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Formation of BN nanoarches: Possibly the key to cubic boron nitride film growth

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The formation of epitaxial nanotubes (nanoarches) on the surface of hexagonal BN (*h*-BN) during electron irradiation is reported. In addition to implications in terms of understanding fullerene based structures, we suggest that these act as the nucleation sites for cubic BN (*c*-BN) growth and may lead to improved film growth. We also report a strong dependence upon the microscope vacuum, which may be critical in understanding irreproducibility in film growth. © *1998 American Institute of Physics.* [S0003-6951(98)02503-0]

Cubic BN coatings could find widespread use in the cutting tool industry owing to its high hardness (second only to diamond) and to its chemical inertness towards ferrous alloys (diamond reacts with iron at high temperatures) and oxidation resistance.[1] It also has potential uses as a wide band-gap semiconductor. While there have been a few reports of *c*-BN grown in thin film form using laser ablation[2] or metal–organic chemical vapor deposition,[3] most research in the field has employed ion-bombardment assisted growth techniques to obtain the cubic phase.[4–12] However, the exact role the ions play in the nucleation and growth process is poorly understood; understanding and then controlling it would represent a significant step towards achieving a viable production process for making high quality films, since the ion bombardment is responsible for compressive stresses which lead to cracking and delamination for a film thickness of only 200 nm.[4]

The actual microstructure of *c*-BN films will have some bearing later, and will therefore be briefly described here. High resolution electron microscopy (HREM) studies of cross-sectional samples reveal a layered growth sequence.[5,6] First, a layer of amorphous material ~ 2 nm thick forms between the BN and the substrate [typically Si(001)]. Next an ordered layer of turbostratic BN (*t*-BN) extends for ~ 5 nm. Turbostratic BN has the same sp^2 bonded sheets found in *h*-BN, but there is both rotational and translational disorder between the graphitelike layers along the *c* axis. The *t*-BN seen in the HREM studies is oriented such that the *c*-axis lies in the plane of the growing film with the edges of the sp^2 bonded sheets exposed on the growth surface. Finally, the *c*-BN is seen to form on top of the oriented *t*-BN layer. Recent results show that the *c*-BN crystals are preferentially oriented with (111) type planes parallel to the oriented sp^2 bonded sheets in the *t*-BN layer.[7] The texture seen in the films is noteworthy, and it has been postulated that the exposed edges of the sp^2 bonded sheets serve as nucleation sites for the cubic phase.[8]

In most of the published models, nucleation is treated as secondary and the emphasis is placed on growth. In the compressive stress model the ions serve to build up enough compressive stress to make the cubic phase thermodynamically favorable.[9] The preferential sputtering model holds that the ions sputter away the unwanted hexagonal phase and leave the cubic phase intact.[10] And in the subplantation model, instead of preferential sputtering, preferential damage of the hexagonal phase is assumed to occur due to a lower displacement energy threshold relative to the cubic phase. Also, displaced atoms sitting in interstitial sites lead to a densification of the film, thus favoring sp^3 bonding.[11] All of these models offer explanations of how bombardment sustains *c*-BN deposition, but it may be that the key effect of the ions is to form the initial *c*-BN nuclei, and that the bombardment is unimportant for further homoepitaxial growth. It has already been recognized that the optimal conditions for nucleation may differ significantly from those for growth.[12] If the ions are only required for nucleation, then relatively thick films of *c*-BN might be grown free of the ion-induced compressive stresses which contribute to cracking and delamination.

The *h*-BN used in our study was prepared by crushing a 99.5% pure bulk sample in methanol and then dispersing the suspension on a 1000 mesh gold grid. Samples were then placed into transmission electron microscopes and subjected to intense electron bombardment. One set of images was collected at 1 MeV electron energy and 20 A/cm^2 current density, while a second set of images was recorded at 300 keV and ~ 50 A/cm^2. Electrons with 1 MeV (300 keV) energy can impart up to 431 eV (85 eV) to boron atoms and 307 eV (60 eV) to nitrogen atoms in direct knock-on collisions with the atomic nuclei. Assuming that the energy required to displace an atom from the *h*-BN lattice is close to the value found for graphite, 30 eV,[13] the electron irradiation will be able to produce atomic displacements in the BN sample. The bombardment used to grow *c*-BN is typically 200–1000 eV argon ions. Since the mass of argon is close to the masses of boron and nitrogen, an argon ion will be able to transfer most of its energy to either a boron or nitrogen atom in an elastic collision. Therefore, the atomic displacements produced by the electrons in our study occur in the same energy range as those produced by ion irradiation during growth of a *c*-BN film.

Figure 1 shows HREM micrographs of a region of *h*-BN before and after 10 min of intense electron irradiation at 300 keV. The electron beam was oriented perpendicular to the $(1\bar{2}10)$ planes in the *h*-BN lattice. In the 1 MeV electron irradiation experiments, the curling seen in Fig. 1(b) occurred with less total irradiation time even though the beam

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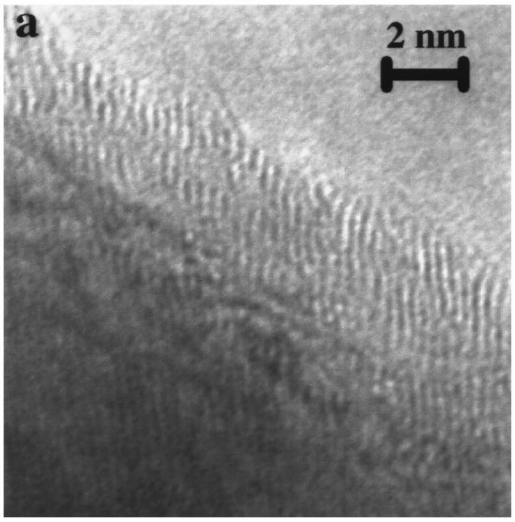

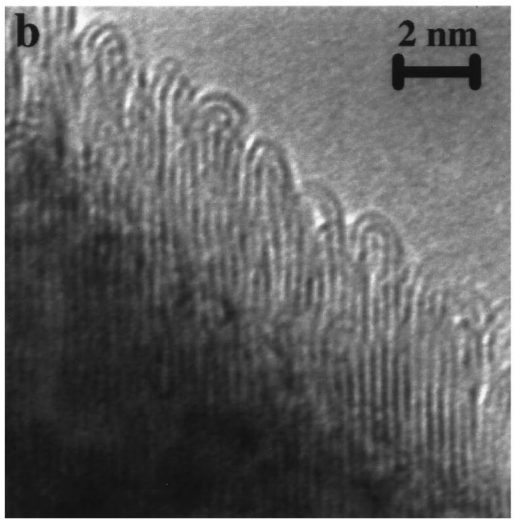

FIG. 1. HREM pictures taken in Hitachi H-9000 microscope operating at 300 kV beam voltage. (a) Hexagonal BN sample looking perpendicular to (1210) plane before intense electron irradiation. Dark lines correspond to sp^2 bonded sheets viewed edge-on. (b) Same region after 10 min exposure to 50–100 A/cm^2 electron beam with 300 keV incident energy.

current was less. This indicates that knock-on events are important, so electron irradiation is a good model of what will be taking place under ion bombardment during growth. The nanoarches are essentially half nanotubes epitaxially capping the ends of the sp^2-bonded sheets. The cylindrical nature and epitaxy was verified by tilting the specimen and observing that the fringe contrast disappeared. Most of the half nanotubes have widths of 1–1.7 nm, corresponding to four to six sp^2 sheets across the diameter of a tube. Figure 2 depicts a simple model structure for a 1 nm diameter tube. Using 1 nm as the tube diameter and taking the B–N bond distance to be unchanged from the 0.145 nm sp^2 value, we find that a B–N–B bond is bent by $\sim 12°$ as projected along the tube axis. This is a significant fraction of the corresponding value of 54.7° for the projected angle for pure sp^3 bonds suggesting a

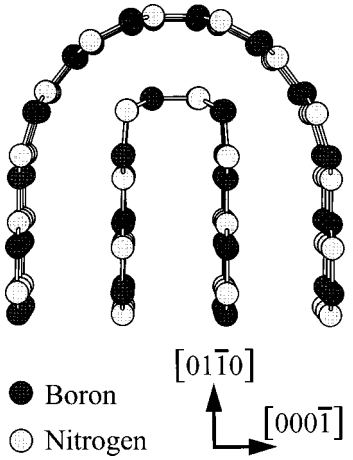

FIG. 2. Simple model depicting atomic structure of a nanoarch.

strong sp^3 character for the bonds in the tube. The bending angle could be even greater for some bonds if the curvature is not symmetrically distributed along the circumference of the tube. EELS spectra from BC_2N nanotubes showed that the boron atoms stay in sp^2 hybridized states while the nitrogen atoms alter their bonding towards sp^3 hybridization.[14]

An additional result that has practical implications in terms of the growth is worth mentioning: curling of the *h*-BN graphitic sheets was sensitive to the vacuum conditions. The pictures in Fig. 1 were obtained on a specially-designed Hitachi H-9000 microscope operating at 1×10^{-10} Torr vacuum in the specimen region. The same results were obtained on a high voltage microscope in Japan operating at 1×10^{-8} Torr for the 1 MeV irradiations. However, when the experiment was repeated several times in two other Hitachi H-9000 microscopes operating at $\sim5\times10^{-7}$ Torr, no curling of the graphitic sheets was seen for electron irradiations up to an hour at 300 keV incident energy and ~50 A/cm^2 current density. This result does not indicate an instability in the nanoarches, since exposure of arches produced in the 1×10^{-10} Torr vacuum to air did not affect their structure in any way determinable through HREM. Rather, we believe that the poorer vacuum environments blocked the formation mechanism of the arches.

The curling of sp^2-bonded sheets under intense electron bombardment and the formation of onionlike structures has been well-documented in the case of carbon,[15–17] and more recently for *h*-BN.[18] However, the well ordered semicylindrical capping every four to six graphitic layers seen in this study has only been reported previously for high temperature and/or high pressure treatments.[19,20] Interestingly, total energy calculations suggest that the interface between the basal plane edges in *h*-BN or *t*-BN and the (112) plane of *c*-BN is stable,[8] and nucleation of diamond along the basal plane edges in graphite has been observed experimentally.[21] We believe that these additional results taken together with ours make a compelling case that nanotube formation is the key to *c*-BN formation, and depends not just upon the flux and energy of the ions during growth but also upon a previously hidden variable, the residual vacuum. This mechanism of *c*-BN nucleation suggests exciting possibilities for the ion-free homoepitaxial growth of relatively thick films which do not crack and delaminate from the substrate; for instance,

higher energies may be appropriate (plus stringent vacuum control) to nucleate the cubic phase but not for subsequent growth.

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