

Microstructure of highly oriented, hexagonal, boron nitride thin films grown on crystalline silicon by radio frequency plasma-assisted chemical vapor deposition

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We present a high-resolution electron microscopy study of the microstructure of boron nitride thin films grown on silicon (100) by radio-frequency plasma-assisted chemical vapor deposition using B_2H_6 (1% in H_2) and NH_3 gases. Well-adhered boron nitride films grown on the grounded electrode show a highly oriented hexagonal structure with the c -axis parallel to the substrate surface throughout the film, without any interfacial amorphous layer. We ascribed this textured growth to an etching effect of atomic hydrogen present in the gas discharge. In contrast, films grown on the powered electrode, with compressive stress induced by ion bombardment, show a multilayered structure as observed by other authors, composed of an amorphous layer, a hexagonal layer with the c -axis parallel to the substrate surface and another layer oriented at random. © 1996 American Institute of Physics. [S0021-8979(96)04422-2]

In recent years, an important research activity has been directed to the preparation of boron nitride (BN) thin films by several low-pressure physical vapor deposition (PVD) and chemical vapor deposition (CVD) methods, to be used as protective coatings and as dielectric layers in many optical, mechanical, and electronic applications.¹⁻³ This is due to the outstanding properties of BN, such as optical transparency, chemical inertness, hardness, high electrical resistivity, high thermal conductivity, and low dielectric losses. In thin film form, BN can crystallize in various phases depending on preparation conditions. Among them are the hexagonal (h -BN) structure, similar to that of graphite but insulating, the cubic (c -BN) structure analogous to that of diamond, and an amorphous (a -BN) structure. Successful deposition techniques of c -BN, considered as a promising material for tribological and high-temperature electronics applications, all make use of ion bombardment during deposition, thought to be an essential condition. However, this involves a high compressive stress, which limits the film thickness and often leads to poor adherence or even cracking and delamination.⁴ Such problems do not occur in the case of noncubic BN, believed a good candidate dielectric material for sub-half-micron microelectronics technology.⁵

Since the work of Kester *et al.*,⁶ several researchers have reported cross-sectional high-resolution transmission electron microscopy (HRTEM) studies of the structure of BN films obtained by ion beam-assisted PVD methods⁷⁻¹⁰ and radio frequency (rf) bias magnetron sputtering.¹¹ These studies revealed a multilayered structure of the films, composed of an initial few-nanometer-thick a -BN layer next to the Si substrate, followed by an h -BN layer with the c -axis parallel to the substrate surface, and finally by a c -BN layer. The preferred orientation of the intermediate h -BN layer is

thought to be a result of the increasing biaxial compressive stress in the film, induced by ion bombardment.¹² Without bias or ion assistance, it has been shown that the hexagonal layer grows with the c -axis normal to the substrate and c -BN is not formed. For BN films prepared by CVD methods, there is a lack of similar HRTEM studies in the literature, although infrared absorption measurements of films grown by inductively coupled rf plasma CVD^{13,14} and magnetic field-enhanced rf plasma-assisted CVD¹⁵ are in agreement with the layered structure observed in PVD films.

We report here, for the first time, a cross-sectional HRTEM analysis of BN films obtained by rf plasma-assisted CVD (RF-PACVD). The films were prepared in an rf (13.56 MHz) capacitively coupled planar diode reactor by glow discharge decomposition of B_2H_6 (1% in H_2) and NH_3 (pure) gases. Optical transparent films, with thicknesses between 100 and 800 nm, were deposited on polished crystalline Si(100) substrates with native oxide layer, placed either on the powered electrode (cathode) or on the grounded electrode (anode). After heating the substrates at 300 °C in a vacuum (10^{-4} Pa) for several hours, NH_3 and B_2H_6 - H_2 gases were consecutively admitted to the reaction chamber through separate gas lines and their flows were regulated by mass flow controllers. The deposition conditions were: substrate temperature, 300 °C; pressure, 30 Pa; rf power density, 0.5 W/cm²; B_2H_6 - H_2 flow rate, 50 sccm; and NH_3 flow rate, 5 sccm. Anodic films, deposited at a rate of 1 nm/min, showed good adherence to substrate, whereas cathodic ones (5 nm/min) did not and often cracked when exposed to atmosphere. The infrared spectra of both films showed absorption peaks at about 1400 and 800 cm⁻¹, characteristic of h -BN and/or a -BN, but did not show the c -BN absorption at about 1100 cm⁻¹. It should be noted that successful PACVD processes for the growth of c -BN films use N_2 and inert gases because it is considered that hydrogen inhibits the growth of

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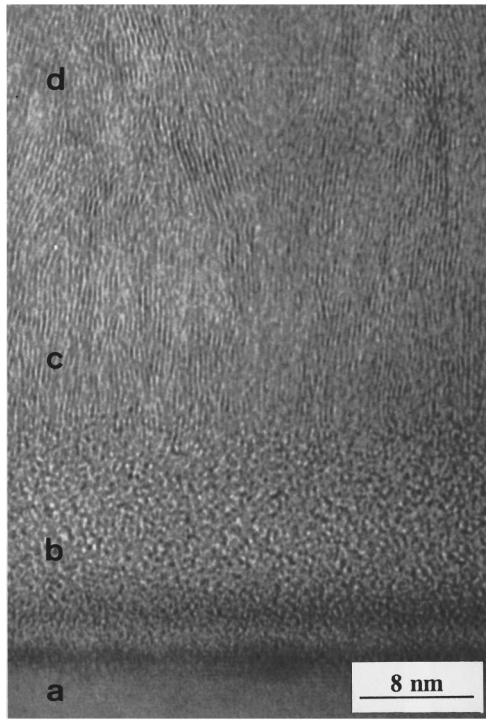


FIG. 1. Cross-sectional HRTEM image of a 600-nm-thick BN film grown on the cathode showing (a) Si substrate, (b) α -BN interfacial layer, (c) h -BN oriented layer, and (d) h -BN randomly oriented layer.

c -BN,^{3,15} which differs from the CVD synthesis of diamond films. In spite of the high concentration of hydrogen in the plasma, the hydrogen content in the films was less than about 5%, as evaluated from the very weak N–H absorption bands which appeared in the infrared spectra. Adherent films were stable and did not show noticeable changes in their infrared spectra after being exposed to air for several months.

Cross-section specimens were prepared using a standard sandwich-type procedure, including diamond saw cutting, sample glueing, mechanical grinding and polishing, and argon-ion milling at room temperature. HRTEM and dark field (DF) images as well as selected area diffraction (SAD) patterns were recorded using a Philips CM30 electron microscope operating at 300 kV. Figure 1 shows a cross-sectional HRTEM image of a BN film grown on the cathode. A layered microstructure is observed. Close to the Si substrate there is an amorphous layer about 15 nm thick, most possibly α -BN although an Si–O–B–N mixing layer cannot be ruled out. Above there is a 15-nm layer showing fringes highly oriented perpendicular to the substrate surface. The SAD pattern of this layer [Fig. 2(a)] shows two arcs indexed as (002) reflection of h -BN, along with continuous rings corresponding to (100) and (110) reflections of h -BN. The structure observed is consistent with the turbostratic modification of h -BN observed in PVD films, namely h -BN crystallites with the c -axis oriented parallel to the substrate surface but randomly oriented in this plane. Above this layer, the film exhibits numerous domains without preferred orientation and the (002) reflection on the SAD pattern [Fig. 2(b)] shows a continuous circle instead of arcs. It should be noted that the preferred texturing of the intermediate h -BN layer, with the

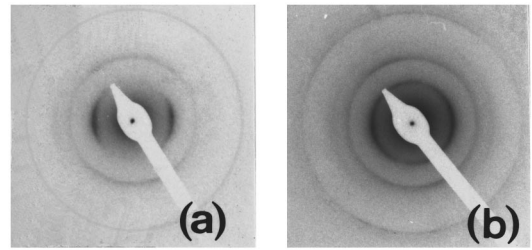


FIG. 2. SAD patterns of h -BN regions shown in Fig. 1 near (a) and far (b) from the interface with substrate.

c -axis parallel to surface substrate, is a prerequisite for growing c -BN films. The observation of this texturing in the film grown on the cathode agrees with the compressive stress model proposed by McKenzie¹² since, as a result of the self-bias voltage developed in the substrate electrode (–180 V), the impact energy of incident ions onto the growing film is high enough, in our case, to promote a preferential texturing of the h -BN layer but not high enough for the formation of c -BN.

Figure 3 shows a cross-sectional HRTEM image and SAD pattern of a BN film grown on the anode. The absence of amorphous interface should be emphasized, although the native Si oxide layer was not removed before deposition. The low film deposition rate, combined with the cleaning effect of an hydrogen-rich plasma on Si oxide surfaces,¹⁶ could explain the reduction of Si native oxide during the first stages of BN growth. Interestingly, a textured microstructure is observed throughout the film, showing h -BN lattice fringes aligned nearly perpendicular to the substrate with an interplanar distance of about 0.35 nm. The SAD pattern

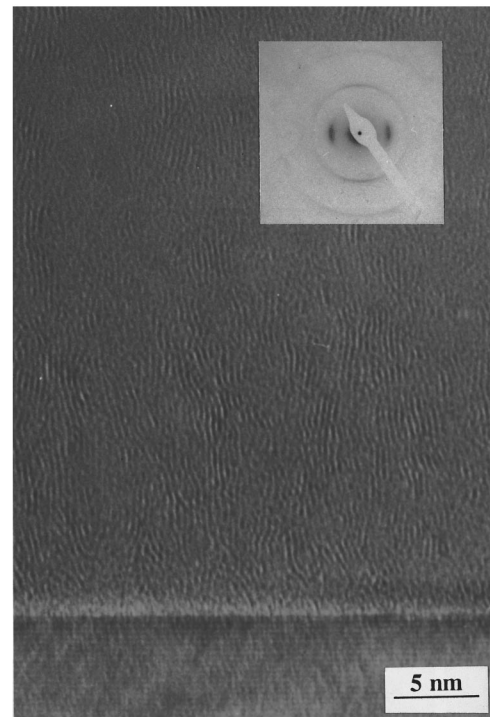


FIG. 3. Cross-sectional HRTEM image and SAD pattern of a 150-nm-thick BN film grown on the anode showing a h -BN oriented structure.

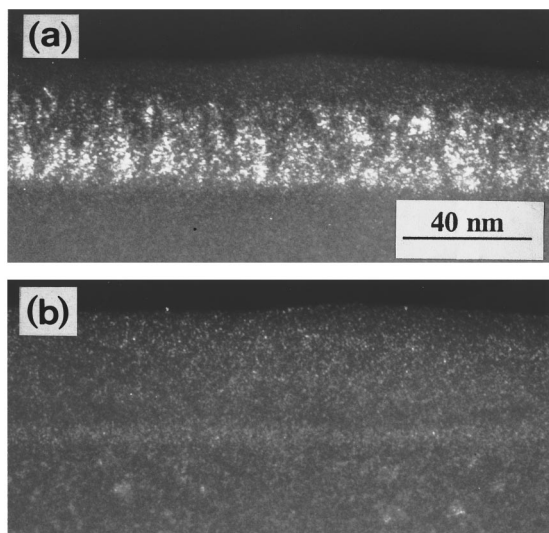


FIG. 4. TEM dark field images of film shown in Fig. 3. Bright areas in each picture show the (002) *h*-BN planes (a) perpendicular and (b) parallel to substrate Si(100) surface. The whole film thickness is not shown because of the ion milling hole on top.

shows two bright arcs, corresponding to *h*-BN(002) reflection along with continuous rings ascribed to (100) and (110)*h*-BN reflections. This orientation is corroborated in the DF image shown in Fig. 4(a), obtained by tilting the incident beam so that the beams diffracted towards the arcs passed through the objective aperture. In such conditions, bright areas denote *h*-BN crystallites contributing to (002) reflection and having their *c*-axis parallel to the substrate surface. However, such a contrast is not observed in the DF image of Fig. 4(b) made using the dark part of the (002) *h*-BN ring.

It should be noted that this textured *h*-BN growth, without an interfacial amorphous layer, has been achieved without the need of high compressive stress induced by ion bombardment since, for films grown on the anode, the energy of incident ions is only of a few tens of eV, the same order as the plasma potential. One possible explanation for the observed texture of *h*-BN in the absence of strong ion bombardment conditions might be related to an etching effect of hydrogen atoms present in the gas discharge, favoring the growth with the *c*-axis parallel to the substrate surface. The same textured growth has been observed in sputtered aluminum nitride films with a gas mixture containing H₂, whereas

without H₂ the films grew with the *c*-axis normal to the substrate.¹⁷ This result would allow the subsequent growth of *c*-BN, and even of diamond, by lattice matching in analogy with the enhanced nucleation of diamond at the edges of vertically arranged graphite planes,¹⁸ and thus it could help to elucidate whether the compressive stress is a necessary condition for the growth of *c*-BN.

In conclusion, we show the possibility of growing textured *h*-BN films that adhere well to crystalline Si substrates, without an interfacial amorphous layer, in a low-temperature PACVD process under soft ion-bombardment conditions. This texturing is a first requisite for the growth of *c*-BN films and should allow the growth of diamond on these films.

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