Nucleation and Growth of Cubic Boron Nitride Films Produced by Ion-Assisted Pulsed Laser Deposition

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ABSTRACT

X We are studying the boron nitride system by using a pulsed excimer laser to ablate from hexagonal BN (hBN) targets to form cubic BN (cBN) films. We are depositing BN films on heated (25 - 800°C) Si (100) surfaces and are using a broad-beam ion source operated with Ar and N₂ source gasses to produce BN films with a high percentage of sp³-bonded cBN. In order to understand and optimize the growth and nucleation of cBN films, parametric studies of the growth parameters have been performed. The best films to date show >85% sp³-bonded BN as determined from Fourier-transform infrared (FTIR) reflection spectroscopy. High resolution transmission electron microscopy (TEM) and selected area electron diffraction confirm the presence of cBN in these samples. The films are polycrystalline and show grain sizes up to 30- 40 nm. We find from both the FTIR and TEM analyses that the cBN content in these films evolves with growth time. Initially, the films are deposited as hBN and the cBN nucleates on this hBN underlayer. Importantly, the position of the cBN IR phonon also changes with growth time. Initially this mode appears near 1130 cm⁻¹ and the position decreases with growth time to a constant value of 1085 cm⁻¹. Since in bulk cBN this IR mode appears at 1065 cm⁻¹, a large compressive stress induced by the ion bombardment is suggested. In addition, we report on the variation in cBN percentage with temperature.

INTRODUCTION

There are at least four crystalline phases of BN. The two sp²-bonded phases are hexagonal BN[1] (hBN) (similar to graphite) and rhombohedral BN[2] (rBN). hBN is the stable room temperature phase. rBN differs from hBN in the stacking and rotation of the graphite-like BN layers. The two sp³-bonded phases are a hexagonal phase (wBN) with wurtzitic structure[3] and the metastable cubic phase (cBN) with a zinc-blende structure[4]. In addition there is a turbostratic BN (tBN) phase which consists of a spectrum of disordered graphite-like structures. tBN is characterized by a larger separation between the hexagonal BN planar networks. In addition, these planar networks fall out of registry with each other and show severe curvature in transmission electron microscopy (TEM) lattice images.

In recent years there have been several successful methods employed to grow cBN films. We[5, 6] and others[7] have used ion-assisted pulsed laser deposition (IAPLD). Examples of other successful techniques include e-beam evaporation of boron with a broad-beam ion source of nitrogen[8, 9, 10], ion plating[11], and rf-plasma deposition[12]. All of the successful methods require the presence of an activated nitrogen source (N₂, N, N₂⁺ or N⁺ of energies > 100 eV) to produce high quality films (> 80% sp³-bonded cBN). This suggests that a common mechanism is responsible for the production of the sp³-bonded cBN phase.

Kester and Messier[9] have observed that the momentum per deposited atom (momentum/atom) transferred into the film by the bombarding ions controls the phase formation.

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In a narrow window of momentum/atom transfer the cBN phase is nucleated. Below this window only the hBN phase is formed, and above this window the deposited film is totally resputtered away by the ion beam. We have also observed similar behavior in our films[5]. This observation, however, does not explain the mechanism for cBN conversion. Kester et al. [10] reported that the initial BN material is deposited as hBN/tBN oriented such that the c-axis is parallel to the plane of the substrate. The cBN material was found to nucleate from this oriented hBN layer. McKenzie et al.[13] have shown in situ stress measurements that reveal the BN film is under high compressive stress during nucleation and growth of the cBN phase, and the amount of cBN in the film correlates to the stress level in the film. They propose a conversion model based upon compressive biaxial stress induced in the c-axis oriented hBN by the ion bombardment. This compressive stress, combined with local melting of the hBN/tBN structure along the ion tracks (a "thermal spike"), places a local region of the material in the portion of the pressure-temperature phase diagram where cBN is the stable phase.

We have reported microstructural characterization[14, 15] of cBN films that show similar layered behavior as described above by Kester et al.[10]. In addition, we have found two other sources of the sp^2 -bonded tBN material in our films. First, TEM lattice images show that small pockets of the tBN phase are also found in the inter-grain region between the cBN crystallites. This indicates that the conversion process is not 100% effective even after cBN nucleation. Second, lower resolution TEM images reveal the presence of particulates incorporated into the films. These particulates are generated by the pulsed-laser-deposition (PLD) process and are unconverted hBN material from the target. We find that they also shadow the ion beam from part of the growing film, thus preventing conversion of this region to cBN. Importantly, we find cBN crystallites of 30-40 nm that show intra-grain twins on only one type of {111} plane.

In this paper, we report on our observations of the nucleation and growth of cBN films as a function of growth time and temperature based mainly upon Fourier infrared transform (FTIR) spectroscopy.

EXPERIMENTAL

The IAPLD vacuum chamber (Fig. 1) is capable of attaining a base pressure of 1×10^{-10} Torr and is equipped with in situ Auger electron spectroscopy (AES) and a broad-beam ion source. An aperture constructed from pyrolytic BN was placed 10 cm downstream from the ion gun in order to eliminate contamination from sputtering of the chamber walls by the spreading ion beam. Thus BN samples were deposited on Si (100) substrates with an area irradiated by the ion beam, and with an area that was not irradiated by the beam. This allowed for a direct comparison between the two regions of every sample, and provided an easy means of determining the affect of the ion beam on film content. The ion current striking the sample was measured by a probe circuit that biased the sample substrate at -30 volts in order to repel electrons from the surface. A more complete description of the experimental procedure and deposition conditions is described elsewhere[5].

Characterization of the samples was accomplished mainly through FTIR spectroscopy, which serves to quickly determine bulk film characteristics. For sp^2 -bonded BN (crystalline hBN or turbostratic BN[16]), there are two characteristic peaks at 1370 cm^{-1} and 800 cm^{-1} associated with the in-plane B-N bond stretch and the out-of-plane B-N-B bond bend, respectively[17]. cBN,

Fig. 1 A diagram of the chamber used to deposit the films.

Fig. 2 IR reflection vs. wavenumber for a BN film. One spectrum was taken in a region irradiated by the ion beam, and the other was taken from a non-irradiated region.

Fig. 2 depicts two FTIR spectra taken from the irradiated and non-irradiated regions of the same sample. The affect of the ion beam is dramatic and clear. The irradiated region shows a mixed phase sample that is > 85% cBN. The non-irradiated region shows no evidence of cBN.

The crystallinity of the films has been assessed using transmission electron microscopy (TEM) and selected area diffraction. This work is reported in more complete detail elsewhere[14, 15] and is briefly summarized here. Fig. 3 is a plot of the azimuthally-averaged electron diffraction intensity versus inverse lattice spacing for the sample whose FTIR spectra are shown in Fig. 2. The peaks in the irradiated region index to those of cBN, while those in the non-irradiated region index to the disordered tBN phase. This result is in good agreement with the FTIR spectroscopy data. Importantly, high-resolution TEM lattice images show that the cBN is heavily twinned on {111} planes with grain sizes up to 30 - 40 nm.

Fig. 3 The average azimuthal electron diffraction intensity obtained from TEM specimens for irradiated and non-irradiated regions of a film.

with sp^3 bonding, has an IR-active TO mode at 1065 cm^{-1} [18]. Reflectance spectra were obtained at nearly normal incidence and were ratioed to the spectrum of a silicon wafer that was cleaned by the same NH_4F dipping process as the deposition substrates. The spot size of the IR beam was 0.04 mm^2 , allowing separate spectra to be taken of both the region irradiated by the ion beam and the area outside the ion beam. The percentage of cBN in the samples was estimated by taking the ratio of the peak height of the cBN mode at $\sim 1065\text{ cm}^{-1}$ to the sum of the peak heights of the hBN mode at 1370 cm^{-1} and the cBN mode at $\sim 1065\text{ cm}^{-1}$. Computer simulations of the IR reflection spectra[5] show that this procedure estimates the actual cBN percentage to within $\pm 5\%$.

Cross-sectional TEM images reveal an amorphous layer ($\sim 3\text{ nm}$ of presumably BN) followed by a hBN/tBN layer (30 nm) oriented with the c-axis in the plane of the substrate upon which the cBN phase nucleates. This result is essentially the same as that reported by Kester et al.[10] for films deposited in a slightly different manner.

A parametric study was undertaken in order to optimize the deposition process and produce films with the highest fraction of sp^3 -bonded cBN. Samples were deposited using various combinations of the

deposition parameters described in detail elsewhere[5]. The present paper focuses on the initial stages of growth and the temperature dependence of the growth process.

DISCUSSION

In order to observe the BN phase nucleation and evolution, depositions were performed as a function of growth time while holding all other variables constant. The FTIR spectra for a series of samples grown at 400 °C are shown in Fig. 4. The cBN IR mode appears after several minutes of growth and steadily increases in strength with time. As can be seen from the relative change in peak heights, the cBN percentage as measured by FTIR evolves from zero and grows with time. These spectra show that the BN deposited from the target initially goes down as sp²-bonded material even while being irradiated by the ion beam, consistent with the high resolution TEM observations[14].

Also evident in Fig. 4 is a pronounced upward shift of the cBN IR mode from its bulk value. For three growth temperatures, the difference between the cBN IR mode and its bulk crystalline value of 1065 cm⁻¹ is plotted in Fig. 5 as a function of growth time. In the most extreme case, the cBN IR mode first appears at 1137 cm⁻¹. At the three temperatures studied, the

Fig 5 Peak shift of the TO IR mode of cBN from the bulk crystalline position of 1065 cm⁻¹ as a function of growth time at different temperatures.

Fig. 4 IR reflection spectra for films grown for varying deposition times. The initial deposition is sp²-bonded material, and the cBN peak height increases relative to the peak height of the hBN modes. Note how the peak position of the cBN IR mode decreases with increasing time (thickness).

peak position decreases to a constant level of 1085 cm⁻¹ (i.e. above the bulk value of 1065 cm⁻¹) as the growth time (thickness) increases. The presence of high compressive intrinsic stresses in cBN films as a function of growth time has been reported in reference [13]. (Upward shifts in lattice mode frequencies with increasing pressure due to vibrational anharmonicity are quite common, and this phenomenon has been reviewed extensively for inorganic compounds[19].) The shift in the cBN IR mode with time is probably related to the intrinsic stress in the film, since others have reported[13] a shift in the cBN IR mode from ~1085 cm⁻¹ to near 1050 cm⁻¹ upon delamination of the film. If so, this indicates

that nucleation of the cubic phase occurs at a time of very high stress, and that the stress decreases to a constant value (above that of bulk cBN) as the films grow in thickness.

Deposition of cBN films was performed at substrate temperatures between 65 and 800 °C. The results are shown in Fig. 6. We find that the optimum temperature range for growing cBN is between 150 and 500 °C. The cBN percentage drops rapidly below 150 °C and the films are totally resputtered near 100 °C for the current density used. The cBN percentage falls off more gradually as the temperature is increased above 500 °C. Increasing the ion current at high temperature only increases the resputtering rate and does not result in a higher cBN percentage. Elastic recoil detection spectroscopy shows (Fig. 6) reveals these samples are stoichiometric over the 100 to 800 °C temperature range. This is in contrast to films grown by unassisted PLD in which the nitrogen content of the films varies from N/B ~ 0.30 - 0.70 from 25 - 600 °C[20].

On a general level, ion-induced phase transformations can result due to the accumulation of damage in the bombarded structure[21]. This raises the free energy till conversion to a higher energy metastable phase becomes possible. Such transformations are dependent upon the initial structure of the bombarded material. In this light, the temperature dependence of the cBN percentage is interesting and is possibly intimately connected with the structure and crystallinity of the deposited surface layers during growth.

Specifically, using in situ AES, we have observed that even under ion bombardment the surface of the growing cBN film is sp²-bonded[5]. This suggests that even after nucleation of the cBN phase, the ablated material is deposited on the film surface in the tBN/hBN structure. The conversion to cBN occurs below the growing film surface as the compressive stress grows. Studies conducted on unassisted PLD grown BN films show that the ordering as well as the stoichiometry in the deposited tBN/hBN phase is temperature dependent[20]. If this is also true of the tBN/hBN deposited on the ion-irradiated films, then the conversion efficiency to cBN should be directly affected. For instance, at the optimum temperature for growth the ordering/disordering in this tBN/hBN surface layer may be optimum for the conversion to cBN. Above this temperature the ordering in the surface layer becomes closer to that of hBN (lower free energy) resulting in less favorable conversion to the cubic phase. Below this temperature, the surface layer becomes more disordered so that formation of cBN is suppressed.

The nucleation of cBN in these samples may also be temperature dependent and affect the cBN content of the films. The rapid reduction in the cBN content below 150 °C with a concurrent rise in the resputtering rate suggests that nucleation of the cBN phase is being altogether suppressed. It is not known whether the c-axis oriented hBN/tBN layer is required for the nucleation of cBN under ion bombardment. If it is, then below 150 °C this layer may not form or be significantly disordered, thus rapidly suppressing the nucleation of cBN. Above the optimum growth temperature this layer may gradually increase in crystallinity (again due to higher atom mobility) leading to less favorable arrangements for cBN conversion.

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CONCLUSIONS

Films containing >85% sp³-bonded cBN have been grown using IAPLD. Using FTIR spectroscopy, we find that the initially deposited film is sp²-bonded BN, and that the cBN concentration increases with growth time. This result is consistent with TEM cross-section

Fig. 6 cBN content and N/B ratio as a function of temperature.

analysis that shows that the initial layer on the Si (100) substrate is amorphous followed by a hBN/tBN layer oriented with the basal plane perpendicular to the plane of the Si substrate. The cBN nucleates and grows on this oriented hBN/tBN. A significant upward shift in the position of the cBN IR mode indicates that the cBN is under high compressive stress when it nucleates. With growth time, this stress decreases quickly to a constant value.

The temperature range over which films with a cBN percentage above 70% can be grown is between 150 and 500 °C. At high temperature, the cBN percentage does not recover to that of the lower temperature data upon increasing the ion current, indicating that the conversion process is less-favored at these temperatures. There is a dramatic reduction in the cBN concentration below 150 °C that is accompanied by a rise in the resputtering rate till the entire film is nearly sputtered away near 100 °C. As temperature is increased above ~500 °C, the cBN percentage falls off more slowly as a function of temperature than for samples grown below 150 °C. Elastic recoil detection spectroscopy shows that the films grown from 100 to 800 °C are stoichiometric (N/B = 1).

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