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Linköping University Post Print

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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.

Keywords

Boron Nitride, epitaxy, XRD, TEM, FTIR, Cathodoluminescence

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 understand 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 (111) 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.

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 (0001) 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 Kα_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 Brucker 80V FTIR/Raman spectrometer with an incidence angle of 15º 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 100x 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 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 ºC, 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.1.a illustrates a typical XRD θ−2θ scan diffractogram of one of the layers. The sharp peak of highest intensity at 41.69º is associated to the reflection from the (0006) plane of the sapphire substrate and more weakly the reflection from the Al_2O_3 (0003) plane is detected at 20.50º. 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 36.04º corresponding to the (0002) 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 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 (≥ 3.35 Å) and a lack of stacking sequence. Peaks observed in the range from 44º to 46º originate from the sample holder and the sharp peak at 37.51º is due to the CuK_β line diffraction on the sapphire (0006) planes. The peaks associated with r-BN are at the 2θ angles of 26.71º and 55.06º (with an error of +/- 0.01º) which correspond to reflections from the (0003) and (0006) planes, respectively. It should noticed here that reflections from the (0002) and (0004) 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 (3.325Å and 3.33 Å 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 (26.71º) 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 26.71º, the peak at 55.06º can be distinguished from the background and the intensity ration 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 30º rotated with respect to the sapphire substrate [8]. The rotation is in fact due to the 30º 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 50.15º and 45.57º for h-BN and

r-BN, respectively, corresponding to the reflection of the {01$\underline{1}$2} planes has been used. For the case of h-BN six peaks around the Φ axis should be observed with a separation of 60°, (Fig.2.a) whereas only 3 peaks with 120° separation are predicted for r-BN (Fig.2.c). In the measurement using a 2θ angle of 50.15° (Fig.2.b) only three distinct peaks are observed. Due to the limited thickness and low electron density of the sp^2-BN film and the fact that the measurement is done without monochromatic beam, contribution for the substrate can be expected which will complicate the interpretation of the results. This is the case here since sapphire has a diffraction from {02$\underline{2}$4} at 52.533° and those three peaks are attributed to the sapphire substrate. With a 2θ angle of 45.57° (Fig.2.d) 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.

More close investigation of the 0003 peak (Fig.3), reveals that the peak is a contribution of two different peaks: a sharp peak at 26.71° with a full width at half maximum (FWHM) of only 0.16°, being the smallest reported value for any sp^2 BN phase, to the best of our knowledge, and a weak and broad (FWHM=1°) peak at 26.3° which is associated to the less ordered form of sp^2-BN, the turbostratic (t-BN). The t-BN peak at 26.3° appears when the growth is done at unfavorable conditions or when the r-BN lattice is damaged due to e.g. stress. An example of XRD pattern where only t-BN is visualized is given in Fig.1.b.

Since the 0003 peak of bulk r-BN is expected to be at 26.717° [10] XRD measurements show that we did obtain high quality r-BN films. However, this is achieved only with low growth rate (less than 200 nm/h). Increasing the B/H$_2$ ratio in the gas phase allows an increase of the growth rate, but with a degradation of the crystal quality as observed by an increasing basal plane spacing; the 0003 peak of r-BN is shifted from 26.72° to 26.56° for the samples grown at B/H$_2$ ratios of 0.01% and 0.07%, respectively. This increase of the basal plane spacing is proposed to be favored by incorporation of impurities such as carbon and/or oxygen atoms. Moreover XRD measurement reveals that films grown in presence of Si atoms exhibit better crystal quality, typically as presented in Fig.1.a, than those grown without Si which show generally a turbostratic structure as shown in Fig.1.b. When trying different types of coating (SiC, TaC and hot-pressed BN powder) for the susceptor we found that any presence of water and/or oxygen during BN CVD leads to deposition of mainly boron oxide films via incorporation of species containing a very strong B-O bond. We showed by thermodynamic calculations that these B-O bonds are formed already in the gas phase. Any oxygen contamination of the growth chamber thus prohibits the growth of high quality BN [12].

XRD ω-scan measurements have also been performed and confirm the formation of r-BN. The peak is rather broad with a FWHM of 1.1° which reveals stress in the material (see Fig.3.b).

3.2 SEM, TEM and exfoliation problem

The surface of an r-BN layer as observed with SEM is shown in Fig.4.a. Similar morphology has been observed for all investigated layers irrespectively of the sp^2 phase, r-BN or t-BN. The surface is rather rough with nanosize features on the surface. When manipulating the material an exfoliation is easy observed and examples with cross section SEM are given in Fig.4. In Fig.4.b part of the r-BN epilayer is lifted from the substrate and a rather dense r-BN material is observed with a thickness of about 2 μm covered by nanorods which could be as high as 2 μm without specific ordering or orientation. This is also visualized in Fig.4.c where part of the layer is still attached to the substrate (left and right part on the image) whereas others parts are exfoliated from the substrate, as at the center of this picture which shows an undulation of the layer. The total thickness of the dense layer is less than 1 μm whereas nano-sized rods reach few μm high. A second example is given in Fig.4.d, which occurred when preparing the sample for TEM investigation using polishing technique. The 400 nm thick layer is lifted from the substrate and a total ripple of the layer is observed. This shows the difficulty of preparing samples for further investigations such as TEM. As we have reported [8] in the case of the growth of high quality r-BN some amount of the t-BN can be formed and observed at the interface r-BN/AlN. t-BN could be formed due to the deterioration of the crystal structure which is mainly due to the difference in the in-plane linear thermal expansion coefficient between sp^2-BN and AlN/sapphire. While sapphire and AlN have a positive in-plane linear thermal expansion coefficient which increases with temperature, sp^2-BN has a negative coefficient in a wide temperature range. This results in severe stress in the grown material as it cools down after deposition at high temperature. In addition at high temperature (typically more than 1400 ℃) voids can appear in the sapphire substrate at the interface AlN/Al$_2$O$_3$ enhancing the exfoliation [13]. However, we succeeded to prepare specimens for cross sectional TEM and the image (Fig.4.e) shows up to 40 BN layers which is the largest number reported up till now in the literature, to the best of our knowledge. However, some stacking faults and grain boundaries are seen and other defected areas are also observed associated to the t-BN structure.

3.3 Optical characterization

FTIR measurements have been widely used for the characterization of BN, particularly for the phase composition when mixture of sp^2 and sp^3 forms appears. The peaks of interest for h-BN are at ~783 and 828 cm^{-1} corresponding to the out of plane vibration modes (B-N-B mode, transversal and longitudinal) and ~1367 and 1610 cm^{-1} which are from the in-plane stretching vibrations (B-N mode) [14]. Polarization dependence [15] as well as pressure dependence [16] have been reported for the sp^2 h-BN. However, to the best of our knowledge, r-BN has not been considered. As its crystalline structure is very close to that of h-BN we would expect similarity for the optical properties of these both phases. Typical spectra recorded for few films are shown in Fig.5 where the main structure below 1000 cm^{-1} is related to the sapphire substrate. The contribution from the AlN buffer layer is observed close to 675 cm^{-1}, and can be slightly shifted in wavenumber position from sample to sample. This peak is related to the transversal optic mode and the slight shift observed from the bulk value (671.6 cm^{-1}) [16] is interpreted as a consequence of the strain existing in the AlN buffer layer which also is at the origin of the broadening of the 0002 AlN peak observed at 36.04° in the XRD θ-2θ scan (see Fig.1). In the FTIR spectra the two peaks observed at 802 and 1370 cm^{-1} as indicated by an arrow in Fig.5 are associated to the out-of-plane bending vibration and in-plane stretching modes in r-BN. In addition, the B-N-B mode sometime has a broad background as in the case of Fig.5.d) which is not understood yet. The splitting of the B-N observed in Fig.5.a and b) is attributed to the two optical modes, transverse and longitudinal.

Most important is the appearance of these peaks which is found to be independent of the sp^2 phase (r-BN or t-BN, in our case) when compared with the XRD analysis. The labeling of each layer is noted in Fig.5 together with the results obtained from the XRD θ-2θ scans: as first example the curve a) and b) in Fig.5 are very similar whereas their associated XRD diffractograms differ in the same way than the both displayed in Fig.1. A second example is for the curve Fig.5.d, where the B-N-B mode is well observed whereas the B-N vibration is not detected and the XRD pattern for this layer is characteristic for r-BN. As mentioned the addition of small amount of SiH_4 to the gas mixture during sp^2-BN deposition improves the crystalline quality of the growing film and contributes to the growth of high quality epitaxial r-BN instead of less ordered t-BN film. SIMS composition measurements revealed an average concentration of Si in the low 10^{19} cm^{-3} range [9]. Nevertheless there are no indications of Si-N bonds in the FTIR spectra where a peak at about 850 cm^{-1} is expected.

Using Raman spectroscopy the characteristic peak for the in plane vibrations of sp^2 hybridized B-N is found at 1369 cm^{-1} (Fig.6). The peak is almost at the same position than previously reported for h-BN [14], similar peak position is expected for r-BN material since

same chemical bonds exist in h-BN and r-BN. In addition as indicated in Fig.6, the FWHM is found to be 30 cm^{-1} which reveals the high crystalline quality of the r-BN grown layer.

Low temperature CL measurements show difference in the luminescence spectra for layers grown with or without intentional addition of Si during the growth. Fig.7 shows the CL spectra recorded from two different layers and the inset of the figure shows the same spectra but with normalized intensity. First the total intensity is found to be 20 times higher when there is no Si addition to the gas mixture during the growth. We should notice here that due to the experimental set-up it was not possible to record the spectra at higher energy; the near band gap emission is thus probably not visualized in the recorded range. Moreover various bands are observed. The band at about 350 nm which is the most intense for the sample grown without addition of Si and decreases significantly in intensity when small amount of Si is added to the gas mixture, is typically assigned to carbon and oxygen related luminescence in h-BN [17]. In h-BN a band at 400 nm was assigned to native surface defects which are sensitive to oxygen ambient [18]. We observe other broad bands around 430, 505 and 570 nm which prove that the quality of the material needs further improvement.

4. Conclusions

Various characterization techniques, structural and optical, can be used to investigate the quality of sp^2-BN layers. Sharp XRD peaks at 26.71º and 55.06º are associated to the reflection from the (0003) and (0006) planes of the r-BN phase, whereas larger peak at 26.3 º is related to t-BN form. Pole figure measurements reveal a twinning of the r-BN structure. Using FTIR measurements vibration modes are observed at 802 and 1370 cm^{-1} and with Raman spectroscopy the in-plane vibration is found at 1369 cm^{-1}. However FTIR and XRD conducted on the same layers give different results; their complimentary is needed for a more fundamental understanding of the properties of the material especially for the r-BN phase which has not been investigated until now. Improvement of the crystalline structure is also confirmed by cathodoluminescence measurements which show a decrease of the intensity of the luminescence associated to defects for samples grown with addition of silane to the gas phase. Special preparation as for TEM or cross section experiments can influence the mechanical properties and induces change or destruction of the original phase. More work is needed to understand, more deeply, the growth mechanism of r-BN and its structural, physical and optical properties and thereby push the state-of-the-art quality of r-BN.

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Figure captions

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.

Fig.2: (102) pole figures of a) h-BN as predicted for a angle $\theta = 51.15°$ and b) as measured and (012) pole figures of c) r-BN as predicted for an angle $\theta = 45.57°$, and d) as measured. The red circles in the measured pole figure are for a better visualization of the peak positions.

Fig.3: a) High resolution XRD θ-2θ scan over the 0003 BN peak showing the contribution of r-BN and t-BN and b) ω-scan for the same layer. The peak positions obtained from the fitting procedure are indicated in the figure for the r-BN and t-BN, respectively. Their FWHM are found to be $0.16°$ and $1°$, respectively. For the w-scan the FWHM is $1.1°$.

Fig.4: a) Top view SEM image of a r-BN layer, b) and c) cross section SEM images showing exfoliation from the substrate, d) TEM image illustrating the total ripple of the r-BN layer and e) cross section TEM of a r-BN layer showing more than 40 basal planes.

Fig.5: FTIR spectra of 4 different BN layers. The spectra have been shifted along the Y-axis for a better visualization. The label of each layer is indicated as well as the phase association resulting form the XRD analysis.

Fig.6: µ-Raman scattering spectrum of r-BN film.

Fig.7: CL spectra of layers a) grown with addition of Si to the gas mixture and b) without addition of Si. The other growth parameters were the same (T=1500 ºC, p=70 mbar, B/N= 650 and B/H_2= 0.02%).
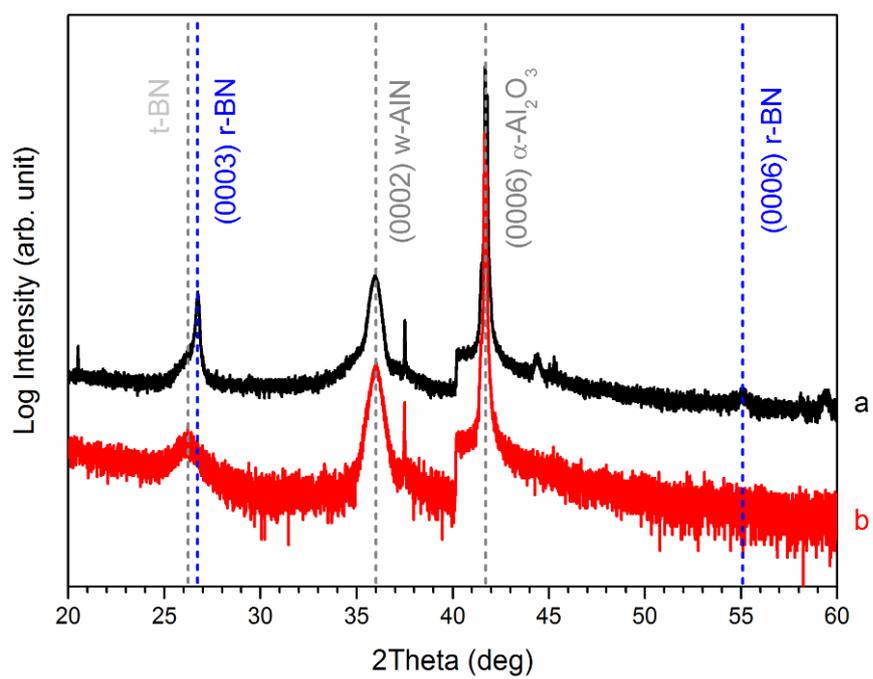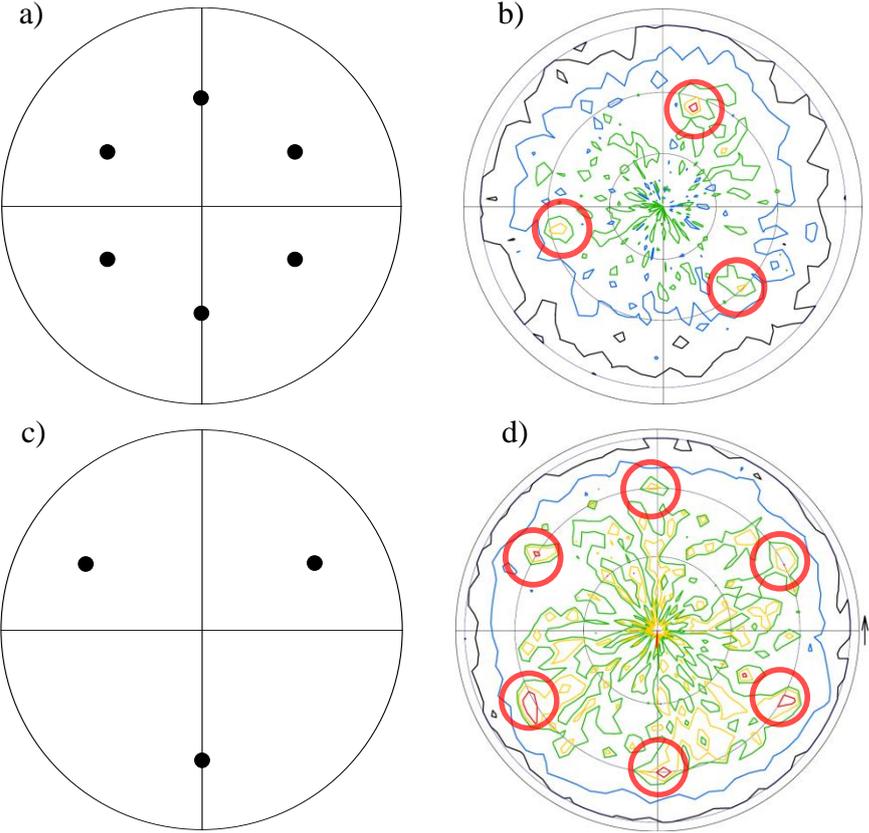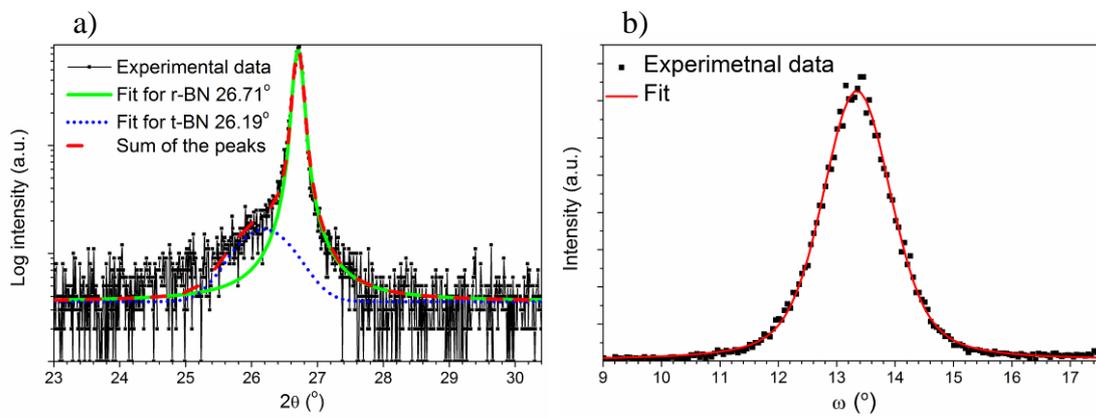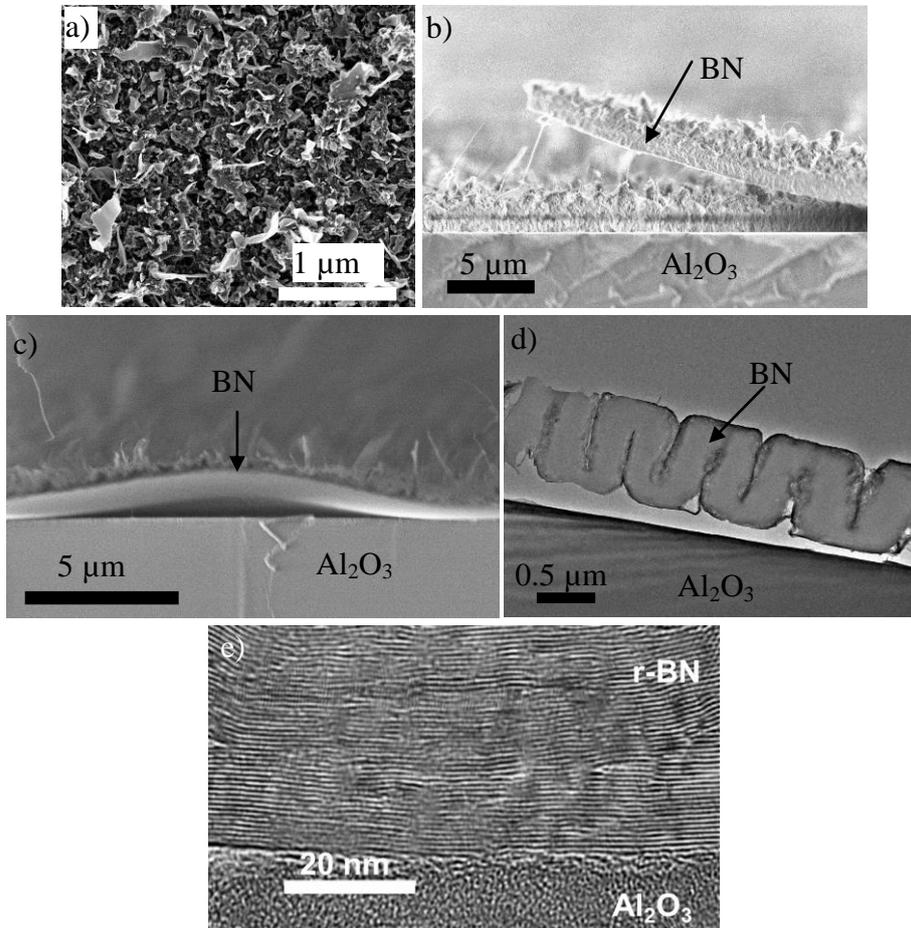
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