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Orientation effects in *t*BN/*c*BN interfaces: A transmission electron microscopic study

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The orientation between cubic boron nitride (*c*BN) crystallites and the *t*BN layers on which they grow was studied using high-resolution transmission electron microscopy. BN films were prepared by radio-frequency magnetron sputtering under conditions leading to the formation of ~100% *c*BN films grown on a preceding *t*BN layer. Two types of orientations were observed: (i) *c*BN layers grown on the edges of the *t*BN(0002) planes so that the *c*BN{111} planes are parallel to the *t*BN(0002) planes (as reported previously by many authors), (ii) *c*BN layers grown on curved *t*BN(0002) planes with no orientation to the *t*BN planes. The first type of *c*BN growth is associated with stress leading to delamination of *c*BN films thicker than 100 nm. The second type is associated with reduced stress enabling the growth of much thicker (~500 nm) films at a relatively low (450 °C) substrate deposition temperature. These results may be helpful in the fabrication of thick *c*BN films and improving our understanding of the *c*BN nucleation process. © *2002 American Institute of Physics.* [DOI: 10.1063/1.1431394]

Cubic boron nitride (*c*BN) films have significant technological potential due to their superior properties including high hardness, high thermal conductivity, chemical inertness, wide band gap, and their ability to be both *p*- and *n*-type doped.[1] BN films with a high (>85%) *c*BN component can be deposited by different techniques using energetic species.[1–8] The compressive stress formed by the ion impact, however, limits the maximal thickness of these films to ~200 nm, beyond which delamination occurs. High-resolution transmission electron microscopy (HRTEM) studies of the BN films show that *c*BN layers are not formed directly on the substrate. The initial layer is amorphous, then an oriented *t*BN layer, with the (0002) basal plane perpendicular to the surface, is formed. The *c*BN layer seems to nucleate on the edges of the (0002) *t*BN planes with the (111) planes parallel to the *t*BN basal planes. The formation of both these oriented layers is associated with the significant compressive stress discussed earlier. In this letter, we show that under the proper conditions curled (0002) *t*BN planes are formed, on the top of which the nucleation and growth of *c*BN crystallites is random. This type of *c*BN growth is associated with a reduced amount of stress.

The BN films were deposited on Si substrates using rf magnetron sputtering as described elsewhere.[9] A 1-in.-diam 99.99% *h*BN sputter target was used. Typical deposition conditions were: (i) an Ar/N_2 mixture of 1:1, (ii) a total pressure of 10 mTorr, (iii) a target self-bias of -50 to -100 V, (iv) a substrate temperature of 450 °C, (v) a 75 W rf power, and (vi) a deposition rate of 100 nm/h. Regular depositions were performed after achieving a base pressure on the order of 10^{-9} Torr. The chemical composition of the films was determined by x-ray photoelectron spectroscopy (XPS) using a monochromatic Al $K\alpha$ source. The BN phase composition was determined by a Fourier transform IR (FTIR) spectroscopy. Cross-sectional HRTEM was performed on samples prepared by the conventional sequence of sandwich gluing, mechanical polishing, dimpling, and ion milling using a Philips CM 200 FEG HRTEM (200 kV, point resolution of 0.19 nm). Measurements and calculations based on the imaging conditions used show that delocalization effects can be neglected.

Films had a *c*BN fraction of 85% as determined from FTIR spectra (Fig. 1) in the conventional way.[1] XPS showed a stoichiometric BN composition with residual O and C concentrations less than 3% and 2%, respectively. Cross-sectional HRTEM microscopy performed on films deposited using a bias voltage of -120 eV was consistent with previous reports.[1,7,10,11] The initial BN layer grown on the Si substrate is amorphous (Fig. 1) and is followed by a *t*BN layer in which the (0002) basal planes are perpendicular to the surface. The *t*BN layer is not ordered. The plane spacing of *t*BN is not uniform. In some parts of the film, the spacing of the *t*BN(0002) plane is rather small (~3.4 Å), close to that of *h*BN. In other parts the spacing is greatly enlarged. The *c*BN layers start to form on the top of *t*BN layers, i.e., on the edges of the (0002) planes (Fig. 2), which are exposed to the growth direction. The *c*BN crystals are preferentially oriented with their (111) planes parallel to the (0002) *t*BN planes [the preferred orientation is also evident in the transmission electron diffraction (TED) pattern of Fig. 1]. In some locations the orientation is not perfectly parallel and it deviates up to 5°. The disorder of the *t*BN(0002) planes and enlarged planar spacing in some areas affect the ideal 3:2 ratio between the *c*BN and the *t*BN planes, which is not always observed. Reducing the substrate bias from -120 to

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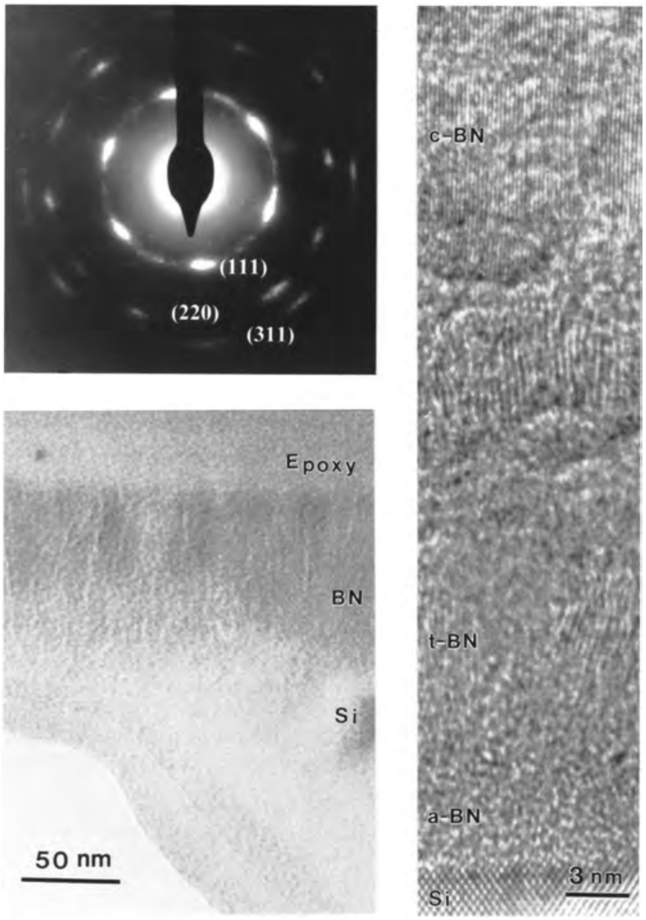

FIG. 1. TEM of the BN film deposited with a base pressure of 10^{-9} Torr; bottom-left corner: low-magnification image of the film and substrate; right: a HRTEM image showing the layered growth of the BN film; upper-left corner: a TED pattern taken at the top of the BN film indicating (111), (220), and (311) *c*BN planes. Note the oriented growth nature of the TED pattern.

-50 eV induces a significant change in both the *t*BN and *c*BN structures by introducing a second type of orientation which is mixed with the conventional one described earlier. The *t*BN in this region is more randomly oriented with large curvatures of the (0002) planes. The curling of the *t*BN basal planes is randomly distributed in different directions, so that most of the film growth surface in this region consists of curved *t*BN planes rather than plane edges. The *c*BN crystals in this region seem to start nucleating on the *t*BN basal planes (Fig. 3) with no preferential orientation between the *c*BN and *t*BN planes, and a random orientation to the substrate. The *t*BN thickness needed to initiate *c*BN nucleation increases with decreasing bias (and formation of *t*BN curled planes) from $\sim$25 to $\sim$150 nm. The stress buildup in the second type of *c*BN neighborhood seems to be much smaller than in the first one so that the maximal thickness obtainable without delamination was 100 nm ($\sim$75 nm net *c*BN) and over 500 nm ($\sim$350 nm net *c*BN) for biases of -120 and -50 V, respectively.

The formation of the oriented *t*BN layer is generally considered to result from the compressive stress induced by the ion bombardment. McKenzie and co-workers[8,12,13] argue that the observed orientation is due to the reorganization of the *t*BN layers in their most compressible way, minimizing the Gibbs free energy (GFE). Cardinale *et al.*[14] show that the minimal GFE is achieved for a 45° tilt of the basal planes from the substrate leading them to suggest that the plastic deformation of the BN results in the observed orientation of the *t*BN basal planes. An alternative explanation suggested by Lifshitz and co-workers[15–17] for carbon films is the preferential displacement of atoms in the direction perpendicular to the basal planes (C–C bond energy $\sim$0.8 eV) with respect to the displacements in the plane (bond energy 7.4 eV). It is interesting to point out that Kulik *et al.*[16] and Lifshitz *et al.*[17] indeed found a compression in oriented graphitic layers grown at elevated substrate temperatures in accord with a stress-induced mechanism. The reported spacing of the *t*BN layers is, however, larger by 5%–15% than that of crystalline *h*BN, in accord with our present work, similar to the carbon films obtained by Lifshitz *et al.* for high-energy (20 keV), room-temperature depositions.[17] This may indicate the significance of the preferential displacement in orientation of the *t*BN layers rather than the role of compressive stress, which should lead to smaller spacing of the basal planes with respect to the hexagonal graphite phase rather than the ob-

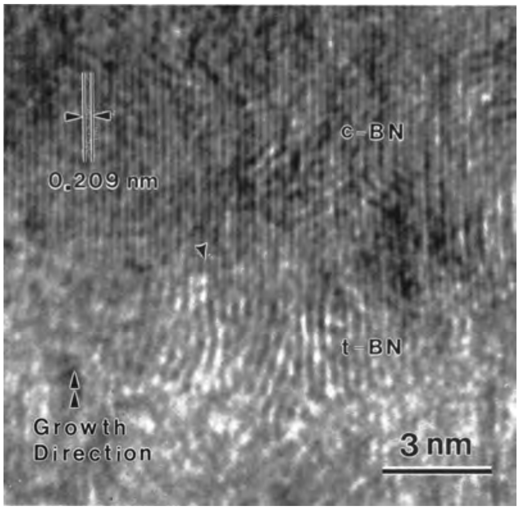

FIG. 2. High-resolution image taken at the *c*-BN/*t*-BN interface. The cubic phase nucleate at the very edge of the oriented *t*-BN(0002) plane, with the *c*BN(111) planes along the growth direction.

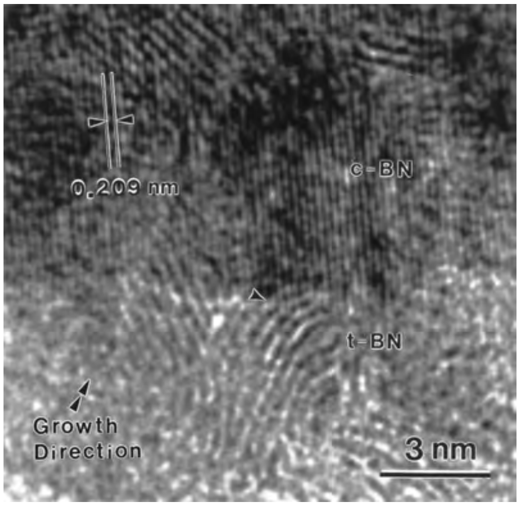

FIG. 3. High-resolution image taken at the *c*-BN/*t*-BN interface. The cubic phase nucleated at the curled plane of the *t*-BN is not oriented either to the *t*BN planes, or to the growth direction.

served larger spacings. The formation of curled *t*BN planes for lower bias conditions (lower ion energies) reported here may be either due to a smaller amount of displacements or owing to conditions favoring reorganization to the minimal GFE state (as suggested by Cardiole *et al.*[14] In both cases it is unclear whether a significant local stress in the films already exists at the *t*BN layer or only evolves later in the subsequent *c*BN layer.

The next issue is the nucleation of *c*BN crystallites on the top of *t*BN layers. This nucleation and orientation relation is associated with the geometrical similarity and the close match (a ratio of ~3:2) between the *h*BN(0002) spacing (3.33 Å) and the *c*BN(111) spacing (2.06 Å).[1,11,18,19] The nucleation of *c*BN (cubic diamond) on the edges of (0002) planes of *h*BN (graphite) was proven to be energetically favorable.[18,19] The edges of the (0002) planes thus provide nucleation sites for the formation of the cubic phase. The additional conditions necessary for the formation of critical cubic nuclei (*c*BN or cubic diamond) are still unclear and different mechanisms[1] have been suggested (sputter, stress, thermal spike, subplantation). Our present data, however, show the existence of another type of nucleation sites different from the (0002) edges, i.e., curved (0002) planes. Collazo-Davila and co-workers,[20,21] who studied BN nanoarches, proposed without experimental evidence that curling sp^2 structures might serve as *c*BN nucleation sites due to the sp^3 character of B–N–B bonds in curled sp^2 bonded sheets. The present work is in accord with their speculation. This nucleation site is different from the previous one in at least two ways: (i) it leads to a randomly oriented growth of *c*BN with respect to the *t*BN layers or the initial substrate, and (ii) the further growth of the *c*BN layer is associated with a reduced stress. At present, we cannot suggest any clear mechanism for the formation of the critical *c*BN nuclei on the curled *t*BN plane although it is most probably associated with less stress than on the *t*BN edges, supporting the likelihood of one of the other mechanisms (not related to stress).

The stress buildup in the *c*BN layer (responsible for most of the stress accumulation and BN film delamination) can be associated with two different reasons: (1) oriented growth of *c*BN layers on (0002) *t*BN edges, and (2) energetic ion impact. The stress reduction reported here can thus be attributed to either the formation of a nonoriented *c*BN component or to the reduction of the ion energy. Recent data of Zhang and Matsumoto[22] indicate that ~10-μm-thick, low-stress *c*BN films can be grown using a slightly larger bias than ours (-85 to -150 V), where the *c*BN crystallites are 100% nonoriented. The films deposited by us contain a mixture of *c*BN crystallites with a maximal fraction of nonoriented *c*BN of ~30%. This means that our films still contain a significant amount of stress due to the oriented *c*BN component. By the similarity to the work of Zhang and Matsumoto[22] it is reasonable that by optimizing our deposition conditions to acquire only the second type of *c*BN crystallites we could remove the stress generated in *c*BN layers and be able to deposit thick *c*BN films. It should be noted that some reduction of stress buildup and increase of *c*BN film thickness was claimed to be achieved by reducing the bias after completion of the nucleation stage,[1,23,24] indicating that the ion energy *per se* may also affect the stress buildup. We, nevertheless, emphasize that our deposition temperature was relatively low (450 °C, compared to 900–1200 °C for the thicker, low-stress films produced using lower ion energies). It would be thus difficult to distinguish between temperature annealing and ion energy effects in the cited works.

To summarize, we have identified a growth environment for *c*BN crystallites additional to its oriented growth on the edges of (0002) *t*BN planes. We have shown that nonoriented *c*BN crystallites are grown on curled (0002) *t*BN planes. The film stress is reduced and the maximal thickness of the BN films before delamination increases with the increasing fraction of the nonoriented *c*BN component from ~0% to 30%. Both growth types require a UHV base pressure since O is deleterious to *c*BN growth. These findings contribute to the understanding of *c*BN growth mechanisms and may be optimized for the formation of thick, stress-free *c*BN films.

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