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Structural evolution of boron nitride films grown on diamond buffer-layers

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Abstract

Boron nitride films on diamond buffer layers of varying grain size, surface roughness and crystallinity are deposited by the reaction of B_2H_6 and NH_3 in a mixture of H_2 and Ar via microwave plasma-assisted chemical vapor deposition. Various forms of boron nitride, including amorphous α-BN, hexagonal h-BN, turbostratic t-BN, rhombohedral r-BN, explosion E-BN, wurzitic w-BN and cubic c-BN, are detected in the BN films grown on different diamond buffer layers at varying distances from the interface of diamond and BN layers. The c-BN content in the BN films is inversely proportional to the surface roughness of the diamond buffer layers. Cubic boron nitride can directly grow on smooth nanocrystalline diamond films, while precursor layers consisting of various sp^2-bonded BN phases are formed prior to the growth of c-BN film on rough microcrystalline diamond films.

Keywords: Cubic boron nitride; Nanocrystalline diamond film; Boron nitride

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1. Introduction

Cubic boron nitride is the second hardest material next to diamond. However, it is superior to diamond in some applications owing to its higher temperature oxidation resistance and higher chemical inertness to ferrous materials. Nevertheless, for most BN films prepared by various vapor deposition methods, the crystallinity of c-BN film is poor, the film stress is high, and non-cubic BN phases tend to form before c-BN is nucleated, rendering the applications of c-BN films impractical [1–3]. Most researchers have reported that the formation of c-BN film is possible only within a well-defined window of process parameters, e.g., negative substrate bias or the energy of bombarding particles needs to exceed a threshold value. Due to very large film stress, adherent c-BN films have been grown to a thickness less than 1 μm.

A lot of CVD procedures, ion-assisted PVD and hybrid methods are reported for depositing c-BN and diamond films. The primary difference between the deposition of c-BN and diamond films is that ion bombardment during the film growth is essential for the synthesis of c-BN film. Diamond and c-BN are isostructural with only 1.3% lattice mismatch. Therefore, they are ideal templates to each other for epitaxial growth.

Besides the well-known c-BN and h-BN phases, other forms or phases of BN have also been reported. These include the sp^2-bonded BN phases like amorphous BN (α-BN), turbostratic BN (t-BN) and rhombohedral BN (r-BN), and the sp^3-bonded phase wurtzitic BN (w-BN), a transformation of c-BN with varied *a* , *b*, *c* axes. In addition, there is another novel BN phase of mixed bonding of sp^2 and sp^3 called explosion BN (E-BN) [4] or orthorhombic BN (o-BN). Fourier transform infrared spectroscopy (FTIR) has been used extensively to study various BN phases, since their characteristic absorption peaks are quite distinguishable [5,6]. The sp^2-bonded BN phases, like h-BN, have two peaks at 1380 cm^{-1} and 780 cm^{-1}, which stem from the in-plane B–N stretching mode and out-of-plane B–N–B deformation mode, respectively. For sp^3-bonded BN phases, c-BN has a reststrahlen band (TO mode) around 1080 cm^{-1} and w-BN phase has IR absorption bands at about 1085, 1125 and 1250 cm^{-1}. E-BN phase has four peaks in its absorption spectrum occurring at 960, 1250, 1450 and 1600 cm^{-1}. Most of the vapor deposited BN films were not of high c-BN purity, but contained h-BN, t-BN or α-BN phases, and the c-BN grain size was usually in the nanometer scale.

In the past few years, there has been quite significant progress regarding the synthesis of c-BN films. Yamamoto et al.

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reported that thick c-BN films (up to 2.7 μm) were deposited onto Si substrates by an RF diode apparatus using boron carbide (B_4C) targets [7]. Feldermann et al. found that the nucleation of nanocrystalline c-BN film directly onto AlN substrates without the soft turbostratic BN interlayer was indeed possible [8]. Matsumoto and Zhang reported that a thick c-BN film of about 20 μm with high phase purity and low film stress was synthesized on Si substrate by dc-bias-assisted DC-jet CVD through the introduction of the chemical effects of fluorine in an $Ar–N_2–BF_3–H_2$ atmosphere [9].

In this study, we are able to deposit BN and diamond films in the same microwave plasma-assisted chemical vapor deposition (MPCVD) chamber, allowing consecutive growth of diamond/BN bilayers or multilayers. The influence of diamond films with different crystallinity and surface roughness as buffer-layers on the growth of BN films is explored.

2. Experimental

The synthesis of BN and diamond films is performed in a MPCVD system. The MPCVD system allowed independent control of several critical deposition parameters and the details of the system are described elsewhere [2,10]. The diamond buffer layers are deposited for 60 min by the reaction of a constant 1% CH_4 (1 sccm) with various flow ratios of Ar/H_2 of 0/99, 20/79, 50/49 and 90/9 (sccm/sccm) [10], which produced diamond films of varying crystallinity and surface roughness values of 32, 27, 13 and 0.4 nm, assigned as Films A, B, C and D, respectively and listed in Table 1.

The BN layer is then deposited on the diamond film using the same processing parameters. The BN films are deposited by the reaction of 35% NH_3/Ar, 5% B_2H_6/Ar and 60% H_2 mixture, which renders the optimal amount of c-BN content based on our prior study described in Ref. [2]. The substrate-temperature, the microwave power and substrate bias current are controlled at 900 °C, 1000 W and 80 mA, respectively. The deposition is continued for 50 min. The same sample notations of Films A, B, C and D are used for the BN films grown on the diamond buffer layers as listed in Table 1.

A Bomem-DA8.3 infrared spectrometer is used to obtain the FTIR spectra of the BN films. As suggested, the sp^3-bonded BN or c-BN content can be estimated from the peak area (A) intensity ratio $A_{1080}/(A_{1080}+A_{1380})$. We extend the same simple formula to $A_{1080,\ 1125,\ 1250}/(A_{1080,\ 1125\ ,1250}+A_{1380})$ to estimate all the sp^3-bonded BN phases [11].

The morphologies of the BN films are obtained using a Hitachi-S4100 SEM with a field-emission electron gun operating at 15 kV and JEOL JSM-6500F with cold cathode field-emission electron gun. Transmission electron microscopy (TEM) analyses of the BN films were performed using a JEOL JEM 3010 with an acceleration voltage of 300 kV and 0.14 nm point-to-point resolution. Samples were thinned mechanically to a thickness of 10 μm. To complete the sample preparation for TEM, 4.5 keV argon ions with an incident angle of 9° to the sample surface, are used to thin the sample further to electron transparency.

Table 1
Growth condition and surface roughness of the diamond buffer layers and c-BN content in the overgrown BN films

Sample ID film	Growth condition: 1 sccm CH_4 in Ar/H_2 flow	Surface roughness (Ra)	c-BN content (%)
A	0/99 sccm	32 nm	45
B	50/49	27 nm	55
C	70/29	13 nm	73
D	90/9	0.4 nm	90

3. Results and discussion

Fig. 1 shows the Raman spectra of the diamond films with varying roughness from 0.4 to 32 nm. In the Film A, a characteristic peak of diamond at 1332 cm^{-1} and some broad peaks associated with graphite (sp^2 carbon) around 1350 and 1500–1650 cm^{-1} are observed. The graphite species usually appear in the grain boundaries of CVD diamond films. With the increasing Ar fraction in the gas mixture, the 1332 cm^{-1} peak becomes broader in the Films B and C, and disappears in the Film D. In the meanwhile, the characteristic peak of nanocrystalline diamond around 1120 cm^{-1} is found in the Films C and D. The series of diamond films are generally categorized as microcrystalline diamond (MCD) for Films A and B and nanocrystalline diamond (NCD) for Films C and D [10].

Fig. 2 shows the SEM morphologies of the diamond films and the overgrown BN films. The images reveal that the surface grain-size and roughness of the diamond are reduced with the increasing Ar fraction in the gas mixture. The morphologies of the overgrown BN films under the same growth conditions are distinctly different from those of the underlying diamond buffer layers. However, the surface roughness and the grain-size of the BN films follow the same trend as the diamond buffer layers.

Fig. 3 shows the FTIR absorption spectra of the BN films deposited on the diamond buffer layers. The c-BN content is increased following the decreasing roughness of the diamond films. The estimated c-BN content of the Film A is 45% and is up to 90% for the Film D as listed in Table 1. An inverse dependence of c-BN content in the BN films on the roughness of the diamond layers is observed.

The FTIR spectra in Fig. 3 show not only the major h-BN and c-BN phases but also the existence of w-BN and E-BN. The FTIR spectra also indicate the evolution of BN phases among E-BN, w-BN, h-BN and c-BN. As the roughness of diamond buffer layers decreased, the BN films consisting of h-BN, c-BN, E-BN and w-BN changed from h-BN dominant, to more w-BN, to more E-BN, and finally to c-BN dominant BN films. This phenomenon is related to the roughness of the diamond buffer layers which could affect the degree of ion bombardment or the ion to neutral ratio during the ion-assisted deposition of BN films.

Fig. 4 shows the plan-view TEM images of the BN layer of Film D. Fig. 4(a) shows the selected area diffraction (SAD) ring pattern which is indexed as (1 1 1), (2 0 0), (2 2 0), (2 2 2), (3 1 1) of c-BN. The dominant c-BN content in the film is evidenced by the SAD pattern and the prior FTIR results. Fig. 4(b) and (c) show the bright-field and the dark-field images, respectively, of the film. The dark-field image used the (1 1 1) reflection of c-BN.