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Complexity of the microstructure evolution for optimization cBN growth in a four-step ion-assisted deposition process

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Abstract

The changes in microstructure of a specially prepared boron nitride (BN) film as a function of film depth were studied by high resolution transmission electron microscopy (HRTEM) and other materials analysis tools. These changes were then correlated to the changes in processing parameters during film growth. The analyzed film was fabricated by the four-step ion-assisted deposition procedure known to be effective in film-stress engineering for the formation and retention of a thick cubic BN (cBN) layer with a three-step buffer-layer deposition. In this deposition, the energy of the ions assisting cBN formation was increased stepwise from 200 to 280, and then to 360 eV [S.F. Wong, C. W. Ong, G.K.H. Pang, K.Z. Baba-Kishi, W. M. Lau, J. Vac. Sci. Technol. A 22 (2004) 676]. The nominal thickness of the cBN layer was 650 nm and that for each of the three buffer layers was about 160 nm. Both the HRTEM and electron diffraction results confirmed that the top cBN layer, with a thickness of 643 nm, consisted of cBN grains with a preferred orientation of their *c*-axis along the film growth direction. In comparison, the three-step buffer layer deposition yielded complex and intriguing microstructures. In the first buffer layer adjacent to the substrate, grains containing sp^2 planes with a preferred orientation of their basal planes parallel to the film growth direction were the main constituents. The increase of ion energy from 200 to 280 eV for the formation of the second buffer layer first led to an enrichment of the concentration of these sp^2 grains with the preferred orientation. Then, bending of some of the sp^2 planes into curved microstructures was evident. The microstructure became very complex and displayed multiple phases including some amorphous structures. The presence of a cBN-like phase was indeed detected by electron energy loss spectroscopy. This complex microstructure persisted until it was replaced by the cBN structure, without abrupt change when the ion energy was increased from 280 to 360 eV for the deposition of the third buffer layer. It is proposed that small grains with cBN-like sp^3 bonding configurations are present in the 2nd and 3rd buffer layers, probably with crystalline domains less than 5 nm and thus difficult for direct detection even by HRTEM. A sufficient accumulation of these cBN nuclei transformed the buffer layer to the cBN layer.

Keywords: Boron nitride; Growth mechanism; Structural properties; Transmission electron microscopy (TEM)

1. Introduction

Boron nitride (BN) films with a high cubic BN (cBN) content have excellent mechanical properties and promise great applications in surface coating technology [2–5]. It is now widely accepted that cBN-rich films can be synthesized under ion bombardment with energy (U_{assist}) exceeding a certain threshold value. It is also widely accepted that even in a single-step process (where U_{assist} and other deposition parameters were kept constant), the film deposited still exhibits a layered structure. Such a layered structure typically consists of a thin disordered layer (aBN) on the substrate surface, then a layer having randomly packed sp^2-bonded graphite-like planes (often referred as turbostratic BN, tBN), and finally a cBN-rich top layer [6 7]. Different theories, like the static stress model [8,9], dynamic stress model [5], subplantation model [10], quenching model [11] and sputter model [7], have been proposed to describe the

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evolution and growth mechanisms of the cBN phase. A more recent report on ab initio calculations of free energies of various BN phases and studies of their phase transformation further articulate the effects of film stress on the compression of the graphite-like hexagonal BN to the dense and hard wurtzitic BN (the soft rhombohedral BN to the hard cBN). It also explains that defects in these crystalline phases can raise their free energies and thereby facilitate the relevant phase transformation and nucleation during BN film growth [12]. On the whole, the growth mechanisms for various BN phase formations in all known BN film deposition processes are rather complex because different mechanisms may take place at different stages in a BN film deposition process and variations in deposition design can also invoke different mechanisms. The evolution sequence for the mechanisms to take place will be affected by the changes in deposition conditions (e.g. U_{assist}, ion species and their current densities, and growth temperature) during film growth. On the other hand, it will also be reflected by some resultant structural changes as a function of film depth. The extension of research in both experimental studies of microstructure evolution as a function of deposition attributes and theoretical examinations of relevant growth mechanisms are certainly synergetic.

This synergy is shown in a BN film deposition process disclosed recently, a process which was designed by following the theoretical guideline of stress-induced cBN formation and the experimental experience in practical film stress evolution and control. This led to the successful formation and retention of a thick cBN film by adopting a four-step approach (referred as the four-step BN film deposition thereinafter) [1]. In this process, the first three steps comprise of a typical ion-assisted BN deposition procedure at an optimal and constant substrate temperature (680 °C), and a stepwise increase in U_{assist} from 200, 280 and 360 eV for the deposition of a BN film of ~160 nm in each step. This three-step process is known to build up a buffer layer with a gradual increase in film stress [1]. Although the conventional Fourier transform infrared absorption (FTIR) measurements on such buffer films do not show any detectable cBN content, a cBN-rich layer can be formed virtually on top of this buffer layer when U_{assist} is changed to 450 eV. More importantly, the three-step buffer layer deposition also accommodates the formation and retention of a cBN-rich layer of over 500 nm in thickness, whereas a cBN-rich layer of more than 100 nm peels off from the substrate without the buffer layer deposition [1]. The success in this process optimization to improve the cBN film deposition results calls for detailed studies of the associated microstructure evolution, such that further theoretical studies and experimental process optimization can be conducted.

The present article reports on the complex microstructures and their evolutions in the BN film prepared by the four-step BN film deposition. The microstructure data were collected from high resolution transmission electron microscopy (HRTEM), selected area electron diffraction analysis (SAED), FTIR, and electron energy loss spectroscopy (EELS).

2. Experimental methods

The film sample was deposited on Si (100) substrate at 680 °C by using a high vacuum system equipped with two 3-cm Kaufman ion guns (Ion Tech, Inc.) [13]. Boron was sputtered from a 4-in. B target (99.9%) by an argon ion (Ar^+) beam of 70 mA and 1200 eV generated by one ion gun. The substrate was bombarded simultaneously by an Ar^+/N_2^+ ion beam generated by another ion gun. The flow rates of the Ar and N_2 gases admitted into the second ion gun were in a ratio of 1.2:1. The four-step BN film deposition began with a three-step buffer layer deposition, U_{assist} increased stepwise from 200 to 280, and then to 360 eV. Each setting lasted for 20 min, and the beam current (I_{assist}) was kept constant at 20 mA. After the buffer layer deposition process, a cBN-rich layer was deposited, with U_{assist} and I_{assist} set at 450 eV and 30 mA respectively. This step lasted for 180 min.

Cross-sectional transition electron microscopy (TEM) analysis and SAED were conducted by using a JEOL 2010 system (200 keV) and a JEOL 3000 FEG-TEM system (300 keV). The electron beam size was set to have diameters in the range of 2–100 nm. The energy resolution was around 1 eV. Results of FTIR analysis were used to estimate the volume fraction of the cBN content (η_{cBN}) in each layer according to the conventional method [14] and a Nicolet Magna-TR™ System Model 750 was employed. In this analysis, the IR absorption spectrum of a three-layered buffer layer was collected separately from another sample prepared by following the abovementioned procedures. As such, the cBN content in the top layer is deduced by means of proper data subtraction. For the measurements of BN phase composition of the top surface layer of ~1 nm, the technique of EELS was applied, with a Quantum 2000 PHI photoelectron spectrometer [15]. The method deconvolutes the EELS data (arising from the nitrogen 1 s photoelectrons injected by an Al K_α X-ray source) collected from the top surface layer to a phase composition of a mixture of aBN, hBN and cBN, through a comparison of the measured data with those collected from three pure-phase standards. Finally, chemical composition measurements by X-ray photoelectron spectroscopy (XPS) were performed also with the Quantum 2000 PHI spectrometer.

3. Results and discussion

3.1. Layer structure of the BN film

The low magnification cross-sectional TEM image of the film sample (Fig. 1) reveals a layered structure containing a