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Phase identification of boron nitride thin films by polarized infrared reflection spectroscopy

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Six different types of boron nitride films were investigated by polarized infrared reflection spectroscopy. Films with a highly cubic, mixed cubic and noncubic, and exclusively noncubic phase composition were synthesized using ion beam assisted deposition. Additionally, postdeposition argon ion irradiated cubic and noncubic boron nitride films as well as a nitrogen implanted boron sample were analyzed. Using this technique, besides the cubic phase, two different noncubic modifications, layered anisotropic and amorphous, could be distinguished. A preferential orientation of the normal axis of the sp^2-bonded basal planes parallel to the substrate surface was observed. © *1996 American Institute of Physics.* [S0003-6951(96)03627-3]

Infrared spectroscopy is the main characterization tool for boron nitride thin films as the peak positions in the IR spectra of cubic and hexagonal BN are well separated. Mostly absorption measurements in transmission mode[1,2] have been reported, and only a few were performed in reflection geometry on metals using unpolarized light.[3,4] With these techniques, different sp^2-bonded phases have not been identified. According to cross-sectional transmission electron microscopy (XTEM) viewgraphs,[3] *c*-BN containing films exhibit a layered structure. A few nanometers of randomly oriented sp^2-bonded BN are formed at the substrate interface, followed by a vertically oriented sp^2-bonded structure and the cubic phase on top. Albeit, the surface is terminated by an sp^2-bonded layer with a thickness of a few nanometers, as seen in *in-situ* electron loss spectra.[1] The aim of the present communication is twofold. First, we will show that polarized infrared reflection (PIRR) spectroscopy is capable of identifying different, i.e., layered or amorphous, sp^2-bonded phases in BN films. Second, spectroscopic evidence will be presented for the vertical basal planes found by XTEM. However, it is neither possible to resolve the substrate interface nor a superficial layer with a thickness of several monolayers using this technique.

The BN samples were synthesized by ion beam assisted deposition (IBAD),[1,3] using an ion energy of 500 eV and normal angle of incidence, on ⟨100⟩ silicon wafers heated to 400 °C. The ion (nitrogen and argon) to boron atom (I/A) arrival ratio was varied between 1.6 and 2.0, resulting in an increasing cubic fraction in the films with increasing I/A-ratio. Additionally, one sample was prepared by evaporating boron without ion assistance.

Using plasma immersion ion implantation (PIII),[5,6] some BN samples were post-deposition implanted with 40 keV argon ions for modifying the near surface region of the films. In this PIII experiment, the sample is immersed in a plasma and pulsed with a high voltage at repetition rate of 100 Hz or less. This results in a high dose rate of 1.67×10^{16} cm^{-2} s^{-1} during the 30 μs pulses, far beyond the range of commercial ion implanters. A high dose rate may lower the amorphization threshold as reported by Kalish and Prawer.[7] As the average power density is 120 mW/cm^2 or less, the temperature during the implantations remained below 100 °C. For this energy, the mean projected range, as calculated with TRIM,[8] is 26 and 41 nm in cubic (density $\rho = 3.5$ g/cm^3) and noncubic ($\rho = 2.2$ g/cm^3) BN, respectively. The dose was varied between 10^{13} cm^{-2} and 10^{15} cm^{-2}. It can be assumed that at least the highest dose results in an amorphization of the surface region. A 200 nm thick boron film was implanted using PIII with a nitrogen plasma and 20 kV pulses at a dose of 10^{17} cm^{-2} to form an amorphous boron nitride surface layer by direct ion implantation. The projected range corresponds to a quarter of the film thickness. All doses were calibrated by RBS measurements on silicon reference samples.

PIRR spectra were recorded at angles of incidence Φ of 45° or 60° using a wire grid polarizer on a BaF$_2$ or CaF$_2$ substrate. The angle α between the plane of incidence of the IR beam and the plane formed by ion source, substrate, and evaporator during deposition (ISE plane) was rotated in steps of 45°. The PIRR setup and the data acquisition and reduction have been described in Ref. 9.

PIRR spectra at different angles α are shown of a noncubic BN film in Fig. 1(a), a film containing a cubic fraction in Fig. 1(b), and a highly cubic film in Fig. 1(c). The spectra recorded with *s*-polarized light show only the response of the transversal optical (TO) modes and are similar to published transmission spectra,[1,2] whereas the *p*-polarized spectra exhibit a larger dynamic range and additional features due to longitudinal optical (LO) modes. The BN bending mode shows up at 760 cm^{-1} and the TO and LO in-plane stretching mode around 1400 and 1600 cm^{-1}, respectively. The shoulder in the spectra measured with *s*-polarized light at about 1500 cm^{-1} is due to the anisotropy of the *h*-BN crystal.[10] In the following, the changes in the reflection spectra related to the bending mode are not discussed as it is hard to draw definite conclusions from the small changes. Beyond that, in Fig. 1(b) the structure between 1000 and 1200 cm^{-1} arises from the *c*-BN TO mode. Structures due to the *c*-BN LO mode cannot be seen clearly in this figure. Compared to the noncubic film, the low energy side of the sharp

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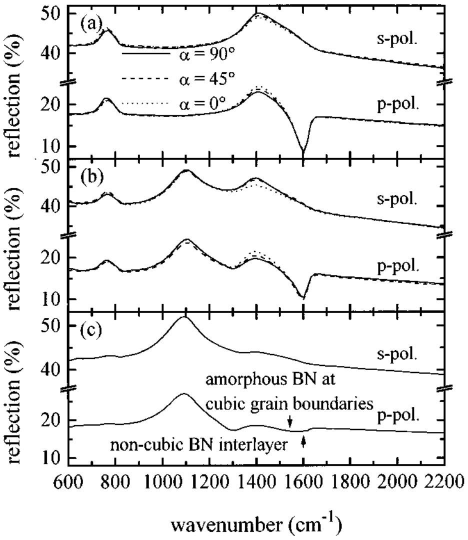

FIG. 1. PIRR data ($\Phi = 45°$) taken at different angles α for (a) a noncubic BN film ($I/A = 1.6$), (b) a *c*-BN containing film ($I/A = 1.8$), and (c) a highly cubic film ($I/A = 2.0$). The plane of incidence of the IR beam was rotated in (a) and (b).

LO stretching peak is asymmetrically broadened. The most striking feature of all the spectra in Figs. 1(a) and 1(b) is that, by varying the angle α, the peak intensity of the anisotropic BN TO stretching mode changes markedly, whereas the shape of the LO peak is not affected. In Fig. 1(c) the spectra of an almost pure *c*-BN sample are shown. Here the *c*-BN LO mode can be detected at 1300 cm^{-1}. Whereas the *s*-polarized spectra do not show any clear feature, a double structure in the *p*-polarized spectra at 1550 cm^{-1}, evolving from the corresponding shoulder in Fig. 1(b), is observed.

Implanting argon with subsequently higher doses into a 150 nm thick film with an initially high cubic fraction results in a decreasing *c*-BN peak intensity, as can be seen in Fig. 2. Albeit the intensity is not reduced to zero as only the upper part of the film is amorphized. Additionally a more prominent feature at 1550 cm^{-1} develops in the *p*-polarized spectra, clearly distinguishable from the LO stretching mode already present. Figure 3 shows a 200 nm thick film of noncubic BN before and after implantation with 10^{15} cm^{-2} Ar. A broadening at the low energy side of the TO stretching mode appears, accompanied by a reduction of the peak height. Near 1550 cm^{-1} a kink appears in the *p*-polarized spectra.

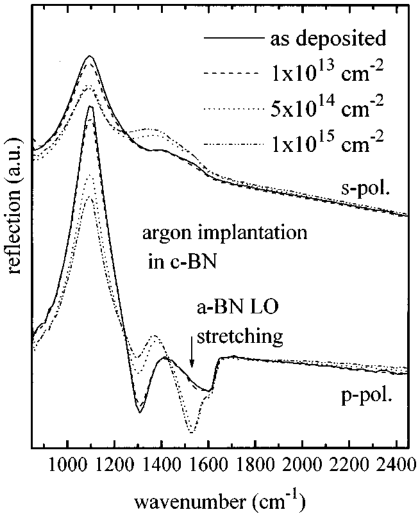

FIG. 2. PIRR data (wire grid polarizer on CaF$_2$ substrate, $\Phi = 60°$, $\alpha = 90°$) before and after implantation with argon (40 keV) at different doses.

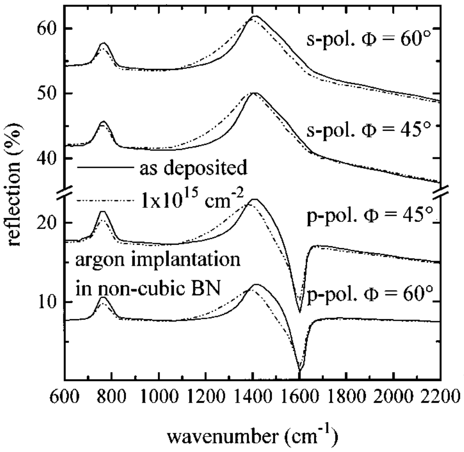

FIG. 3. PIRR data ($\alpha = 90°$) of non-cubic BN before and after argon (40 keV) implantation.

In Fig. 4 the reflection spectra of the boron film with an ion-nitrided, fully amorphous BN surface layer, which superficially look like the spectra of noncubic BN [see Fig. 1(a)], are shown although closely examined, there are outstanding differences. The LO stretching mode appears at 1550 cm^{-1}, with no peak discernible at 1600 cm^{-1}, the maximum of the TO mode is shifted to lower energies (1350 cm^{-1}) and exhibits no anisotropic structure. No changes could be observed in the spectra when the angle α was varied, in contrast to the samples shown in Figs. 1(a) and 1(b).

Summarizing the experimental results, three different BN phases can be detected; cubic BN exhibits a TO and LO mode at 1100 and 1300 cm^{-1}, respectively. Two noncubic sp^2-bonded phases can be distinguished with the help of PIRR. The anisotropic layered phase shows a double peak TO stretching mode at 1400 cm^{-1} and the corresponding LO stretching mode at 1600 cm^{-1}. The modes at 1350 and 1550 cm^{-1} can be attributed to an amorphous sp^2-bonded isotropic BN phase. In this modification the shift of the modes to lower energies can be explained, as suggested by

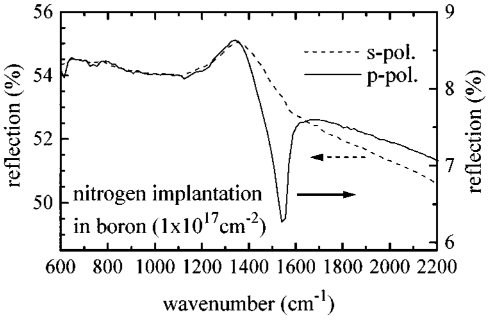

FIG. 4. PIRR data ($\Phi = 60°$) of a boron film with a nitrided surface layer using plasma immersion ion implantion.

Nemanich,[11] by a bond length which is larger than the next neighbor distance in the sp^2-bonded planes. The amorphous phase can be produced by nitriding boron at ion energies large compared to usual IBAD energies (see Fig. 4), or high dose ion irradiation induced damaging of BN thin films (see Figs. 2 and 3), as expected for the present experimental parameters. Furthermore this modification has been observed in the *c*-BN containing film [see Fig. 1(c)]. For this material it can be assigned to sp^2-bonded boundaries at nanocrystalline cubic grains, which were reported by Zhou *et al.*[12] A surface layer is not conceivable as the signal arising from a few monolayers cannot be resolved with the technique used.

A noncubic anisotropic interlayer on top of the silicon substrate, showing vertically oriented sp^2-bonded planes, has been found in XTEM viewgraphs.[3] From these pictures, no information about a preferential orientation of the normal axis can be obtained. The variation of the TO stretching mode at 1400 cm^{-1} with a changing angle α, as seen in the spectra of Fig. 1, is a strong indication of a preferential orientation of the normal axis in the plane of the substrate. This result is surprising as the ions impinge normal to the substrate and the boron atoms arrive at an off-normal angle in our IBAD setup. However, the relative orientation to the ISE plane cannot be inferred at the present stage.

In the films with a high cubic fraction the *p*-polarized reflection spectra related to the isotropic amorphous phase at 1550 cm^{-1} is clearly distinguishable from the contribution arising from the anisotropic modification. This offers the possibility to quantify the relative amounts of noncubic material within the cubic phase compared to the anisotropic BN interlayer next to the substrate.

As these results, i.e., distinction between anisotropic and amorphous sp^2-bonded BN and a preferrential orientation of the basal planes, were only seen in the spectra recorded with *p*-polarized light, PIRR is an ideal method to characterize boron nitride thin films. To resolve the layered growth, obtain the preferential orientation, and quantify the absolute thicknesses of the different phases, a numerical simulation of the spectra is necessary and in progress. In conclusion, PIRR can be used as a routine diagnostic tool which complements selected electron microscopy viewgraphs.

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