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Effect of deposition temperature on the alignment of hexagonal laminates in turbostratic boron nitride thin film

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ABSTRACT

The deposition behavior of turbostratic boron nitride (t-BN) films was investigated with the focus on its microstructure variation in relation to deposition temperature substrate bias voltage. BN films were deposited using the unbalanced magnetron sputtering method. Thin (100 μm) Si strips (3 × 40 mm^2) coated with a nanocrystalline diamond thin layer were used as substrates. A BN target was used, which was connected to a radio frequency power supply set at 400 W. A pulsed direct current power supply connected to a substrate holder was used for negative biasing. The deposition pressure was 0.27 Pa with a flow of Ar (18 sccm)–N_2 (2 sccm) mixed gas. Only t-BN films were deposited with the substrate bias less than −100 V irrespective of the deposition temperature. The orientation of (0002) t-BN laminate alignment changed from normal to parallel to the substrate surface with increased deposition temperature. High resolution transmission electron microscopy and Fourier transform infrared spectroscopy confirmed such behavior. However, the application of bias voltage made the (0002) laminates align normal to the substrate surface even at high deposition temperatures. The films tended to react with moisture in an ambient atmosphere as confirmed by the appearance of O–H absorption peak in the FTIR spectrum. The measured O–H absorption intensity was not influenced by the variation of deposition variables.

1. Introduction

Boron nitride has many allotropes, among which cubic and hexagonal structures are commonly observed. Cubic boron nitride (c-BN) shows excellent physical properties, such as high hardness, thermal conductivity, and oxidation resistance as well as excellent semiconducting properties for high temperature or high power usages [1,2]. Good chemical inertness against ferrous materials makes this material a good candidate for machining applications. Because of these advantages, several studies have been carried out on the fabrication of material in the form of thin film [2–6]. However, to date, no successful application in industry has been reported. One obstacle to the industrial application of film is its poor adhesion to the substrate. The poor adhesion of film is known to be caused either by high compressive residual stress or the existence of a weak turbostratic BN (t-BN) transient buffer layer formed prior to phase formation on the substrate [7].

The role of the t-BN layer in the formation of thin film can be summarized, from the literature survey, as follows: a site for phase nucleation caused by lattice matching [8], compressive residual stress generation due to Ar atom incorporation [9,10], and a reaction site with atmospheric moisture [11–14]. The above phenomena might be influenced by the microstructural characteristics of the t-BN layer, such as its alignment, the degree of curling, and defect density. Recently, moisture reaction, which is harmful to adhesion of deposited film, was reported to be prevented by increasing deposition temperature [15,16], which is probably due to healing of defects in the t-BN layer by high temperature deposition. In spite of the importance of the t-BN layer on the formation as well as the property of film, a systematic study focusing on the t-BN layer itself is very rare, especially on the determining factor of the t-BN laminate alignment. It is thus very important to investigate the structure variation of the t-BN layer in relation to the main deposition variables, which will be used also in designing deposition condition for a film with good adhesion properties. In this study, we investigated the deposition behavior of t-BN films in relation to temperature and substrate bias and analyzed their microstructure variation with Fourier transform infrared spectroscopy (FTIR) as well as high resolution transmission electron microscopy (HRTEM).

2. Experimental

BN films were deposited using the unbalanced magnetron sputtering method on Si strips of 3 × 40 mm^2 with a thickness of 100 μm, upon which a nanocrystalline diamond (NCD) film of about 1 μm thickness

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was coated. The deposition conditions, including the deposition method used for the NCD film, have been described well elsewhere [17]. A hexagonal boron nitride disk of 50 mm in diameter (99.5% in purity, LST chemical) was used as a sputter target. The sputter target was connected to a 13.56 MHz radio frequency (RF) electric power at 400 W. A pulsed unipolar direct current power supply (10 of on/off time ratio) connected to a substrate holder was used to apply a negative bias to the substrate. The distance between the target and the substrate was 75 mm. The substrates were cleaned in acetone and then in methanol before being loaded into a chamber. The chamber was evacuated to less than 1.3×10^{-4} Pa and then maintained at a pressure of 0.27 Pa with a flow of Ar–N_2 sputtering gas. The flow rates of argon and nitrogen were 18 and 2 sccm, respectively. The target was pre-sputtered for 5 min before deposition with the shutter closed. Films were deposited for 15 min, during which films were grown with a thickness of around 100 nm. The substrate was heated using a SiC heater located beneath the substrate holder, whose temperature was measured by a thermocouple attached to the backside of the holder. The real temperature of the front side of the substrate was expected to be higher by at least several tens of degrees C by plasma heating during deposition. The lattice structure and crystal quality of the samples were analyzed using FTIR (PerkinElmer Frontier FTIR) in transmission mode with a resolution of 4 cm^{-1} at normal incidence. The spectrum of a silicon wafer with the NCD film was taken as a background and ratioed from the measured spectra of the deposited films. Due to the interference of overlapping of adjacent peaks, the peak positions, intensity, and full width at half maximum (FWHM) were determined by fitting the IR spectrum of each sample with pure Lorentzian-type peak functions. HRTEM (FEI Titan 300) was used to observe the structure of the t-BN layer. TEM specimens were prepared using a conventional Focused Ion Beam.

3. Results and discussion

Under a substrate bias less than −100 V, only t-BN films were deposited. First, we tried to observe the growth behavior of t-BN film using HRTEM. Fig. 1 shows a macroscopic TEM image of the film grown at 200 °C without substrate bias applied. The surface of the NCD film was rough due to the growth of columnar NCD grains. The surface of the t-BN film, however, looks smooth irrespective of the roughness of the NCD film. No visible evidence of inhomogeneity within the t-BN film was observed. Such macroscopic behavior was not influenced by deposition variables. Although the reason of the formation of the flat BN surface is not clear at this moment, the electric field variation induced by surface roughness of the NCD film might have induced the variation of sticking coefficient of sputtered particles and consequently tended to smoothen the BN film surface.

The orientation of t-BN laminates was analyzed in the HRTEM images of the films. As shown in Fig. 2, we could clearly identify every t-BN (0002) laminate. In the case of the film deposited at 200 °C, most of the t-BN laminates were aligned perpendicular to the substrate surface. (The direction of the substrate surface normal is indicated by an arrow.) On the other hand, laminates composing the t-BN film deposited at 1000 °C were nearly parallel to the substrate surface. Optical diffraction patterns shown in insets, obtained by performing a fast Fourier transform on the HRTEM images also showed clearly a difference of the alignment of (0002) t-BN laminates between the two. This definitely shows that the alignment of the t-BN laminates depends on the deposition temperature. The interlamellar spacing between (0002) laminates was measured to be 0.34 nm within 0.02 nm variation. No variation of this value was observed between samples deposited at different temperatures.

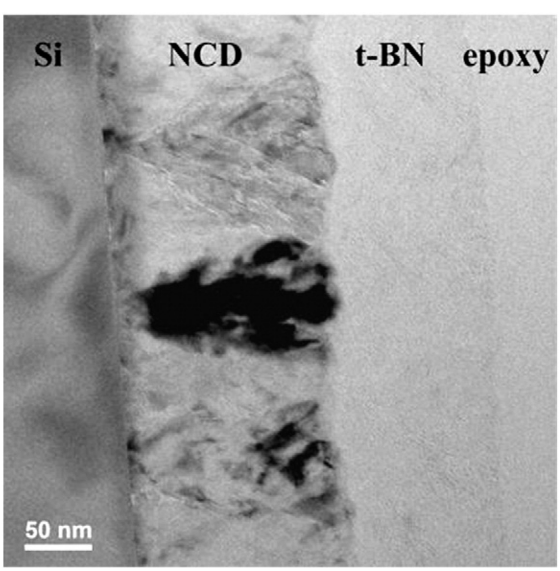

Fig. 1. Cross-sectional TEM image of t-BN film deposited at 200 °C without intentional application of substrate bias voltage.

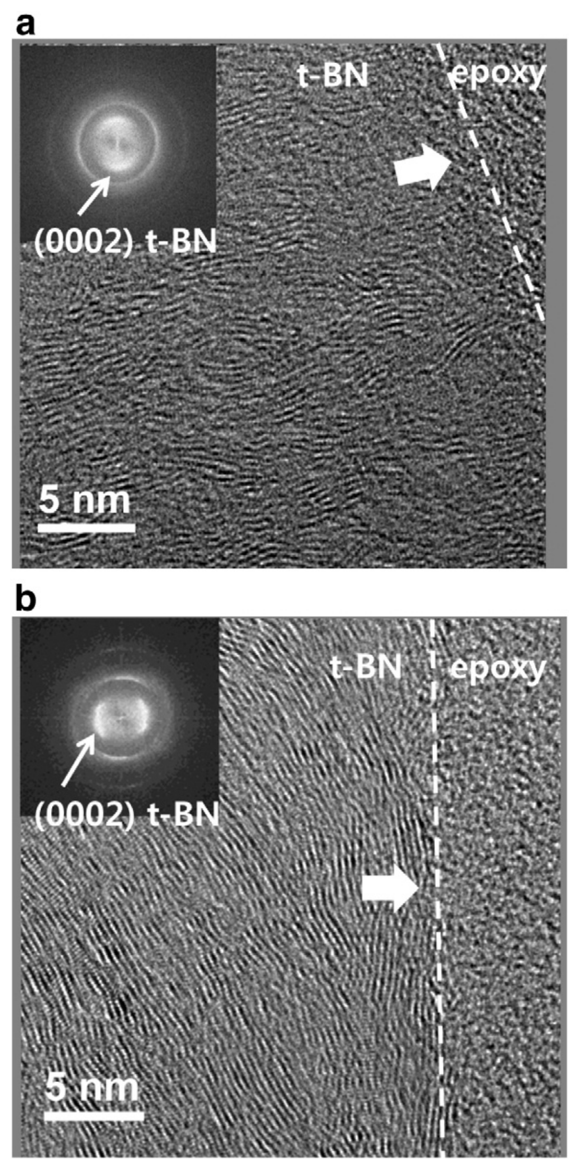

Fig. 2. Cross-sectional HRTEM images of t-BN films deposited (a) at 200 °C and (b) at 1000 °C without application of substrate bias voltage. Insets are fast Fourier transformed optical diffraction patterns and arrows indicate the direction of substrate surface normal.