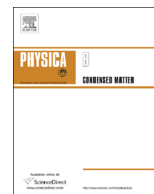




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Boron nitride: A new photonic material



M. Chubarov^a, H. Pedersen^a, H. Högberg^a, S. Filippov^a, J.A.A. Engelbrecht^b,
J. O'Connell^b, A. Henry^{a,*}

^a Department of Physics, Chemistry and Biology, Linköping University, SE-581 83 Linköping, Sweden

^b Nelson Mandela Metropolitan University, Port Elizabeth, South Africa

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ABSTRACT

Rhombohedral boron nitride (r-BN) layers were grown on sapphire substrate in a hot-wall chemical vapor deposition reactor. Characterization of these layers is reported in details. X-ray diffraction (XRD) is used as a routine characterization tool to investigate the crystalline quality of the films and the identification of the phases is revealed using detailed pole figure measurements. Transmission electron microscopy reveals stacking of more than 40 atomic layers. Results from Fourier Transform InfraRed (FTIR) spectroscopy measurements are compared with XRD data showing that FTIR is not phase sensitive when various phases of sp^2 -BN are investigated. XRD measurements show a significant improvement of the crystalline quality when adding silicon to the gas mixture during the growth; this is further confirmed by cathodoluminescence which shows a decrease of the defects related luminescence intensity.

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1. Introduction

Boron nitride (BN) is today the least investigated and hence understood III-nitride material and now gathers researchers' interest due to its amazing properties and close similarities with the polytypes of carbon. BN is a wide band gap semiconductor which can be used for optoelectronic devices working in the UV range; the band gap of BN is comparable to AlN, but its properties are not fully understood since various values have been reported for the band gap energies, in both experimental and theoretical studies, with discussion regarding its nature (direct or indirect). Ultra-violet emission at 215 nm (5.765 eV) has been observed from hexagonal BN (h-BN) small single crystals obtained under high-pressure and temperature conditions [1]. Recently, h-BN epilayers grown by metal organic chemical vapor deposition (MOCVD) were demonstrated to exhibit a very efficient band gap emission close to 5.5 eV, which was found polarized perpendicular to the *c*-axis and with intensity two orders of magnitude higher than AlN. The estimated band edge absorption coefficient was also higher than that of AlN [2]. Kobayashi et al. reported the growth of a 500 nm thick h-BN film on Ni (1 1 1) substrate, which exhibits a near-band-gap ultraviolet luminescence at 227 nm [3]. This group proposed that h-BN film can be used as a release layer for

mechanical transfer of AlGaN-based devices [4] due to its ability of easy exfoliation. These various results are good indicators for BN to be a candidate for optical applications, especially in the deep UV region.

The synthesis of semiconducting BN epilayers of high crystalline quality and with controlled electrical conductivity is urgently needed for the fundamental understanding of this interesting material towards the exploration of possible applications. However, high quality epitaxial thin films of BN are difficult to grow, and in the literature majority of reports shows that the grown films contain significant amounts of various phases. It should be noted that BN can form compounds with either sp^3 -hybridized (cubic (c-BN) or wurtzite (w-BN) form) or sp^2 -hybridized (h-BN or rhombohedral (r-BN) phase) bonds. For the most investigated phase of BN, viz. c-BN, generally polycrystalline films are reported. Ion bombardment during the deposition process is regarded to be necessary for the nucleation of c-BN films and maintaining the sp^3 -hybridization of the bonds [5,6]. Hence, energetic ion-assisted physical vapor deposition including rf and magnetron sputtering as well as ion-beam assisted deposition have been the choice for the c-BN deposition. This means that, due to the growth mechanism, the obtained BN material contains many structural defects, fact which results in poor crystalline quality.

The chemical route represents a more gentle deposition process and CVD techniques operated at high energy regime like plasma enhanced CVD techniques have been used. Very few attempts have been reported on the BN synthesis by processes without the use of energetic deposition and those approaches seem to favor the formation of sp^2 bonded phases.

* Corresponding author. Tel.: +4613 282 414; fax: +4613 142 337.

E-mail addresses: mihcu@ifm.liu.se (M. Chubarov), henke@ifm.liu.se (H. Pedersen), hanho@ifm.liu.se (H. Högberg), stafi@ifm.liu.se (S. Filippov), Japie.Engelbrecht@nmmu.ac.za (J.A.A. Engelbrecht), jacques.oconnell@gmail.com (J. O'Connell), anne.henry@liu.se (A. Henry).

We recently reported the epitaxial growth of sp^2 -BN films on sapphire with an AlN buffer layer using thermally activated CVD [7] and using X-ray diffraction (XRD) pole figure measurements, we demonstrated that the BN films had a twinned rhombohedral crystal structure [8]. High quality r-BN is also found to be promoted by using a Si containing environment during growth [9].

In this paper we describe in more detail results obtained from the characterization of this material and especially reveal some of the difficulties encountered.

2. Material and methods

Epitaxial growth of r-BN is done in a horizontal hot-wall chemical vapor deposition reactor using ammonia (NH_3) and triethyl boron (TEB) as nitrogen and boron precursors, respectively, and (0 0 0 1) sapphire as substrate. An AlN buffer layer is formed by in-situ nitridation prior to the BN growth [7,8]. The growth is carried out at low pressure (typically 100 mbar or lower) with H_2 as carrier gas in the temperature range of 1200–1500 °C and with an N/B-ratio close to 700.

XRD was applied for the characterization of the deposited BN layers and first routinely in the Bragg-Brentano geometry using the $Cu K\alpha_1$ radiation. This was done first in a powder diffractometer (PANalytical X'Pert PRO) for low-resolution θ - 2θ measurements, but a PANalytical EMPYREAN MRD instrument was used for high resolution θ - 2θ and ω measurements as well as to record pole figures. Cross-sectional specimens for transmission electron microscopy (TEM) were produced by two different approaches; either by conventional mechanical polishing followed by Ar^+ ion milling at 5 keV at a grazing angle of 5° or by milling and thinning the sample using a FEI Helios NanoLab 650.

For phase identification we also applied Fourier Transform InfraRed (FTIR) spectroscopy, which is a non-destructive and rapid technique and can be performed either in reflection or transmission mode. We measured FTIR reflectance in a Bruker 80 V FTIR/Raman spectrometer with an incidence angle of 15° and 4 cm^{-1} resolution. Micro-Raman measurements were performed in LabRAM HR800 equipped with a single grating monochromator with an excitation at 659 nm of approx 60 mW and $100\times$ lens. Cathodoluminescence (CL) measurements were performed in a Leo 1550 field-emission gun scanning electron microscope equipped with a MonoCL2 system (Oxford Res. Instr.) at low temperature (typically $T < 10\text{ K}$) and using electron beam energy of 10 keV.

3. Results and discussion

3.1. Growth results and XRD

At optimal growth conditions ($T=1500\text{ °C}$, 70 mbar, N/B=650) rhombohedral epitaxial layers were obtained as proven by XRD analysis and particularly Pole figure measurements revealed a twinned structure of the rhombohedral BN (r-BN) films. Fig. 1a illustrates a typical XRD θ - 2θ scan diffractogram of one of the layers. The sharp peak of highest intensity at 41.69° is associated to the reflection from the (0 0 0 6) plane of the sapphire substrate and more weakly the reflection from the Al_2O_3 (0 0 0 3) plane is detected at 20.50° . Note that this peak corresponds to a forbidden reflection which, as the name implies and according to the structure factor of the sapphire lattice, should not be visible in diffraction experiments but becomes visible due to the kinetic scattering of the X-rays. Contribution from the AlN buffer is also observed at 36.04° corresponding to the (0 0 0 2) plane reflection; the 0002 AlN peak is rather broad which suggests that the buffer layer is thin and strained. We have demonstrated that high quality relaxed AlN layer

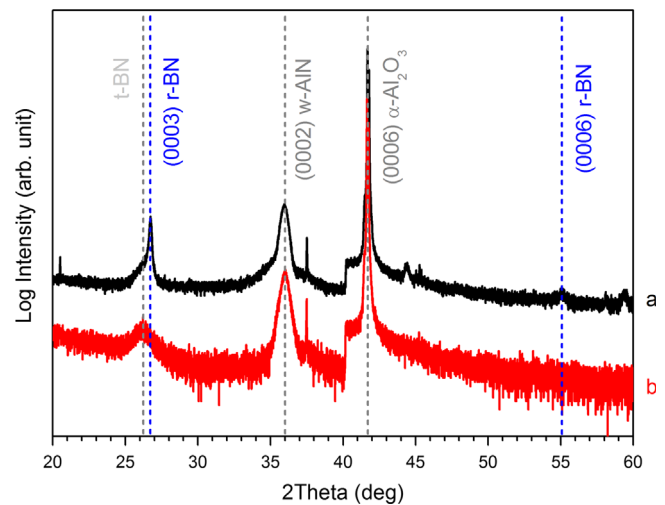


Fig. 1. X-ray diffractions pattern measured in the Bragg-Brentano configuration for (a) a high quality epitaxial r-BN and (b) a t-BN layer.

which exhibits very sharp 0002 peak in θ - 2θ scan XRD does not promote the growth of r-BN and only turbostratic BN (t-BN) is deposited [7]. t-BN differs from the two crystalline sp^2 phases of BN, h-BN and r-BN, by a larger spacing between the basal planes ($\geq 3.35\text{ \AA}$) and a lack of stacking sequence. Peaks observed in the range from 44° to 46° originate from the sample holder and the sharp peak at 37.51° is due to the $CuK\beta$ line diffraction on the sapphire (0 0 0 6) planes. The peaks associated with r-BN are at the 2θ angles of 26.71° and 55.06° (with an error of $\pm 0.01^\circ$) which correspond to reflections from the (0 0 0 3) and (0 0 0 6) planes, respectively. It should be noticed here that reflections from the (0 0 0 2) and (0 0 0 4) planes of h-BN will also give rise to XRD peaks at the same positions since the two sp^2 -BN phases, r-BN and h-BN, have similar spacing between the basal planes (3.325 \AA and 3.33 \AA for h-BN and r-BN, respectively) but differ with their stacking sequences (ABAB... and ABCABC... stacking for h-BN and r-BN, respectively). To distinguish between these two sp^2 phases a first approach is possible with the intensity ratio of these two peaks: the peak at lower angle (26.71°) is 25 times higher in intensity than the peak at higher angle for the r-BN phase and about 17 times for h-BN bulk material [10]. For our layers when a sharp and intense peak is observed at or very close to 26.71° , the peak at 55.06° can be distinguished from the background and the intensity ratio of the two peaks is typically 25, and even as high as 27 for few layers. A second technique is the use of XRD pole figure measurements which reveal that the r-BN layers have a twinned rhombohedral structure 30° rotated with respect to the sapphire substrate [8]. The rotation is in fact due to the 30° rotation of the AlN buffer layer on sapphire [11]; the sp^2 -BN crystal grows directly on the AlN template. During the pole figure measurements an angle 2θ of 50.15° and 45.57° for h-BN and r-BN, respectively, corresponding to the reflection of the $\{0\ 1\ \bar{1}\ 2\}$ planes has been used. For the case of h-BN six peaks around the Φ axis should be observed with a separation of 60° , (Fig. 2a) whereas only 3 peaks with 120° separation are predicted for r-BN (Fig. 2c). In the measurement using a 2θ angle of 50.15° (Fig. 2b) only three distinct peaks are observed. Due to the limited thickness and low electron density of the sp^2 -BN film and the fact that the measurement is done without monochromatic beam, contribution for the substrate can be expected which will complicate the interpretation of the results. This is the case here since sapphire has a diffraction from $\{0\ 2\ \bar{2}\ 4\}$ at 52.533° and those three peaks are attributed to the sapphire substrate. With a 2θ angle of 45.57° (Fig. 2d) 6 weak peaks are visible in the pole figure instead of 3 predicted for r-BN. This behavior reveals a twinning of the rhombohedral crystal structure.

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