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Epitaxial CVD growth of sp^2 - hybridized boron nitride using aluminum nitride as buffer layer

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Epitaxial growth of sp^2 -hybridized boron nitride (BN) using chemical vapour deposition, with ammonia and triethyl boron as precursors, is enabled on sapphire by introducing an aluminium nitride (AlN) buffer layer. This buffer layer is formed by initial nitridation of the substrate. Epitaxial growth is verified by X-Ray diffraction measurements in Bragg – Brentano configuration, pole

figure measurements and transmission electron microscopy. The in plane stretching vibration of sp^2 -hybridized BN is observed at 1366 cm^{-1} from Raman spectroscopy. Time of flight elastic recoil detection analysis confirms almost perfect stoichiometric BN with low concentration of carbon, oxygen and hydrogen contaminations.

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1 Introduction Boron nitride (BN) is a multifunctional material consisting of equal proportion of B and N atoms. BN has a number of excellent properties analogue to diamond and graphite such as mechanical properties but also wide band gap [1;2], low dielectric constant, piezoelectricity and good stability at high temperatures [3]. Further, BN can easily be doped p- and n-type for electronic applications [2]. It is thus a promising material for many applications. However, BN is one of the least investigated semiconductors among the group III-nitrides. In the same way as carbon exists as graphite and diamond, BN can occur in sp^2 -bonded and sp^3 -bonded structures. The sp^3 -bonded forms include cubic (c-BN) and wurzitic (w-BN) phases whereas the hexagonal (h-BN) and the rhombohedral (r-BN) are the sp^2 -bonded phases. The h-BN form has a layer structure with a two-layered stacking sequence (ABAB... structure) whereas the r-BN phase has a three-layered stacking sequence (ABCABC... stacking). The fact that h-BN and r-BN have very similar spacing between the basal planes (3.325 Å and 3.33 Å , respectively) [4] and equal in-plane lattice parameter of 2.50 Å , makes distinction between them extremely difficult. Thus, they cannot be distinguished by common techniques as X-Ray diffraction (XRD) in Bragg – Brentano configuration, transmis-

sion electron microscopy (TEM), Raman spectroscopy, Fourier transform infrared spectroscopy (FTIR) or any composition measurements.

Films with sp^3 -bonded form (mainly c-BN) are generally deposited with “brutal force” such as by energetic ion-assisted physical vapour deposition. The use of more gentle deposition processes will favour the formation of sp^2 -hybridized structures. Synthesis of highly crystalline r-BN nanoplates has been reported [5], but monocrystalline epilayers remains to be demonstrated, to the best of our knowledge. Kobayashi et al. [2;6;7] showed that h-BN can be epitaxially grown by metal-organic chemical vapor deposition (MOCVD) on sapphire ($\alpha\text{-Al}_2\text{O}_3$) (0001), Ni (111) and 6H-SiC (0001) using triethyl boron (TEB) ($\text{B}(\text{CH}_2\text{CH}_3)_3$) and ammonia (NH_3) as precursors. However, their presented XRD data showed very broad h-BN peak. Younes et al. [8] presented CVD growth of h-BN on 6H-SiC and 4H-SiC on-axis (0001) substrates using diborane (B_2H_6) and ammonia with Ar as carrier gas. Broad h-BN related peaks with very low intensity characterized the XRD patterns and their TEM investigations revealed nanocrystalline rather than epitaxial growth of the film. Rye demonstrated hot filament activated CVD of polycrystalline h-BN from borazine ($\text{B}_3\text{N}_3\text{H}_6$) [9], however, no XRD

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measurements were presented although Raman spectroscopy showed a peak from sp^2 -hybridized BN (sp^2 BN). Recently, R. Dahal et al. [10] presented data on the epitaxial growth of h-BN, but confirmation of epitaxy is done by only XRD measurements in Bragg – Brentano configuration.

For the growth of sp^2 BN as semiconductor device material, the substrate should have a low lattice mismatch to h-BN and r-BN and be applicable to the electronic device manufacturing. Wafers of α - Al_2O_3 and 6H-SiC are both used in devices based on III-N materials today, sapphire being the less expensive choice. Both types of substrates have a significant lattice mismatch to sp^2 BN (lattice constants of 4.67 Å and 3.10 Å, respectively [4]). Single crystal Ni (111) shows a better lattice match to sp^2 BN (0001) (lattice constants of 2.49 Å and 2.50 Å, respectively [4,6]).

In this work we apply an AlN buffer layer on sapphire from this the lattice mismatch to sp^2 BN is reduced and the growth of epitaxial sp^2 BN crystalline films is enabled.

2 Experimental A hot wall chemical vapour deposition (CVD) reactor with a SiC coated graphite susceptor was used for the growth. The pressure during deposition was 100 mbar and H_2 was used as carrier gas. It was noted that the reactive chemical environment supplied by the hydrogen gas was needed, since no BN film was formed in experiments with an inert atmosphere of nitrogen or argon as carrier gas. Ammonia and TEB were used as precursor gases. Typical B/ H_2 molar fraction was 0.02 % and a N/B-ratio of 600 was used. Sapphire substrates, α - Al_2O_3 (0001), were employed at a typical growth temperature of 1500 °C. In order to reduce the lattice mismatch between α - Al_2O_3 and sp^2 BN (in-plane axis 4.67 Å and 2.50 Å respectively [4]) an AlN (in-plane axis 3.11 Å [4]) buffer layer was introduced. Formation of the AlN layer was achieved through nitridation of the α - Al_2O_3 surface [11;12] by introducing ammonia in the reactor with a NH_3/H_2 molar fraction of 0.13 % at the growth temperature for 10 minutes. The deposition of the BN film was initiated by adding TEB to the gas mixture and adjusting the ammonia flow after the nitridation step to obtain the required N/B ratio.

For characterization of the grown films, XRD in Bragg – Brentano configuration ($\theta - 2\theta$), pole figure measurements, TEM with energy dispersive X-ray spectroscopy (EDX), Raman spectroscopy with 363.84 nm excitation laser and time of flight elastic recoil detection analysis (ToF-ERDA) were applied.

3 Results and discussion Figure 1 presents diffractograms of the films grown on non nitridized sapphire substrate (FIG 1. A) and on nitridized sapphire (FIG 1. B), respectively. Only a peak from turbostratic BN (t-BN) at 26.3° is observed in the case of non nitridized sapphire substrate (FIG 1. A) while the film grown on nitridized substrate exhibited (0001) orientated sp^2 BN as evident from the XRD pattern (FIG. 1 B). Two peaks are thus observed which are related to either h-BN or r-BN at 26.7°

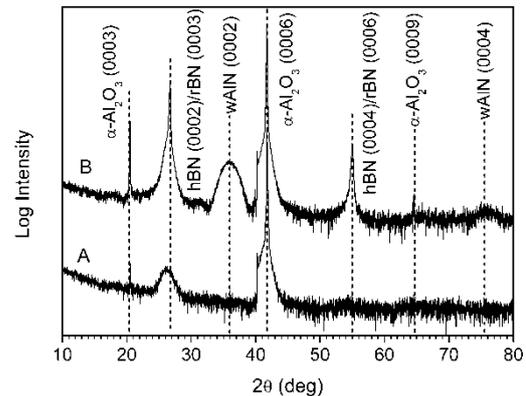


Figure 1 X-Ray diffractogram in Bragg – Brentano configuration of the sp^2 BN film grown on sapphire without AlN buffer layer (A) and with AlN buffer layer (B).

(0002 of h-BN or 0003 of r-BN) and 55.1° (0004 of h-BN or 0006 of r-BN), respectively [4]. The calculated spacing between the basal planes from the XRD-data is 3.30 ± 0.05 Å. The XRD result suggests that the grown sp^2 BN film is highly oriented since only peaks from the (0001) planes are observed for this measurement. Also for the AlN buffer layer only peaks originated from the (0002) and (0004) planes are found at 36.0° and 76.2° respectively, indicating that the AlN formed by nitridation grows as AlN (0001) on α - Al_2O_3 (0001), as previously reported [11;12].

As seen in FIG. 1, the AlN peaks are significantly broadened, which is an indication of a thin film as observed in the TEM image (FIG.2). A slight asymmetry on the left side of the peak at 26.72° of the sp^2 BN is most likely due to the minor inclusions of less ordered material, t-BN, near to the interface with AlN in order to compensate the lattice mismatch. The asymmetry in this case can also be explained by point defects in sp^2 BN near to the interface with AlN.

The cross sectional TEM image (FIG. 2) confirmed the epitaxial growth of sp^2 BN on the AlN buffer layer. In the micrograph the AlN and sp^2 BN planes are clearly discernible and allow a rough estimate of the c-axis lattice parameters for AlN and plane spacing for sp^2 BN which were found to be 2.45 ± 0.05 Å and 3.36 ± 0.05 Å, respectively.

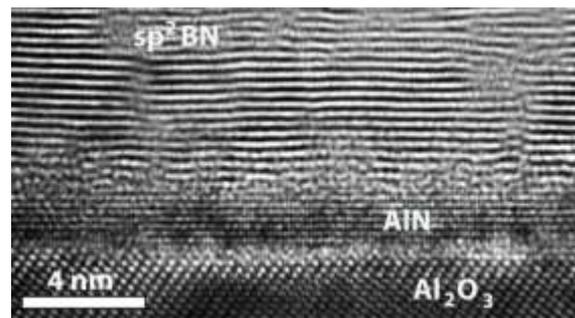


Figure 2 Cross section TEM micrograph of the Al_2O_3 /AlN/BN interface region.

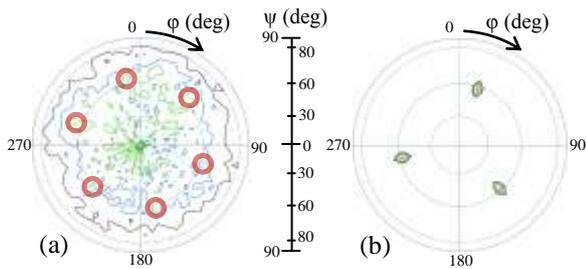


Figure 3 Pole figures of $\{01\bar{1}2\}$ planes of (a) r-BN and (b) Sapphire. The red circles are for a better visualization of the peak positions.

These lattice parameters for AlN and sp^2 BN are close to the previously reported 2.49 Å and ~3.33 Å, respectively [4]. It can also be noted that the c-axis parameter in AlN deviates more from the reference value close to the sapphire. Composition measurements using EDX showed a significant concentration of oxygen in the AlN buffer layer and in the interface between BN and AlN. The interface between BN and AlN appears less ordered in the micrograph. This may be attributed to initially different nucleation orientations or surface roughness, which is soon replaced by ordered epitaxial growth. Some grain boundaries can be seen in the sp^2 BN film, giving rise to seemingly less ordered features.

Pole figure measurements of $\{01\bar{1}2\}$ planes of h-BN and r-BN revealed that the film contains mainly r-BN. It is worth to note, that the detection of h-BN asymmetric reflections in the pole figure measurements is a complicated task since the weak intensity peaks of h-BN overlap with long tails of the high intensity sapphire asymmetric peaks. It is well known fact that AlN epitaxially grown on sapphire is 30° rotated around the c-axis with respect to the sapphire lattice and it is also true for nitridized sapphire [13]. From the pole figure measurements done on sp^2 BN samples and the fact that AlN crystal lattice is 30° rotated with respect to the sapphire lattice, it can be concluded that r-BN crystal directly grows on AlN layer and the r-BN crystal is thus 30° rotated with respect to sapphire (FIG. 3). Raman scattering measurements showed sp^2 -hybridized BN stretching vibrations within the basal planes at 1366 cm^{-1} and a full width at half maximum of 31 cm^{-1} . This Raman peak position is identical to the previously reported data for h-BN powder [14], however a similar peak position is also expected for r-BN material. Broadening of the Raman peak is probably due to the twin structure of the r-BN and also due to the inclusions of t-BN which are distortions in the periodicity of the crystal. Evidence of the twin structure of the r-BN crystal is observed by pole figure measurements (FIG.3 a), since only 3 reflections should be observed for r-BN $\{01\bar{1}2\}$ planes. This phenomenon has been previously observed for CVD grown r-BN nanoparticles [15].

The thickness of the film, as evaluated from TEM images is about 400 nm, corresponding to a growth rate of 100 nm/h.

The elemental composition in the bulk of the film, as evaluated by ToF-ERDA, was found to be 50 at% B and 49 at% N. This is, within the experimental uncertainty of the measurement, very close to what is expected for BN (uncertainty is 1 – 1.5 at% for these elements). The main observed impurities were H, O (~ 0.1 at%) and C (< 0.1 at% close to the detection limit), in total about 1 at% with H being the main contamination element.

4 Conclusions In summary, r- or h-BN with high crystalline quality was grown epitaxially by CVD on α -Al₂O₃ (0001) substrates. The epitaxial growth was enabled by introducing an AlN buffer layer which is formed through the transformation of the sapphire surface by nitridation. These results announce the possibility to further explore sp^2 BN for use in electronic applications.

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