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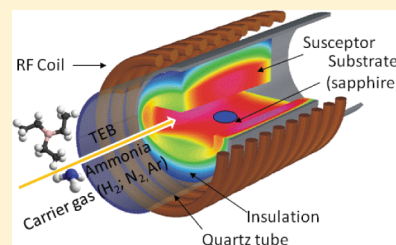
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Growth of High Quality Epitaxial Rhombohedral Boron Nitride

Mikhail Chubarov,* Henrik Pedersen, Hans Högberg, Jens Jensen, and Anne Henry

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

ABSTRACT: Epitaxial growth of sp^2 -hybridized boron nitride (sp^2 BN) films on sapphire substrates is demonstrated in a hot wall chemical vapor deposition reactor at the temperature of 1500 °C, using triethyl boron and ammonia as precursors. The influence of the main important process parameters, temperature, N/B ratio, B/ H_2 ratio, and carrier gas composition on the quality of the grown layers is investigated in detail. X-ray diffraction shows that epitaxial rhombohedral BN (r-BN) film can be deposited only in a narrow process parameter window; outside this window either turbostratic-BN or amorphous BN is favored if BN is formed. In addition, a thin strained AlN buffer layer is needed to support epitaxial growth of r-BN film on sapphire since only turbostratic BN is formed on sapphire substrate. The quality of the grown film is also affected by the B/ H_2 ratio as seen from a change of the spacing between the basal planes as revealed by X-ray diffraction. Time-of-flight elastic recoil detection analysis shows an enhancement of the C and O impurities incorporation at lower growth temperatures. The gas phase chemistry for the deposition is discussed as well as the impact of the growth rate on the quality of the BN film.



INTRODUCTION

The III–nitrides exhibit many interesting properties, in particular as semiconductor materials in optoelectronic devices, such as light emitting diodes (LED) and laser diodes (LD). AlN, GaN, InN, and their alloys cover a wide wavelengths range from IR to UV. Demands for devices operating in the UV range have increased the interest for the B–N system and the binary phases therein. Boron nitride can form compounds with either sp^3 -hybridized or sp^2 -hybridized bonds. The most studied sp^3 -hybridized phase is cubic (c-BN), but there is also a wurtzite phase (w-BN) that is an analogue to the previously mentioned III–nitrides AlN, GaN, and InN. The interest for c-BN mainly stems from the phase similarities to diamond. Unfortunately, high quality epitaxial thin films of c-BN are difficult to obtain, and most of the grown films contain significant amounts of other phases. Furthermore, c-BN films generally appear to be polycrystalline.^{1–4} Ion bombardment during the deposition process seems to be necessary for the nucleation of c-BN films by the formation of the sp^3 bonds. Hence, energetic ion-assisted physical vapor deposition including rf and magnetron sputtering as well as ion-beam assisted deposition have been the choice for BN deposition. The chemical route represents a somewhat more gentle deposition process and chemical vapor deposition (CVD) techniques operated at high energy regime-like plasma enhanced CVD techniques have been used.^{5,6} 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.

The sp^2 -hybridized BN (sp^2 BN) can crystallize into two different phases: hexagonal (h-BN) and rhombohedral (r-BN). These two phases can be regarded as two different stacking sequences of the same basal plane, where h-BN and r-BN have a lattice parameter along the *c*-axis of 6.656 Å and 10.000 Å, respectively (Figure 1). This feature gives a similar spacing between the basal planes for these two polytypes and makes

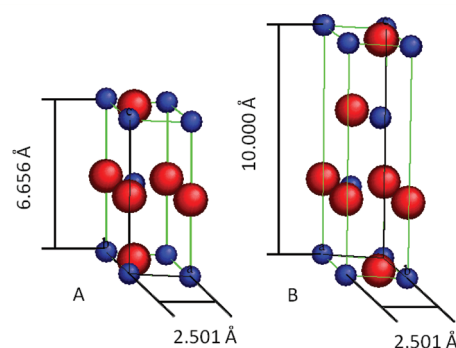


Figure 1. Crystal structures of sp^2 BN. (A) Hexagonal BN; (B) rhombohedral BN. The small blue spheres represent nitrogen atoms and the big red spheres boron atoms.

distinction of these structures difficult by transmission electron microscopy and X-ray diffraction (XRD) in Bragg–Brentano geometry.⁷ In addition, a less ordered form of sp^2 BN, the turbostratic BN (t-BN),⁸ is frequently observed in the growth of both sp^3 and sp^2 BN.

For the growth of sp^2 BN, thermal CVD is generally applied.^{9–12} A first report by Nakamura demonstrated the growth of polycrystalline h-BN at atmospheric pressure, using sapphire and silicon as substrates.¹³ A later study by Jin et al. using Si(100) as substrate reported the influence of various growth parameters on the film properties, but the deposited films exhibited a turbostratic structure.¹⁴ Recently, h-BN epitaxial films were grown on sapphire substrate and graphitized 6H-SiC using thermal CVD.¹⁵ The same group reports the growth of a 500 nm thick h-BN film on Ni(111)

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substrate, which exhibits a near-band gap ultraviolet luminescence at 227 nm. This result is an indicator that h-BN is a potential candidate for optical applications.¹⁶

Different boron precursors have been used in the published studies. An ideal precursor would seem to be borazine ($B_3N_3H_6$), having the desired 1:1 B/N stoichiometry.¹⁷ However, studies show that borazine yields t-BN films, which must be annealed to obtain polycrystalline h-BN films and these will still contain a high amount of t-BN and amorphous BN.^{17,18} In many CVD processes of binary compounds, the ratio of the precursors, e.g., the N/B ratio, is an important process parameter since it is used not only to control the nucleation and morphology of the deposited film but also to control the incorporation of impurities in the grown film. This is a reason to use a combination of separate precursors. As nitrogen precursor, ammonia (NH_3) is almost always used, whereas there are several choices for boron and boron-halides, e.g., BF_3 , BCl_3 , and BBR_3 have been used.^{19–21} For halide based processes, it is necessary to remove the halogen atoms generated from the growing surface, and for this, a high surplus of hydrogen is needed. Also the reaction products formed, i.e., HF, HCl, and HBr, are corrosive gases that may cause etching of the growing films. A less corrosive alternative is diborane (B_2H_6) that easily dissociates into reactive BH_3 species^{22–24} and is a standard gas in the Si industry, but diborane is highly toxic and explosive and should preferably be avoided. The organoboranes, trimethyl boron $B(CH_3)_3$ (TMB) and triethyl boron $B(C_2H_5)_3$ (TEB), are promising alternatives as boron precursors. It has been demonstrated that TMB is a highly reactive molecule that is rapidly decomposed, whereas TEB is more stable.²⁵ This property of TEB is important to better match the reactivity of ammonia. Furthermore, TEB can easily form BH_3 and three ethylene (C_2H_4) molecules,²⁵ thus yielding the same boron chemistry as diborane. The use of TEB as boron precursor has therefore been investigated in CVD of h-BN.^{9–12,26}

The choice of an appropriate substrate material is one of the main issues for the nucleation and the growth of a good quality epitaxial sp^2 BN layer without exfoliation. Silicon has been used to a large extent, probably due to its low cost and the further implementation with its well-established technology, even if there is a large (33%) lattice mismatch between the (0001) plane of BN and the (111) plane of Si. The use of metallic substrates has also been investigated, but when the nucleation of BN is observed, a poor adhesion of the film is reported.²⁷

Recently, we reported epitaxial growth of sp^2 BN films on sapphire, using AlN buffer layer.²⁸ This AlN (3.111 Å) buffer layer was grown to reduce the lattice mismatch between the sapphire substrate (4.671 Å) and the r-BN epilayer (2.501 Å). XRD experiments conducted only in the Bragg–Brentano configuration do not give enough information regarding the phase of the grown layer. Using pole figure measurements twinned rhombohedral crystal structure of the grown films was observed. The twinning of the crystal structure is revealed by the observation of 6 peaks in the pole figure instead of 3 predicted from the crystal symmetry (Figure 2). There were no peaks observed in the pole figure measurements related to the h-BN phase.

In the present article, a detailed investigation of the influence of the process parameters on the quality of the grown material is presented. The process parameters investigated are N/B ratio, deposition temperature, carrier gas, and B/ H_2 ratio. The influence of the buffer layer quality is also studied. The growth

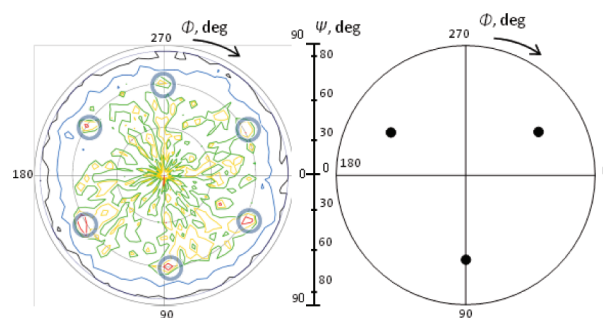


Figure 2. Left: pole figure of r-BN measured at 2θ of 45.57° that corresponds to $\{0112\}$ planes. Right: pole figure calculated for r-BN $\{0112\}$ planes. The blue circles are for a better visualization of the peak positions. The observation of 6 peaks in the measured pole figure instead of 3 predicted by calculated pole figure reveals twinning of the r-BN crystal.

rate dependence on the growth parameters as well as the correlation between growth rate and crystalline quality are discussed. A possible chemical reaction scheme for the deposition of BN is presented.

EXPERIMENTAL PROCEDURES

To enable higher efficiency in the dissociation of the precursors, a hot wall CVD reactor was used for growth; this type of reactor allows for a better lateral and vertical temperature homogeneity compared to a cold-wall CVD reactor and for a higher efficiency of the dissociation of the precursors.²⁹ As substrates, (0001) oriented sapphire cut into 1×1 cm² pieces were used. Prior to deposition, the substrates were cleaned using the RCA cleaning process.³⁰ As carrier gas and diluent, H_2 was mainly used with Ar and N_2 or a N_2/H_2 mixture as alternative carrier gases. The precursor gases were NH_3 as nitrogen source and TEB as boron source. The TEB was stored in a stainless steel bubbler, which was immersed in a water–glycol bath to ensure a constant temperature of $6^\circ C$ producing TEB vapor pressure of 27 mbar. The pressure in the bubbler was controlled using an electric pressure controller that was set to 600 mbar. To avoid parasitic reactions in the gas phase between TEB and NH_3 , these gases were separately introduced into the reactor and mixed 5 cm before entering the hot zone (susceptor).

The growth parameters studied were temperature (1300–1600 $^\circ C$), N/B ratio (300–1000), B/ H_2 ratio (0.005–0.07%), and carrier gas (pure hydrogen, hydrogen mixture with nitrogen, pure nitrogen, or pure argon). In most experiments, the process pressure and the carrier gas flow were kept at 100 mbar and 7 slm, respectively. For investigation of the N/B ratio influence, the concentration of boron in the carrier gas was kept constant at 0.02%, whereas the ammonia concentration was adjusted to achieve the desired N/B ratio. The influence of the B/ H_2 ratio was studied at lower pressure (70 mbar) and lower H_2 flow (5 slm) with the temperature set to 1500 $^\circ C$.

The AlN buffer layer was formed by nitridizing the sapphire substrate surface by feeding ammonia into the reactor³¹ 10 min prior to the r-BN deposition at the growth temperature. The estimated thickness of the obtained AlN layer is typically in the 1.5–3 nm range, as revealed in our previous work with high-resolution transmission electron microscopy.²⁸ The ammonia molar fraction in the carrier gas during nitridation was set to 13%. The growth of BN was then initiated by introducing TEB into the reactor and adjusting the ammonia flow to the desired N/B ratio.

XRD measurements in Bragg–Brentano configuration using Cu $K\alpha$ radiation were used to study the structural properties of the grown films. Time-of-flight elastic recoil detection analysis (ToF-ERDA) was used to investigate the composition of selected films. The thickness of the grown layer was estimated from the weight change of the sample assuming the r-BN density to be 2.277 g/cm³.⁷

RESULTS AND DISCUSSION

Influence of the N/B Ratio. Initial experiments showed that a surplus of ammonia was needed to deposit sp^2 BN, and this is in agreement with previous studies.^{9,10,13–15} Figure 3

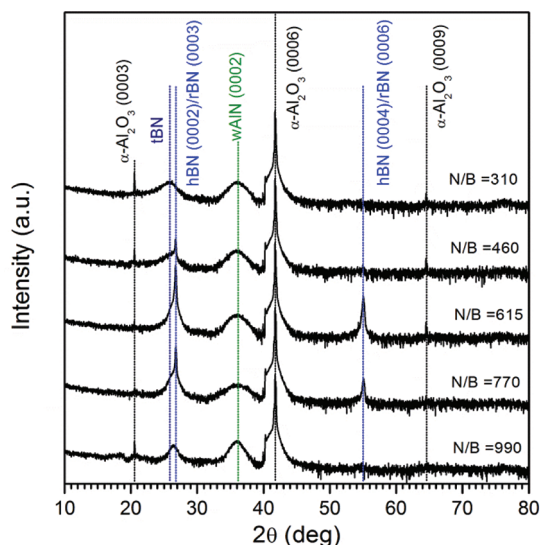


Figure 3. XRD diffractograms illustrating the influence of the N/B ratio on sp^2 BN film quality. The growth was done with H_2 as carrier gas at 1500 °C, 100 mbar, and B/H_2 of 0.02%.

shows diffractograms recorded from films grown with different N/B ratios on (0001) sapphire substrates with AlN buffer layers. For N/B ratios in the range of 615–770, sharp peaks located at 26.7° and 55.1° are seen. These are the 0003 and 0006 peaks from r-BN. Both for higher and lower N/B ratio, the peak at around 55.1° is absent and a broad peak of low intensity is found at 26.3°. This peak originates from t-BN and is shifted to a lower angle compared to the r-BN peak, indicating an increase of the lattice parameter. Its rather broad shape suggests a less-ordered stacking compared to r-BN.

A contribution from t-BN is also visible as a shoulder on the r-BN 0003 peak, see Figure 4. Fitting of the peak was carried out using two bands. The main peak was centered at 26.7° (full width at half-maximum, FWHM, 0.3°) and a second broader peak that is centered at 26.3° (fwhm 2.3°). In our previous study, such growth behavior was attributed to the formation of a t-BN layer in order to compensate the lattice mismatch between the r-BN film and the AlN buffer layer or to point defects between these layers.²⁸

For the growth of a 1:1 stoichiometry binary material such as r-BN, it is reasonable to assume that the ratio of precursors should be close to 1. Although, for the chemically related III–nitride materials AlN, GaN, and InN, this is not the case.³² To obtain semiconductor grade material for AlN, the N/Al ratio is typically in the range from 50 to 800.³³ In the case of GaN growth, the N/Ga ratio is approximately 1000. To achieve good quality InN epilayer, the N/In ratio should be higher than 100 000.^{34,35} Therefore, it is not surprising that the present study shows that an N/B ratio in the range of 615 to 770 is needed for the deposition of high quality r-BN films. Lower N/B ratio than 615 favors the growth of t-BN, which is supported from previous study.¹⁰ In our study, higher N/B ratio than 770 also leads to the formation of t-BN, which is similar to a previous study when low density films were obtained when using high

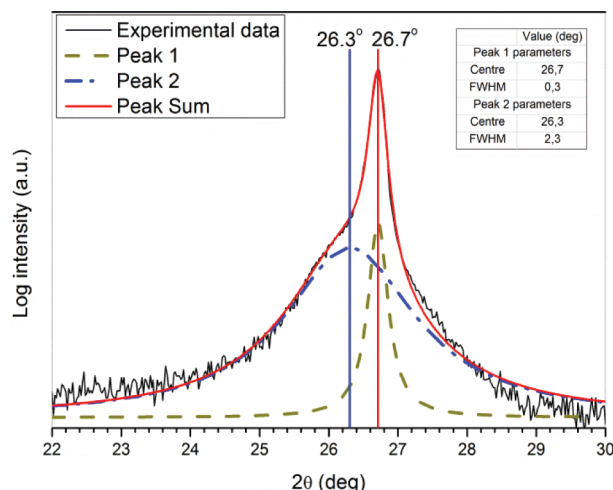


Figure 4. Experimental data (black curve) compared with the deconvolution of the t-BN/r-BN XRD peak fit (red curve). The growth was done with H_2 as carrier gas at 1500 °C, 100 mbar, N/B of 615, and B/H_2 of 0.02%.

N/B.¹⁴ High NH_3 content in the gas phase is supposed to disturb the ordering of the sp^2 BN crystal.

Influence of the Growth Temperature. From the diffractograms obtained from films grown in the temperature range 1300–1600 °C, sharp peaks from (0003) and (0006) planes are only observed when the growth temperature was set to 1500 °C (see Figure 5). Both lower and higher temperatures

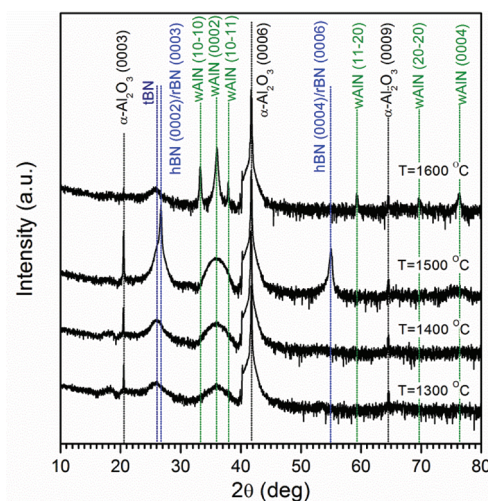


Figure 5. XRD diffractograms showing the growth temperature influence on the sp^2 BN film quality. The growth was done with H_2 as carrier gas at 100 mbar, N/B of 615, and B/H_2 of 0.02%.

favor the growth of t-BN. The growth of t-BN at lower temperatures can be explained by the increased incorporation of carbon and oxygen, revealed by the ToF-ERDA of such films. In the films grown at 1500 °C, the carbon and oxygen levels were typically 0.5 and 0.8 atom %, respectively, whereas in the films grown at 1200 °C, carbon and oxygen content increased to 0.7 and 1.3 atom %, respectively (sensitivity for C and O is 0.1 atom %). Concentration of the contamination elements is an average value acquired from depth profile through the BN layer. In addition, the highest concentration of O and C atoms was found at the top surface of the BN layers. This is in accord

with previous studies showing that temperature around 1500 °C is necessary to achieve high quality sp^2 BN instead of t-BN.^{10,13} Also, it should be noted that even films grown at optimum conditions contain traces of t-BN; presumably from inclusions or interface structures, which can be derived from a shoulder on the low angle side of the 0003 peak of r-BN in the diffractograms. At high temperatures, the growth of r-BN is hampered by the fact that the AlN buffer layer becomes polycrystalline.

Influence of AlN Buffer Layer Quality. In order to investigate the growth of r-BN films on a high quality AlN epitaxial layer, depositions were carried out on such epitaxial layers pregrown on 4H-SiC, which had a thickness in the range of 500 to 700 nm.³³ In Figure 6, the upper diffractogram is

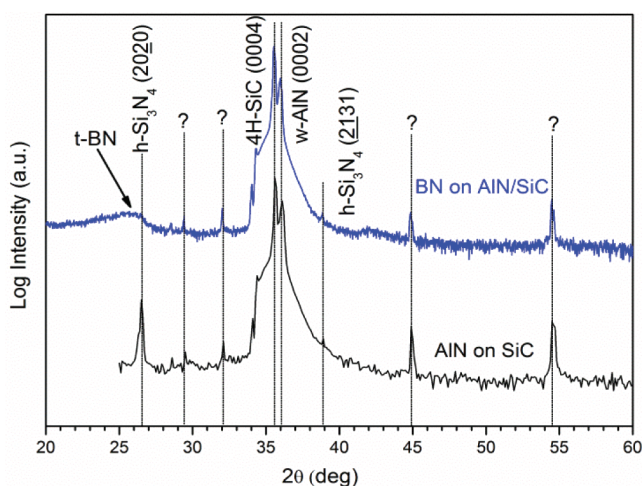


Figure 6. XRD of the AlN on SiC (black; bottom) and BN grown on AlN/SiC (blue; top). The growth was done with H_2 as carrier gas at 1500 °C, 100 mbar, N/B of 615, and B/ H_2 of 0.02%.

recorded from a BN layer grown at optimal conditions (N/B = 615, H_2 carrier gas, $T = 1500$ °C), while the lower diffractogram comes from the AlN/SiC substrate. From the broad t-BN peak in the upper diffractogram, it is obvious that not even a high quality epitaxial AlN buffer layer will support the nucleation of epitaxial r-BN growth. Both this and our previous study show that a thin and strained AlN layer promotes the growth of epitaxial r-BN, but the properties of the buffer layer must be controlled.²⁸

In addition, the diffractogram from the AlN/SiC substrate shows peaks from Si_3N_4 at the 2θ angles of about 26° and 39°. The Si_3N_4 phase is probably formed by a solid-state reaction between the SiC substrate and the AlN film. There are also unidentified peaks in the diffractogram that are labeled with question marks. These peaks are suggested to originate from a ternary $Al_xC_ySi_z$ compound that can form during the AlN growth.

Influence of the Carrier Gas. The deposition of BN films from TEB and ammonia was found to be dependent on the amount of hydrogen in the reactor. Figure 7 presents XRD diffractograms of samples grown with different carrier gases. As can be seen, pure hydrogen ambient seems to be necessary to support the growth of r-BN layers as no peaks originating from any BN phases were found when either pure Ar or N_2 were used as carrier gases. Although, it was possible to nucleate t-BN when a 1:1 mixture of H_2 and N_2 was used. These results

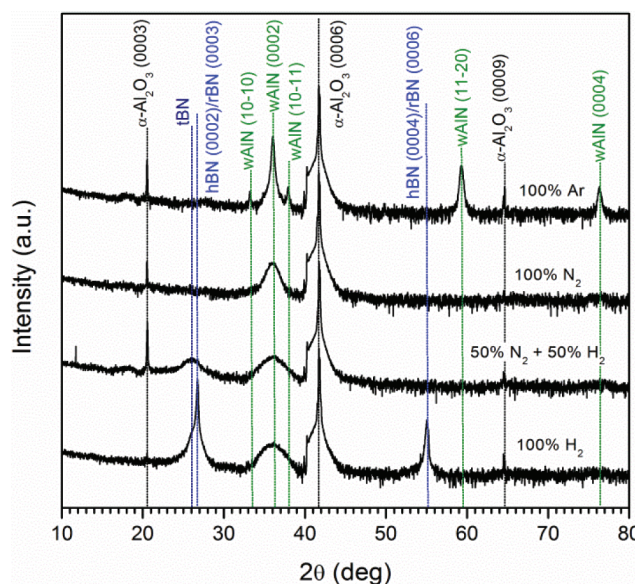


Figure 7. XRD diffractograms showing the carrier gas influence on the quality of sp^2 BN film. The growth was done at 1500 °C, 100 mbar, N/B of 615, and B/ H_2 of 0.02%.

indicate that H_2 is necessary in order to make the gas phase chemistry for the growth of epitaxial r-BN function properly.

Fourier transform IR spectrum measurements were done on the films grown in Ar and N_2 atmosphere and showed weak peaks from B–N vibrational modes, but no peaks corresponding to B–C or N–C vibrations were detected.

A previous study using B_2H_6 and NH_3 as precursors showed that h-BN nanocrystals embedded in an amorphous matrix could be deposited in an inert atmosphere of argon.²² A higher boron concentration (1% B_2H_6 diluted in Ar) in the gas phase could allow the growth of sp^2 BN in argon atmosphere.²² From this study, we particularly note that the applied boron precursor was diborane, a molecule that contains no carbon and with a H/B ratio of 3. To our knowledge, there is no publication where the growth of BN by thermal CVD has been demonstrated from a carbon containing precursor such as TEB in an atmosphere different to H_2 .

Influence of the B/ H_2 Ratio. The influence of the B/ H_2 ratio on the quality of the grown film was studied at growth conditions 70 mbar and 5 slm of H_2 flow, which is slightly different compared to the 100 mbar and 7 slm that was applied in the experiments described above. It is worth noting that, with the 100 mbar, 7 slm, and B/ H_2 = 0.02% process conditions, the growth rate for the r-BN was typically 100 nm/h for high quality material.²⁸ When the H_2 flow was lowered from 7 slm to 5 slm, all the other growth parameters were recalculated to obtain the same gas speed in the reactor, the same ammonia concentration, and a N/B ratio of 615. X-ray diffraction data recorded from films where the B/ H_2 ratio is increased from 0.01% to 0.07% show that both the 0003 and 0006 r-BN XRD peaks are shifted to lower angles; the 0003 peak from 26.72° to 26.59° and 0006 from 55.1° to 54.85°, see Figure 8. The largest 2θ angle recorded for the 0003 peak of r-BN in Figure 8 was 26.72°, which is close to the reported value of 26.717° for r-BN 0003.⁷ As the boron concentration in the precursor mixture is increased, the peak shifts to lower diffraction angles. This indicates an increase of the c -axis lattice parameter when the growth conditions favor the nucleation of t-BN. However, with the lowest B/ H_2 ratio of 0.005% (not included in Figure 8 since

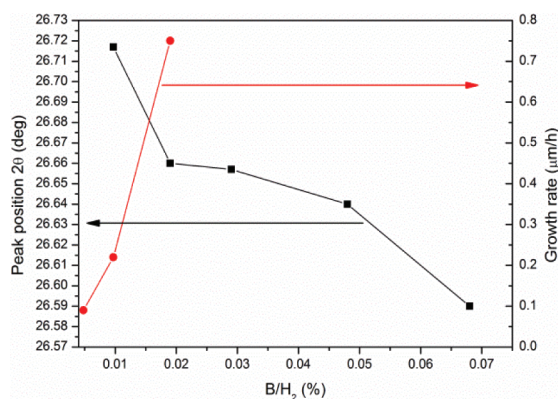


Figure 8. r-BN 0003 XRD peak position (black squares) and growth rate (red circles) as a function of the B/H₂ ratio. The growth was done with H₂ as carrier gas at 1500 °C, 70 mbar, and N/B of 615.

it is outside the scale), only a broad t-BN peak with low intensity at 26.3° is observed indicating that, at very low growth rate, t-BN is predominantly formed. These observations highlight the importance of controlling the TEB concentration in the gas mixture in order to enable growth of epitaxial r-BN.

In addition, with a B/H₂ ratio of 0.01%, keeping the other growth parameters identical but increasing the N/B ratio from 615 to 700 by increasing the NH₃ flow, the 0003 r-BN peak in the XRD diffractogram is slightly shifted to an angle of 26.74°, i.e., away from the optimal value of 26.717°, which further indicates that an N/B ratio of 615 is optimum in our process.

Variation of the lattice parameter deduced from the XRD peak position has been previously reported upon changing the growth temperature⁹ or the N/B ratio¹⁰ but not when varying the B/H₂ ratio, to the best of our knowledge. As it was already pointed out, it is not obvious if the films in those reports were h-BN or r-BN since no pole-figure measurements were presented.

Growth Rate. The growth rate of the grown films was estimated by weighing the samples grown at 70 mbar with 5 slm H₂ flow. The density of the grown film was considered to be 2.277 g/cm³ as for the bulk BN material. With B/H₂ = 0.01% and B/H₂ = 0.005%, the growth rate was found to be 220 nm/h and 90 nm/h, respectively (growth rates for some boron concentrations are presented in Figure 8 with red circles and the growth rate axis on the right). The growth rate reduction is connected to the reduction of boron and nitrogen containing species in the gas phase since the B concentration is decreased but the N/B ratio was kept constant making the N/H₂ ratio decreasing also.

In comparison, the growth rate of sp² BN film using diborane and ammonia and a growth temperature of 1600 °C has been reported to be in the range of 6 to 10 μm/h.²² Here, it should be pointed out that these films are of poor quality as they consist of h-BN nanocrystals embedded in an amorphous matrix. For the growth of sp² BN using TEB and NH₃ as precursors and H₂ as carrier gas, film thickness was reported to be around 300 nm, using different growth times with different N/B ratios; a reduction of the growth rate was observed when the N/B ratio was increased.¹⁰ For example, a 300 nm film was grown during 4 h at N/B ratio of 630, which gives a growth rate of 75 nm/h.¹⁰ This value is comparable to our achieved growth rate with about the same N/B ratio.

The main trend observed in the literature is that a lower growth rate results in a better crystalline quality of the film,

while processes with high growth rate render polycrystalline, turbostratic, or amorphous BN films or film consisting of nanocrystals in an amorphous matrix.^{10,22,36,37} However, comparison is complicated since, in most studies, the deposition temperature is lower than 1500 °C and the growth conditions differ and are often not completely described. The films in the present study may spontaneously delaminate from the substrate when the film thickness is higher than 1 μm, but for films thinner than one micrometer, no delamination was observed.

Films grown with high B/H₂ ratio exhibited rough surface with milky white appearance, while the films grown with low B/H₂ (<0.02%) showed shiny reflective surface.

Proposed Chemical Reaction Scheme for sp² BN Deposition. Lewis et al. studied the properties of several organoboranes, including TEB, for boron–carbon film CVD.²⁵ Already at a temperature of 300 °C, the ethyl groups of the TEB molecules are dissociated from the TEB molecule as ethylene (C₂H₄), leaving a B–H bond instead of the B–C bond. If all three ethyl groups are abstracted from the TEB molecule, the end product will be borane (BH₃), i.e., a homolytically cleaved diborane (B₂H₆) molecule. This reaction scheme suggests similarities in chemistry between TEB and diborane but with the important difference that also hydrocarbons are formed in the gas phase. In our study, the growth of r-BN from TEB is performed at 1500 °C, i.e., in a temperature region where the hydrocarbons released from the TEB molecule will undergo several gas phase reactions to form reactive species, e.g., C₂H₂.³⁸ Such precursor fragments could be present on the surface during the growth of r-BN film and are likely to hamper the nucleation of any binary BN compound if not removed. The amount of contaminations was investigated by ToF-ERDA. As mentioned above, the carbon and oxygen concentration in the BN films increased when the temperature was decreased. This could be explained by a less effective surface chemistry for the removal of adsorbed carbon and oxygen containing species at lower temperatures. Such species are most likely removed by atomic hydrogen that is generated from the homolytic cleaving of hydrogen gas or from the decomposition of hydrocarbons formed from TEB or from NH₃. All these reactions should be more efficient at higher temperatures, thus leaving more atomic hydrogen to abstract unwanted carbon and oxygen contaminants from the surface of the growing films. This important property of hydrogen provides an explanation why the growth of epitaxial r-BN is restricted when the carrier gas is not 100% hydrogen. It should be noted that the amount of hydrogen observed in the samples by ToF-ERDA was lower than 1 atom %.

For the nitrogen precursor, ammonia, the main species contributing to the growth of AlN and GaN were found to be NH₃, NH₂, and NH since the concentration of atomic nitrogen is very low.³⁹ We expect here a similar behavior in the case of BN.

CONCLUSIONS

The influence of fundamental process parameters on the quality of the grown r-BN films is investigated. Successful growth is limited to a narrow window of temperature and N/B ratio. The N/B ratio should be around 615 to achieve a good quality, state of the art, r-BN film, and the temperature should be around 1500 °C. If the temperature is lower by 100 °C, t-BN is formed on nitridized sapphire. If the temperature is 100 °C higher than the optimal temperature, the growth of a polycrystalline AlN

buffer layer prevents the formation of the r-BN film. The use of pregrown, high quality AlN on SiC does not favor the formation of r-BN. Pure hydrogen as carrier gas is found to be necessary for the sp^2 BN deposition since it is expected to be needed for the gas phase chemistry and to remove carbon containing species from the growing surface since no BN is formed on the substrate using inert carrier gas. The B/ H_2 ratio influences the quality of the grown film; a decrease of the B/ H_2 ratio is accompanied by a decrease of the *c*-axis lattice parameter. The growth of high quality r-BN is achieved only with low growth rate to avoid possible contamination from carbon. A possible chemical reaction scheme for the deposition of BN is presented.

AUTHOR INFORMATION

Corresponding Author

*Phone: +46 13 288983. Fax: +46 13 137568. E-mail: mihails.cubarovs@liu.se. Webpage: www.ifm.liu.se/semicond/.

Notes

The authors declare no competing financial interest.

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