Thermal chemical vapor deposition of epitaxial rhombohedral boron nitride from trimethylboron and ammonia

Running title: CVD of epitaxial r-BN from B(CH$_3$)$_3$ and NH$_3$

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Epitaxial rhombohedral boron nitride films were deposited on $\alpha$-Al$_2$O$_3$(001) substrates by chemical vapor deposition, using trimethylboron, ammonia, and with a low concentration of silane in the growth flux. The depositions were performed at temperatures from 1200 to 1485 °C, pressures from 30 to 90 mbar and N/B ratios from 321 to 1286. The most favorable conditions for epitaxy were: a temperature of 1400 °C, N/B around 964, and pressures below 40 mbar. Analysis by thin film X-ray diffraction showed that most deposited films were polytype-pure epitaxial r-BN with an out-of-plane epitaxial relationship of r-BN[001] $\parallel$ w-AlN[001] $\parallel$ $\alpha$-Al$_2$O$_3$[001] and with two in-plane relationships of r-BN[110] $\parallel$ w-AlN[110] $\parallel$ $\alpha$-Al$_2$O$_3$[100] and r-BN[110] $\parallel$ w-AlN[110] $\parallel$ $\alpha$-Al$_2$O$_3$[100] due to twinning.
I. INTRODUCTION

The trialkylboron triethylboron (TEB, B(C₂H₅)₃) is commonly used as boron precursor in chemical vapor deposition (CVD) of boron-based thin films as it is less corrosive than the halides BF₃ and BCl₃, and less poisonous than diborane (B₂H₆). In a seminal study, Lewis et al.¹ compared the triarylborons TEB, trimethylboron (TMB, B(CH₃)₃) and tributylboron (TBB, B(C₄H₉)₃) and suggested that TEB was the most suitable for depositing boron carbon films, judged mainly by the high B/C ratio obtained. A recent study on the thermal gas phase chemistry of TEB in CVD² confirmed that the molecule is an efficient boron source at temperatures below 1000 °C. TEB has been employed for CVD of boron carbides²⁻³, phosphides and arsenides⁴ and, of particular interest for this study, boron nitrides.⁵⁻¹³ TEB decomposes primarily by β-hydride elimination, offering a low-temperature synthesis route for boron-rich films¹². On the contrary, a drawback is that the ethyl ligands are suggested to form C₂H₄ upon β-hydride elimination², which will be reactive as CVD precursors at the high temperatures needed for the growth of boron nitride (around 1500 °C)⁵⁻⁹ and can therefore lead to carbon impurities in the BN films. In this regard, TMB is a promising alternative to TEB. TMB was recently shown to be an efficient boron precursor for high temperature deposition and suggested to form less reactive CH₄ in an α-elimination decomposition.¹⁴ Studies on CVD of boron-based compounds using TMB are scarce. Manasevit et al. successfully deposited boron monophosphide and boron subarsenide from TMB⁴. For boron-nitride-based neutron detectors, Maity et al. deposited films from ¹⁰B-enriched TMB and ammonia in a nitrogen ambient,¹⁵ but did not report on any characteristics of the process. Here, we investigate CVD of epitaxial rhombohedral boron nitride (r-BN) using TMB and ammonia in hydrogen ambient at
temperatures ranging from 1200-1485 °C, pressures from 30 to 90 mbar and N/B ratios ranging from 321 and 1286.

II. EXPERIMENTAL DETAILS

BN films were deposited on α-Al2O3(001) for 120 min at temperatures of 1200, 1300, 1400, and 1485 °C in a hot-wall CVD reactor kept at a base pressure below 10^-7 mbar. The substrates were cut in 10x10 mm^2 pieces and were cleaned according to the following procedure: 3 min in an ultrasonic bath in acetone at 80 °C, 3 min in an ultrasonic bath in ethanol at 80 °C, followed by standard clean 1 (SC1, NH3:H2O2:H2O with relative concentrations 1:1:26 at 80 °C)\(^\text{16}\) and standard clean 2 (SC2, HCl:H2O2:H2O with relative concentrations 1:1:22 at 80 °C)\(^\text{16}\). The substrates were placed in the center of a tantalum-carbide-coated elliptical susceptor. Prior to BN deposition, the α-Al2O3 substrates were heated to 1100 °C during 5 min in palladium membrane purified hydrogen gas (H\(_2\)), after which ammonia (NH\(_3\), 99.999 \%, further purified with respect to water by a getter filter) was introduced and the temperature ramped up to the selected growth temperature for 10 min to form an in-situ aluminum nitride buffer layer as previously reported in \(^\text{8,9,12}\). H\(_2\) was used as carrier gas for the boron precursor TMB (99.99 \% purity, Voltaix/Air Liquide Advance Materials, FL) as well as the nitrogen source NH\(_3\). TMB was flowed in a separate quartz liner to avoid the formation of the NH\(_3\):B(CH\(_3\)_3) adduct\(^\text{17}\). The N/B ratio was varied between 321 and 1286. From previous works\(^\text{18}\), silane (SiH\(_4\), 99.999 \% purity, 2000 ppm diluted in 99.9996 \% H\(_2\)) was inserted 2 min prior to growth. The process pressure was in the range of 30 to 90 mbar and regulated by a throttle valve. The growth temperature was monitored by a pyrometer (Heitronics KT81R, calibrated by silicon melting).
The deposited films were characterized by thin film X-ray scattering, electron microscopy and ion beam analysis. All diffractograms and reflectograms were acquired using Cu Ka radiation. The 2θ/ω diffractograms were acquired with a PANalytical X’Pert PRO, using a Bragg-Brentano HD mirror with 1/2° divergence and anti-scatter slits as primary optics and an X’Celerator detector with a 0.5 mm anti-scatter slit, 0.04 rad Soller slits and nickel Kβ filter as secondary optics. In plane measurements, as azimuthal scans (φ-scans) and Glancing-Incidence Diffraction (GID) were acquired with a Phillips X’Pert MPD, using cross-slits (2x2 mm²) with nickel Kβ filter as primary optics and a proportional detector (PW1711/96) equipped with a parallel plate collimator. The thickness of the film was estimated from scanning electron microscopy (SEM) using an accelerating voltage of 5 kV and an in-lens secondary electron detector. The analysis of the composition was performed by time-of-flight energy elastic recoil detection analysis (ToF-E ERDA). The measurements were carried out with a 36 MeV 127 iodine ion beam. The incident angle of primary ions and exit angle of recoils were both 67.5° to the sample surface normal giving a recoil angle of 45°. The measured ToF-E ERDA spectra were converted into relative atomic concentration profiles using the Potku code19.

III. RESULTS AND DISCUSSION

A. Structural characterization of the BN films

Figure 1 shows 2θ/ω diffractograms recorded from sp²-BN films deposited at 1200, 1300, 1400, and 1485 °C. At 1400 °C there are clear peaks positioned at 26.5° and 54.5° originated from the diffraction of sp²-BN(00ℓ) and the second order diffraction (002ℓ), suggesting highly-oriented pyrolytic BN20 or textured h-BN21 or r-
BN\textsuperscript{22} on the nitridated \(\alpha\)-Al\textsubscript{2}O\textsubscript{3}(001). We note that the growth temperature of 1400 °C is 100 °C lower than the temperature previously reported for TEB at similar growth conditions\textsuperscript{9}. Increasing temperature to 1485 °C or decreasing it to 1300 °C, decreases the intensity of the 00\(\ell\) peak and the second order diffraction peaks are no longer visible. At 1200 °C, no diffraction peak is visible. As for deposition with TEB\textsuperscript{9}, the deposition of high-quality \(sp^2\)-BN films seems to be constrained to a narrow temperature window, albeit at 100 °C lower temperature. In addition, to the high-intensity 006 peak from the sapphire substrate in all investigated films, the 002 diffraction peak of w-AlN was detected from 1200 °C and with 100 and 110 peaks visible for growth at 1485 °C. SEM measurements of cross sections showed that the average film thickness increased from 896 ± 87 nm at 1200 °C to 1308 ± 194 nm at 1400 °C, corresponding to an average growth rate from 7.5 ± 0.7 nm/min to 10.9 ± 1.6 nm/min.
Fig. 1. 2θ/ω diffraction patterns from BN films deposited at (from top to bottom) 1485, 1400, 1300, and 1200 °C for 120 min, using a process pressure of 70 mbar and N/B = 643. The bulk of the carrier flow consisted of 5000 sccm H₂, the TMB flow was set to 0.7 sccm diluted in 150 sccm H₂ and the Si/B ratio was 0.037. The NH₃ flow applied for nitridation of the α-Al₂O₃(001) substrate was 500 sccm.

Using a combination of glancing incidence diffraction (GID) and φ-scans, we concluded that the films deposited on AlN/α-Al₂O₃(001) were epitaxial already at 1300 °C. The films deposited 1400 °C were most cases polytype-pure rhombohedral BN. The epitaxial relationships were sp²-BN[001] || w-AlN[001] || α-Al₂O₃[001] (Figure 1) out-plane and, sp²-BN[110] || w-AlN[110] || α-Al₂O₃[100] in-plane as shown by the GID diffractogram in Figure 2.(a).
Fig. 2. (a) GID diffractogram aligned on r-BN(110) \((\varphi = 124.48^\circ, \psi = 89.43^\circ)\) revealing the epitaxial relationship of a sp\(^2\)-BN film deposited at 1400 °C and 55 mbar. The bulk of the carrier flow consisted of 6400 sccm H\(_2\), the TMB flow was set to 0.9 sccm diluted in 191 sccm H\(_2\) and the N/B and Si/B ratios were 707 and 0.037,
respectively. (b) GID diffractogram of the same film as in Figure 2.(a), but rotated 30°
($\varphi = 154.48^\circ$, $\psi = 89.39^\circ$), showing extinction of the (100) planes of sp$^2$-BN.

The \{110\} planes of sp$^2$-BN cannot be used to determine the BN polytype. By
rotating the sample by 30°, it is possible to use GID to investigate the presence of the
\{100\} planes of h-BN, as this family of planes is extinct in the case of r-BN.$^{22,23}$ The
result is shown in Figure 2.(b), where only diffraction from the aluminum nitride
buffer and the sapphire substrate is detected. This shows that it is possible to obtain
polytype-pure r-BN films from TMB. In a few films, diffraction of h-BN inclusions
could be detected by GID, as previously reported in$^{24}$.

The twinning of the r-BN films was also investigated by acquiring azimuthal
scans of the \{101\} of planes of r-BN. These planes have a three-fold symmetry as
dictated by rhombohedral crystal system, whereas the $\varphi$-scan in Figure 3 shows six
peaks for r-BN\{101\}. This originates from the presence of twin crystals that are
rotated by 60°. From this result, two in-plane epitaxial relationship can be determined
to: r-BN[110] $\parallel$ w-AlN[110] $\parallel$ $\alpha$-Al$_2$O$_3$[100] and r-BN[110] $\parallel$ w-AlN[110] $\parallel$ $\alpha$-
Al$_2$O$_3$[100]. Twinning of r-BN has been reported in previous works for films
deposited on sapphire$^9$ and SiC$^{10}$ and is to be expected due to the 6-fold symmetry of
the AlN buffer layer and of the hexagonal polytypes of silicon carbide, respectively.
Fig. 3. XRD φ-scans of r-BN(101) (2θ = 42.6835°, ψ = 77.61°) and α-Al₂O₃{202} (2θ = 46.161°, ψ = 72.20°). Diffraction from crystals oriented -30° with respect to the substrate is indicated by circles, diffraction from crystals oriented +30° is indicated by crosses.

B. Deposition process

In contrast to r-BN deposited from TEB⁹, epitaxial films were obtained in a wider range of N/B ratios and lower pressures using TMB at 1400 °C. At fixed pressure, NH₃/TEB ratios below 460 and above 770 were shown to strongly affect r-BN epitaxy⁹, whereas NH₃/TMB between 321 and 1286 resulted in epitaxial r-BN, without having any influence on the crystal quality from 2θ/ω scans for N/B ratios above 643, as shown in Figure 4 (a) by the full width at half maximum (FWHM) values from 0/20 scans of r-BN(003). For comparison, the FWHM of 20/ω diffractograms of α-Al₂O₃(006) was 0.06°. Figure 4 (b) indicates an optimal N/B ratio of 964. This is higher than the value observed for decomposition of TEB (N/B around
615-640) and can be explained by the fact that at a lower process temperature the activation of the NH$_3$ molecule is less favorable$^{25}$. In Figure 4 (c), the crystal quality is shown to increase while decreasing the process pressure as illustrated by the proportional decrease in FWHM of 0/2θ scans of r-BN(003) with decreasing process pressure from 90 to 30 mbar. Interestingly, Figure 4 (d) shows that at fixed N/B ratios, the pressure does not affect the total amount of coherently diffracting domains along the c-axis, i.e. the proportion of crystallites is independent of the total pressure at these experimental conditions.
(a)\[\text{FWHM (°)}\] vs \(\text{N/B ratio}\) 
(b) \(\text{Normalized Intensity}\) vs \(\text{N/B ratio}\) 
(c) \(\text{FWHM (°)}\) vs \(\text{Pressure (mbar)}\) 
(d) \(\text{Normalized Intensity}\) vs \(\text{Pressure (mbar)}\)
Fig. 4. (a, b) Dependence of the FWHM (a) and of the normalized intensity (b) of 20/ω diffractograms from r-BN(003) for films deposited at 1400 °C, 50 mbar and N/B ratios ranging from 321 to 1286. The carrier gas flow was changed to keep the same residence time inside the hot zone. To discard the effects of the buffer layer, the NH₃ flow during nitridation was adjusted so that the partial pressure of NH₃ was the same for each sample. (c, d) Evolution of the FWHM (c) and of the normalized intensity (d) of 20/ω diffractograms of r-BN(003) for films deposited at 1400 °C, N/B = 643 and pressure from 30 to 90 mbar. The nitridation conditions were the same for each film i.e. 636 sccm NH₃ in 6400 sccm H₂ at 40 mbar. The TMB flow was 0.9 sccm and mole fractions were the same as in Figure 1. Lines are guide for the eyes.

Similarly as reported for TEB¹⁸, the deposition process using TMB is dependent on the background silicon concentration. In the absence of silane, the intensity of the (003) diffraction peak of r-BN is significantly reduced and the peak broadens as shown in Figure 5. ToF-ERDA gives 44.5 at% B, 46.1 at% N (B:N ratio of 1:1.04), 4.3 at% C, 3.8 at% O and 1.1 at% H in an r-BN film deposited at 1400 °C, 40 mbar, 0.9 sccm TMB and NH₃/TMB ratio of 643. This can be compared to the B:N ratio of 1:0.98; O, H of 0.1 at%, 1 at%, respectively, and C being less than 0.1 at% (below detection threshold) for a film deposited at 1500 °C, 70 mbar, 0.7 sccm TEB and B/N = 643.⁸ A reason for the increased carbon content in the film deposited from TMB may be the fact that TMB cannot undergo β-hydride elimination. This may restrict the removal of all ligands from the TMB molecule and result in a less favorable surface chemistry for the removal of the methyl groups, leading to the incorporation of carbon in the films. Similar trends have been observed for the pairs
trimethylaluminum/triethylaluminum and trimethylgallium/triethylgallium for $\text{Al}_x\text{Ga}_{1-x}\text{As}$, $\text{GaAs}$, $\text{In}_x\text{Ga}_{1-x}\text{As}$ and $\text{GaN}$.

**IV. CONCLUSIONS**

We demonstrate a deposition process for epitaxial r-BN on $\alpha\text{-Al}_2\text{O}_3(001)$ from a reaction between TMB and NH$_3$ in hydrogen. Epitaxial growth was achieved at 1300 °C and with the best conditions at a deposition temperature of 1400 °C. The epitaxial relationships are: r-BN[001] $\parallel$ w-AlN[001] $\parallel$ $\alpha\text{-Al}_2\text{O}_3[001]$ out-of-plane and in-plane r-BN[110] $\parallel$ w-AlN[110] $\parallel$ $\alpha\text{-Al}_2\text{O}_3[100]$ and r-BN[110] $\parallel$ w-AlN[110] $\parallel$ $\alpha\text{-Al}_2\text{O}_3[\overline{1}00]$ due to twinning. At 1400 °C, the deposition process is shown to have a more favorable process window for epitaxy at investigated N/B ratios and process pressures and where the crystal quality of the films was the highest for a N/B ratio of 964 and a deposition pressure below 40 mbar. ToF-ERDA gives 44.5 at% B, 46.1 at% N, 4.3 at% C, 3.8 at% O and 1.1 at% H, where the C and the O contents in the
investigated film are higher compared to a film deposited with TEB under similar conditions.

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