for cBN phase formation to 1000 °C [6]. Experimental results have revealed that the threshold ion energy is typically 50 eV to a few hundreds of eV for sputtering and plasma CVD and more than a few hundreds of eV for ion beam deposition [1–3]. The resulting cBN films usually have low crystallinity (nanometer-sized grains), high residual compressive stress (10–20 GPa), and low adhesion to the underlying substrates. Most work has been concentrated on the solution of the stress/adhesion problem to obtain thick cBN films [7–11]. An exception is the use of single crystal diamond substrates to improve cBN crystallinity by accommodating different lattice constants and surface free energies of cBN and the substrate [12]. However, overcoming the above problems requires fundamental improvement of deposition techniques.

In the early 2000s, a marked progress in cBN film deposition was made by introduction of the chemistry of fluorine into the CVD process using a direct-current (dc) plasma jet. High-quality cBN films with micrometer-sized grains and low compressive stress were successfully deposited at high rates [13]. The role of fluorine has been argued as (i) preferential etching of sp^2-bonded BN phase consisting typically of turbostratic and amorphous BN (tBN and aBN) phases, leaving rigid cBN phase and (ii) stabilization of the growing cBN surfaces in the form of sp^3 bonding [14–16]. tBN has a hexagonal structure with distorted interplanar spacing. But the high gas pressure (6.7 kPa) and high substrate temperature (~1000 °C) conditions in dc plasma jet CVD may provide only limited applicability for electronic devices.

In our previous work, cBN films were deposited under low-energy ion bombardment (<40 eV) by low-pressure inductively coupled plasma (ICP)-enhanced CVD using the chemistry of fluorine [17]. The threshold ion energy and the substrate temperature were reduced to a few eV and ~730 °C, respectively. The resultant films consisted of micrometer-sized grains with crystallographic morphology and in-depth cBN fractions up to ~70 vol.% [18,19]. The low film stress (~4 GPa) enabled one to deposit thick cBN films directly on WC-Co [20,21]. The great reduction

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in ion energy was attributed to a high ion to boron flux ratio, however, it has not been verified quantitatively.

In this paper, the deposition mechanism of cBN films in our ICP is examined in terms of ion energy, ion flux, and ion to boron flux ratio onto the substrate. The results are compared with other deposition techniques with and without the chemistry of fluorine.

2. Experiment

A schematic of the ICP-CVD apparatus and the electrical circuit is shown in Fig. 1. BN films were deposited in the high-density source region of the ICP with a three-turn helical copper coil wound around a water-cooled silica glass tube. Inside the silica tube, a sintered BN tube 45 mm in inside diameter was suspended to suppress both impurities from the silica tube and capacitive coupling between the coil and the plasma [22]. Top and bottom ends of the ICP source were sealed with a grounded flange and a grounded diffusion chamber, respectively. Prior to deposition, $11 \times 11 \times 0.5$ mm^3 n-type Si(100) substrates were cleaned ultrasonically in ethanol, dipped in a HF solution to remove the native oxide layer, and rinsed in ethanol. The substrate was then loaded on a Mo holder and covered with a sintered BN frame cover. The actual coating area exposed to the plasma was about 10 mm in diameter. A gas mixture of He, N_2, H_2, and BF_3 at flow rates of 96.2, 10.0, 10.0, and 1.8 sccm, respectively, was introduced through mass flow controllers. BF_3 was pre-mixed at the dilution rate of 10 vol.% in He. The radio-frequency (rf) plasma power at 13.56 MHz and total pressure were kept at 1.0 kW and 40 Pa. The substrate was heated by plasma without a heater and its temperature measured with an infrared pyrometer was about 730 °C. The temperature variation was estimated to be within ±20 °C.

The electron (ion) density near the substrate measured with a single Langmuir probe was around 3×10^{11} cm^{-3}. A positive or negative dc bias (V_s) was applied to the substrate in reference to the grounded stainless steel chamber to control the sheath potential $\Delta V_{sheath} = V_p - V_s$, where V_p is the plasma space potential near the substrate measured with an emissive probe. A simple calculation of the sheath thickness and the ion mean-free-path showed that the value of ΔV_{sheath} corresponds to the mean ion-impact energy when V_s is positive [17]. Fourier transform infrared spectroscopy (FTIR, Perkin Elmer Spectrum 100) was used to characterize the films.

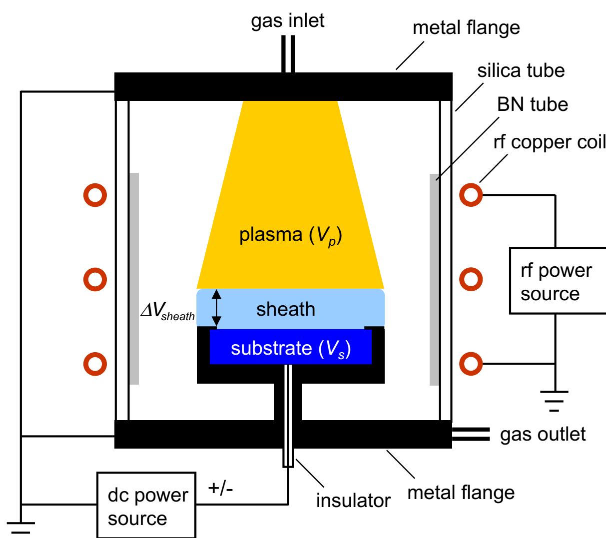

Fig. 1. Schematic of the ICP-CVD apparatus and the electrical circuit. V_p, V_s, and ΔV_{sheath} denote the plasma potential, substrate bias, and sheath potential, respectively.

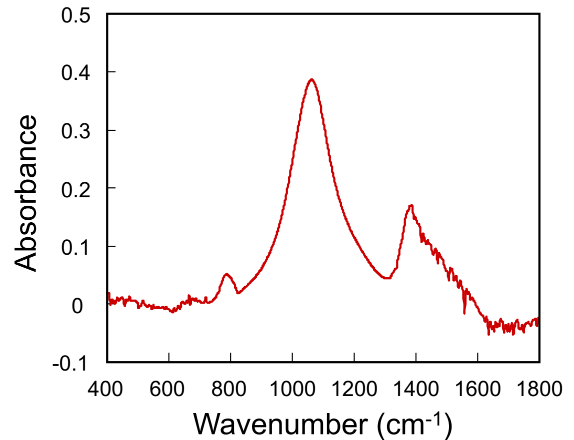

Fig. 2. Typical FTIR transmittance spectrum of a cBN film obtained with $V_s = +50$ V after the duration of 30 min.

3. Results

A typical FTIR transmittance spectrum of a cBN film obtained with $V_s = +50$ V after duration of 30 min is shown in Fig. 2. The absorption peaks at around 780 cm^{-1} and 1380 cm^{-1} are attributed to the out-of-plane B–N–B bending mode of sp^{2}BN and the in-plane B–N bond stretch mode of sp^{2}BN, respectively. The primary absorption peak at around 1065 cm^{-1} is attributed to the Reststrahlen band of cBN. The thicknesses of cBN and sp^{2}BN phases were determined from the values of absorbance of cBN and sp^{2}BN phases at around 1065 cm^{-1} and 1380 cm^{-1} by using the IR absorption coefficients of cBN (17,000 cm^{-1}) and sp^{2}BN (22,000 cm^{-1}) phases for our films [20]. For the spectrum in Fig. 2, the total film thickness and the cBN fraction are about 305 nm and 75 vol.%, respectively. The majority of the sp^{2}BN phase is located between the cBN layer and the Si substrate, while the rest is on the cBN layer. A small amount of sp^{2}BN phase on the surface is attributed to the residue of preferential etching by fluorine atoms during deposition [14,17]. The ratio of boron to nitrogen atoms at the film surfaces determined by X-ray photoemission measurement is around 0.9. The fluorine concentration at the film surfaces is typically ~1 at.%. The presence of hydrogen is expected, but we have not tried to detect them.

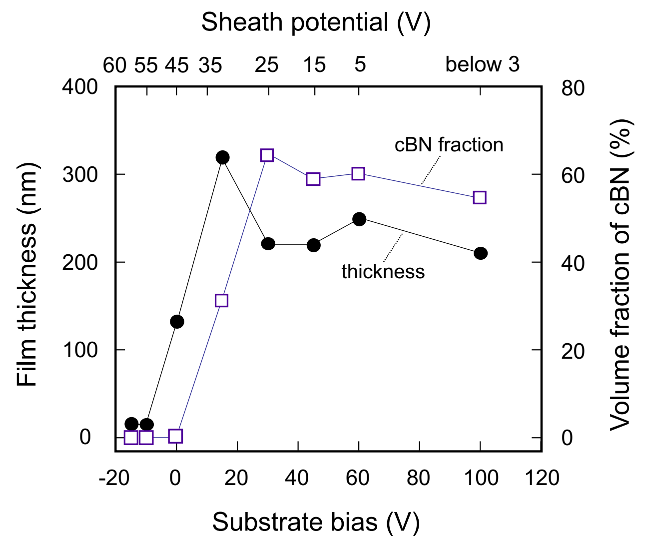

Fig. 3. Total film thickness (left axis) and cBN fraction in the film (right axis) obtained after the duration of 15 min as functions of substrate bias V_s (bottom axis) and sheath potential ΔV_{sheath} (top axis).

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