Chemical vapor deposition of $sp^2$-boron nitride films on $Al_2O_3$ (0001), (1120), (1102), and (1010) substrates

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ABSTRACT
Thin films of boron nitride in its sp²-hybridized form (sp²-BN) have potential uses in UV devices and dielectrics. Here, we explore chemical vapor deposition (CVD) of sp²-BN on various cuts of sapphire: Al₂O₃ (1120), Al₂O₃ (1102), Al₂O₃ (1010), and Al₂O₃ (0001) using two CVD processes with two different boron precursors triethylborane and trimethylborane. Fourier transform infrared spectroscopy shows that sp²-BN grows on all the sapphire substrates; using x-ray diffraction, 2θ/ω diffractogram shows that only Al₂O₃ (1120) and Al₂O₃ (0001) rendered crystalline films: and using phi(φ)-scans, growth of the rhombohedral polytype (r-BN) films on these substrates is confirmed. These films were found to be epitaxially grown on an AlN interlayer with comparatively higher crystalline quality for the films grown on the Al₂O₃ (1120) substrate, which is determined using omega(ω)-scans. Our study suggests that Al₂O₃ (1120) is the most favorable sapphire substrate to realize the envisioned applications of r-BN films.

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I. INTRODUCTION
Epitaxially grown hexagonal and rhombohedral boron nitride [h-BN (Ref. 1) and r-BN (Ref. 2)] thin films are materials that have various applications in the fields of UV devices,3–6 as piezoelectric materials,7,8 and in graphene technology.9–11 Similarly, other less ordered forms of BN including turbostatic BN and amorphous BN (a-BN) have been studied to understand film nucleation and have potential electronic applications as dielectrics.12–14 Thin film growth of sp²-hybridized boron nitride (sp²-BN) is typically done using chemical vapor deposition (CVD). Growth of epitaxial sp²-BN thin films requires high growth temperatures, above 1200 °C,15–19 this is a limiting factor for the substrates that can be used for this process. It should be noted that metallic substrates have been used to deposit a few layers of sp²-BN at lower temperatures. Hitherto, substrates for epitaxially grown h-BN and r-BN phases include 3C-SiC(111), 4H- and 6H-SiC(0001) on-axis substrates, ZrBr₂ and α-Al₂O₃.15,17,19–23 These substrates resulted in epitaxially grown [0001]-oriented sp²-BN films, here it is challenging to distinguish between the h-BN and r-BN phases.12 Therefore, it is of interest to study epitaxial sp²-BN film growth in other crystal orientations. Growth of sp²-BN films on other cuts of sapphire (Al₂O₃) provides a potential route to explore this possibility. These cuts include Al₂O₃ (1120), Al₂O₃ (1102), and Al₂O₃ (1010) henceforth referred to as a-cut, r-cut, and m-cut, respectively. Previously investigated Al₂O₃ (0001) called c-cut substrate is also included for comparison. We have previously employed an AlN buffer layer to facilitate epitaxial growth of sp²-BN on c-cut sapphire.18,23 AlN growth on r-cut Al₂O₃ also showed a-plane (1120) oriented growth suggesting that growth orientations can be altered based on the substrates used.24 Other studies on AlN growth on c-cut and a-cut Al₂O₃ showed that the growth direction of AlN was identical on both cuts of Al₂O₃.25 This is relevant since the surface nitridation of Al₂O₃ is observed and expected for thermal CVD at such high temperatures. Notably, a recent study on the surface properties of the substrate
comparing h-BN growth using diborane (B₂H₆) on a-cut and c-cut Al₂O₃ revealed the former to be less likely to modify under growth conditions in the absence of an AlN buffer layer.²¹ It is noteworthy from this study that when B₂H₆, a carbon-free boron precursor, was used to deposit BN without nitridizing the surface, h-BN films were observed.

This study investigates the possible growth of sp²-BN using thermal CVD, comparing the differences in growth of the material on a-cut, r-cut, m-cut, and c-cut substrates. This growth was done using two different boron precursors trimethylboron (TMB) and triethylborane (TEB), which have been investigated in previous studies.¹⁹,²⁶ Crystalline growth of sp²-BN in the polytype r-BN was observed in these studies. The most suitable substrates for specific growth applications will be realized as we identify the major characteristic differences between each substrate.

II. EXPERIMENT

A. Film deposition

These films were deposited using hot wall CVD with two different boron precursors, TMB, B(CH₃)₃ (99.99% purity, Voltaix/Air Liquide Advanced Materials, FL) and TEB, B(C₂H₅)₃ (semiconductor grade quality, from SAFC Hitech). The precursor used for nitrogen was ammonia (NH₃, 99.999%, further purified with respect to water using a getter filter) with H₂ (palladium-membrane with H₂ to avoid the formation of intermediate adducts prematurely. A pyrometer (Heitronics KT81R, calibrated by a silicon melt test) was used to monitor the growth temperature. The process pressure was maintained using a throttle valve. As observed from prior studies, the addition of silane (SiH₄) had proved useful to promote better crystallinity in the films grown by this process hence was introduced during growth using both the precursors.²⁷

Previously developed process parameters were selected from past studies on TEB and TMB.¹⁹,²⁶ For both processes, the base pressure was kept below 2 × 10⁻⁷ mbar. Carrier gas flow was maintained at 5000 SCCM H₂. The growth temperature for the process based on TMB was 1400 °C and BN was grown for 60 min with a process pressure of 50 mbar, while the process based on TEB growth was done at 1500 °C and BN was grown for 120 min with a process pressure of 70 mbar. The NH₃/TMB ratio was kept at 96.6. Silane (SiH₄, 99.999% purity, 2000 ppm diluted in 99.9996% H₂) was supplied with a flow corresponding to 16.5 SCCM 2 min prior to BN deposition. The NH₃/TEB ratio was kept at 642. SiH₄ (99.999% purity, 2000 ppm diluted in 99.9996% H₂) was supplied with a flow corresponding to 13 SCCM 2 min prior to film deposition.

All substrates used are sized at 10 × 10 mm² except for the m-cut substrates, which were 20 × 20 mm². The c-cut, a-cut, and r-cut wafer are 2 in., 330 μm thick on axis substrates manufactured at The Roditi International Corp. Ltd. The m-cut wafer is 2 in., 430 μm thick substrates are manufactured at MTI Corporation (Materials Tech. Intl.). They were cleaned with the same procedure, which includes 3 min in an ultrasonic bath with acetone at 80 °C, 3 min in an ultrasonic bath with ethanol at 80 °C, followed by standard clean 1 (SC1, NH₃:H₂O₂:H₂O with relative concentrations 1:1:26 at 80 °C) and standard clean 2 (SC2, NH₃:H₂O₂:H₂O with relative concentrations 1:1:22 at 80 °C).²⁸ The substrates were then placed in the heating part of the reaction cell (susceptor), this elliptically shaped susceptor is coated with tantalum-carbide (TaC). The depositions on these different substrates were done separately, and they were placed in the same position inside the susceptor for each deposition. To form an in situ aluminum nitride buffer layer, NH₃ was introduced prior to BN deposition process as described above. As previously reported, this pretreatment is applied to favor the growth of crystalline BN on the α-Al₂O₃ substrates.²⁹,³⁰ NH₃ was introduced at 1100 °C and maintained as the temperature was ramped to the respective growth temperatures for each precursor process as described above. Following this, the NH₃ flow was maintained for an additional 10 min at 1400 and 1500 °C for the processes with TMB and TEB, respectively.

B. Film characterization

Fourier transform infrared spectroscopy (FTIR) transfectance spectra were measured using a Bruker Vertex70 FTIR spectrometer, with a globar MIR light source and a DLaTGS detector, the software used here was BRUKER OPUS 7.5. The incident s-polarized light is kept at an angle of 60° with respect to the sample surface normal. The spectra were acquired at room temperature, after a 30 min N₂ purge, with 2 cm⁻¹ resolution that averaged over 50 scans. A thin film of gold was used as a reference. The FTIR peaks were fitted using a Lorentzian profile and linear base line using SCIFIT software (version 1.22).

X-ray diffraction (XRD) was used to investigate the structural properties and the crystallographic relationship to the buffer layer and the film orientation. All diffractograms were recorded using Cu Kα radiation (Cu Kβ removed by a nickel filter). The 2θ/ω diffractograms were recorded in a PANalytical X’Pert Pro diffractometer with a Bragg-Brentano HD and 1/2° slit as primary optics and X’celerator detector with a 5 mm anticatter slit on the secondary side. The azimuthal scans (ω-scans) were recorded in a Phillips X’Pert MPD diffractometer with crossed slits (2 × 2 mm²) and 1/2° slit as primary optics and proportional detector (PW1711/96) equipped with a parallel plate collimator on the secondary side. Since BN diffracts poorly, longer scan times were used for these ω-scans, which is why a background subtraction and signal smoothing was applied. The same instrumentation was used to obtain XRD ω-scan (rocking curve) on the crystalline samples. ω-scans give a measure of the crystal quality of the deposited films. The full width half maximum was calculated using PANAlytical DATA VIEWER software version 1.3b.

The compositional analysis of the films was performed using time-of-flight energy elastic recoil detection analysis (ToF-ERDA). The measurements were done using a 36 MeV 127I+8 beam. The incidence angle of primary ions and the exit angle of recoils were both 67.5° to the sample surface normal constituting a recoil angle of 45°. The measured ToF-ERDA spectra data were then converted into relative atomic concentration profiles using the POTKU code.³¹

The surface morphology of the sp²-BN films was analyzed using scanning electron microscopy (SEM) 1550 Gemini. The microscope was operated with conventional and immersion lens
(in-lens) secondary electron detectors and was set at an accelerating voltage of 3 kV. SEM was also used for thickness measurements; these measurements were performed on the aligned cross sections of the samples. The samples were scratched using a diamond tipped pen and then cracked. The resulting film thicknesses were estimated to be around 300 nm for all films grown using TEB. While varying film thicknesses were estimated for TMB grown films, 700 nm for the c-cut, 1000 nm for the a-cut and very thin, approximately 100 nm for the r-cut, and 150 nm for m-cut substrates.

III. RESULTS AND DISCUSSION

A. Chemical bonding states

Figure 1 shows the FTIR transflectance spectrum on all cuts of Al₂O₃ after film deposition. Here, the transflectance is the sum of reflectance from the film surface and twice the transmittance through the film. For all the investigated samples, we observe the transversal optical in-plane mode peaks for sp²-BN at 1369 cm⁻¹, as well as the longitudinal optical out of plane mode of sp²-BN at around 820 cm⁻¹. Hence, we can conclude that sp²-BN films were grown on all studied cuts of Al₂O₃. On these latter bands, sharper absorption bands were observed on c-cut and a-cut for both the precursors. These sharp edges were suggested to indicate the crystallinity of these samples. Since, for amorphous material, there is a variation in the frequency of the vibrational modes which gives broader peaks compared to crystalline films, suggests that the sp²-BN films grown on r-cut and m-cut Al₂O₃ were amorphous.

B. Thin film x-ray diffraction

Figures 2(a)–2(d) show the 2θ/ω diffraconogram of the films deposited on different cuts of Al₂O₃ using TEB and TMB. In Figs. 2(a) and 2(b), for the c-cut and a-cut substrates, they show relatively weaker diffraction peaks at 2θ = 26.5° and 2θ = 54.8° which originate from sp²-BN (000½) and sp²-BN (0002½), respectively. AlN (0002) and AlN (0004) peaks were also observed for both of these samples. The hkl½ here signifies that the long-range order is in the direction normal to the surface. Samples with TEB as a boron precursor have comparatively lower intensities. From thickness measurements we know that for the samples grown using the TMB precursor, we observe thicker films deposited during growth which is reflected in the peak intensity. In Figs. 2(c) and 2(d), there are no sp²-BN peaks, confirming the FTIR analysis suggesting that the sp²-BN films present are amorphous on the r-cut and m-cut Al₂O₃. In Fig. 2(d), i.e., the r-cut sample shows AlN (1120) growth, this growth orientation on this substrate has been observed in the past few studies and for the m-cut samples in which AlN (1000) and (1013) growth is observed, the latter of which has been reported previously.

φ-scans for sp²-BN are used to determine the epitaxial relationship of the films grown on the c-cut and a-cut Al₂O₃, which were conducted to confirm the polytype growth using the TMB precursor, as shown in Fig. 3. As the φ-scan peaks are measured at the characteristic psi(ψ) and 2θ angles for r-BN (1011) planes for the r-BN polytype, we can confirm the presence of the r-BN film growth on these samples. There are no overlapping planes of other phases of sp²-BN or AlN, which would diffract at these angles. We observe six peaks, which means that there is twinning of the r-BN polytype that is grown for both the cuts; this trend on the a-cut is consistent with the previous results on the c-cut. Using additional φ-scans on AlN [1012] and Al₂O₃ [0112] for the a-cut, we identify the in-plane relationship between them as r-BN [1120] || w-AlN [1120] || α-Al₂O₃ [0001] on the a-cut Al₂O₃. In contrast, on the c-cut, we observe the in-plane epitaxial relationship r-BN [1120] || w-AlN [1120] || α-Al₂O₃ [1010] as previously reported for this substrate. Additionally, we observe twinning of AlN grown on c-cut, which has been observed in the previous studies of AlN growth on c-cut but this is not observed for the AlN grown on the a-cut.
XRD \( \omega \)-scans as shown in Fig. 4 on the films grown using TMB provide information on the difference in crystalline quality of the films grown. The \( a \)-cut sample shows a lower FWHM of 0.98° compared to 1.15° of the \( c \)-cut sample, which is a difference of about 15%, further confirming suggestions of a more suitable substrate in \( a \)-cut Al\(_2\)O\(_3\) for the growth of sp\(^2\)-BN.\(^{21}\) Broadness of the peaks suggests a less ordered film with respect to the substrate.

Samples grown using TMB precursor were analyzed using \( \phi \)-scans and \( \omega \)-scans due to the difference in the amount of r-BN present as described above.

FIG. 2. \( 2\theta/\omega \) diffraction patterns from BN films deposited on the substrates (a) Al\(_2\)O\(_3\) (0001), (b) Al\(_2\)O\(_3\) (1120), (c) Al\(_2\)O\(_3\) (1102), and (d) Al\(_2\)O\(_3\) (1010).

FIG. 3. XRD \( \phi \)-scans of samples (a) on the \( c \)-cut Al\(_2\)O\(_3\) showing the epitaxial relationships between each layer r-BN \( \{10\overline{1}1\} \) measured at \( \psi = 77.76^\circ \), AlN \( \{10\overline{1}2\} \) measured at \( \psi = 61.5^\circ \), and Al\(_2\)O\(_3\) \( \{11\overline{2}3\} \) measured at \( \psi = 61.2^\circ \) and (b) on the \( a \)-cut Al\(_2\)O\(_3\) showing the epitaxial relationships between each layer r-BN \( \{10\overline{1}1\} \) measured at \( \psi = 77.76^\circ \), AlN \( \{10\overline{1}2\} \) measured at \( \psi = 42.75^\circ \), and Al\(_2\)O\(_3\) \( \{01\overline{2}3\} \) (marked separately) measured at \( \psi = 43^\circ \). Both samples are grown using TMB as the boron precursor. The low intensity for a few peaks observed is due to the high tilt sensitivity of the samples at higher \( \psi \) angles.
C. Elemental composition

As observed from the ToF-ERDA results in Figs. 5(a) and 5(b), the samples grown using TEB as the boron precursor show more consistent stoichiometry and a more balanced nitrogen to boron (N/B) ratio compared to the TMB grown samples. We attribute the higher N/B ratio to the higher NH3 flow used with TMB compared to TEB. With respect to the difference in the O content between the two precursor processes, we attribute it to the difference in growth temperatures. Both these differences in the N/B ratio as well as the O content are in line with our previous findings on these precursor processes and their growth on c-cut Al2O3 substrates.26 Furthermore, samples grown using TMB as the B precursor display varying quantities of O in the films, at this stage it is speculated to be a function of the difference in the amount of grain boundaries and whisker growth (Fig. 6) on the films, which leads to oxidation on these sites post deposition. The m-cut sample grown using the TMB precursor displays film growth with the least amounts of O, we speculate that this could be due to a denser amorphous microstructure of the film growth on this cut. Hydrogen content is low (<0.2%) and, thus, it was omitted. Overall, lower quantities of C and higher quantities of B are seen on the film grown using TEB compared to TMB, which agrees with the results from past studies on these precursors.39

D. Surface morphology

Using TEB, plan-view SEM micrographs (Fig. 5) show triangular shaped grains surrounded by less ordered material and whisker growth for r-BN growth on a-cut and c-cut Al2O3. This was previously observed in investigations on c-cut Al2O3.23 For films grown using TMB, the c-cut sample shows similar crystal islands but not shaped as sharply, compared to deposition from TEB. This trend is even more pronounced on the a-cut Al2O3.

E. Differences in film nucleation and growth

From the high crystalline quality of films grown using TMB on a-cut compared to c-cut (Fig. 6) and their difference in film thicknesses, we speculate that the disordered morphology on a-cut could be attributed to the growth of more disordered material in the later stages of deposition. The plan-view SEM of sp2-BN grown films on r-cut and m-cut Al2O3 (Fig. 5) is consistent with the expected amorphous film structure suggested in the XRD (Fig. 2) and FTIR (Fig. 1) results.
XRD results on a-cut Al₂O₃, we can conclude that the out of plane crystalline growth direction for r-BN is still identical to the previously studied c-cut, being sp²-BN (000ℓ) and sp²-BN (0002ℓ). These substrates also show identical AlN 0002 and AlN 0004 peaks; this result of the growth of AlN on the a-cut and c-cut was also observed in a past study on AlN growth on these Al₂O₃ substrates. The potential for a new growth direction of r-BN was not realized for a-cut Al₂O₃ but it shows comparable crystal properties to the c-cut but with better crystalline quality as supported by the ω-scan (Fig. 6) for the growth of r-BN films. These results agree with suggestions from a recent surface study of BN growth on a-cut Al₂O₃, which described it to be more suitable for the growth of h-BN. The presence of AlN 0002 and AlN 0004 peaks on both c-cut and a-cut Al₂O₃ evidently dictates the epitaxial r-BN film growth on these substrates. This is supported by previous studies that have shown that h-BN initially nucleates epitaxially followed by r-BN epitaxial film growth on AlN (0001) grown on c-cut sapphire. In contrast, for r-cut and m-cut Al₂O₃, we do not detect AlN 0002 and AlN 0004 peaks, instead we observe AlN (1120) and mostly AlN (1013) growth on these cuts, respectively. Since we observed that the crystal direction of the AlN film dictates the growth direction of the r-BN film, we would expect growth of crystalline BN films on these substrates in other crystalline directions. Instead, a-BN growth is observed on r-cut and m-cut substrates. We speculate that this could be explained by a high surface energy of the BN planes lattice matched to AlN (1120)/AlN (1013), preventing crystalline BN film growth.

IV. CONCLUSIONS

We report the differences in CVD growth of sp²-BN films with TMB and TEB on different Al₂O₃ substrates [Al₂O₃ (1120), Al₂O₃ (1102), Al₂O₃ (1010), and Al₂O₃ (0001) called a-cut, r-cut, m-cut, and c-cut, respectively]. FTIR shows the presence of sp²-BN films on each substrate, but XRD shows crystalline sp²-BN only on the c-cut and a-cut substrates. Epitaxial growth of the polytype r-BN is confirmed with the in-plane relationships r-BN [1120] || w-AlN [1120] || α-Al₂O₃ [0001] on the a-cut Al₂O₃ and confirmed previously observed r-BN [1120] || w-AlN [1120] || α-Al₂O₃ [0010] on the c-cut Al₂O₃. Our studies show that a-cut Al₂O₃ should be considered as a viable substrate for crystalline growth of r-BN polytype displaying better crystalline quality compared to the commonly used c-cut. This result is promising toward improving crystal quality of r-BN for envisioned applications and studies in...
the future. In addition, our study shows that r-cut and m-cut sapphire are suitable substrates for investigating the growth of amorphous sp²-BN films.

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AUTHOR DECLARATIONS

Conflict of Interest

The authors have no conflicts to disclose.

DATA AVAILABILITY

The data that support the findings of this study are available from the corresponding author upon reasonable request.

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