

SAND21XX-XXXXR**LDRD PROJECT NUMBER:** 223219**LDRD PROJECT TITLE:** Chemical Vapor Deposition of Cubic Boron Nitride**PROJECT TEAM MEMBERS:** PI Anthony Rice (1876) PM Mary Crawford (1800)**ABSTRACT:**

This project explored chemical vapor deposition as a technique to synthesis cubic boron nitride (c-BN) for electronics and coating applications. Current c-BN synthesis techniques are greatly limiting due to requiring high pressure or non-equilibrium energy sources, such as ion bombardment.

INTRODUCTION AND EXECUTIVE SUMMARY OF RESULTS:

Cubic boron nitride (c-BN) offers the smallest, fastest, and most efficient power electronic devices of all known semiconductors. However, c-BN synthesis currently requires either gigapascals of pressure or a non-equilibrium energy source, such as ion-bombardment. The small crystal size and large cost restrict c-BN to niche uses. A metalorganic chemical vapor deposition (MOCVD) technique would greatly increase the feasibility of c-BN power electronics and coatings. Additional detail for potential applications and state-of-the-art synthesis research of c-BN can be found in the addendum.

Multiple researchers have identified c-BN formation under vastly different processing conditions when both AlN and BN are present.¹⁻³ The nature of this interaction is unknown but has been observed in gas phase deposition as well as in solid phase transformation at high temperature and pressure. This project further explores this interaction under conditions compatible with conventional MOCVD techniques.

DETAILED DESCRIPTION OF RESEARCH AND DEVELOPMENT AND METHODOLOGY:

The research plan was divided into 3 thrusts with each attempting to exploit different phenomena expected to yield c-BN. Deposition for all thrusts was conducted in MOCVD Tool 128 in the MESA Microfab. Tool 128 is a Veeco D125 III-nitride reactor that was modified by replacing the original stainless-steel deposition chamber with a water cooled, double-walled quartz tube deposition chamber. Additionally, the original resistive heater system was replaced with an inductively coupled radio-frequency heater system. Tantalum carbide (TaC) coated graphite susceptors were used for all experiments. Reported temperatures are of the susceptor temperature measured by a two-color pyrometer system. Tool 128 includes a KSA Ice reflectance unit that allows *in-situ* deposition rates and thickness to be measured. X-ray diffraction (XRD)

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characterization was performed on an Analytical Pert Pro diffractometer. Fourier transform infrared (FTIR) characterization was performed on a Thermo Fisher Scientific Nicolet 6700 system equipped with a Pike Technologies multi-angle tool for reflectance. Atomic force microscopy (AFM) was performed on an Asylum Research Jupiter XR tool in tapping mode.

Thrust 1 was based on the work of Huang¹ and involved using the interface between AlN and sp2-BN to form c-BN. All deposition for this thrust was conducted on 300 nm thick sputtered AlN on sapphire wafers from Kyma Technology, Inc. These substrates were selected due to the expected difficulty in controlling heteroepitaxial nucleation of AlN on sapphire with varying amounts of AlN, BN, and their alloys coating the susceptor. MOCVD deposition of AlN on the sputtered AlN was done in 3 steps:

- (1) 30 minutes at 900 °C with 36 µmol/min of trimethyl aluminum (TMAI) and 500 sccm of NH₃
- (2) 15 minutes at 1200 °C with 36 µmol/min of TMAI and 2000 sccm of NH₃
- (3) 60 minutes at 1200 °C with 18 µmol/min of TMAI and 25 sccm of NH₃

20 slm of H₂ was used as a diluent and the total pressure was held at 50 Torr throughout AlN deposition. The 3 steps roughly correspond to the processes of roughening, coalescence, and planarization of the AlN film. Typical XRD rocking curves for the AlN (0004) and (10-11) reflections were 200 arcsec and 1000 arcsec, respectively, corresponding to a threading dislocation density of $\sim 7 \times 10^9$ cm⁻².⁴ AlN deposition was followed by BN deposition. Initial conditions were selected to reproduce the work of Huang¹ but were later expanded to include: 30-480 min, 1100-1300 °C, 22-44 µmol/min of triethyl boron (TEB), 100-1000 sccm NH₃, 10-100 Torr, and 20-60 slm of H₂ diluent or mixtures of H₂ and N₂.

Thrust 2 was the use of boron tribromide (BBr₃) to deposit BN instead of the conventional TEB. AlN on sapphire substrates were used for BN sample deposited with BBr₃ utilizes only a single deposition condition. Bare sapphire substrates were used when multiple individual BN layers were deposited sequentially on a single sample. The bare sapphire substrates were prepared by *in-situ* H₂ etching for 20 minutes at 1100 °C at 500 Torr with 16 slm of H₂ and 16 slm of N₂ of gas flow. The choice to used two different types of substrates was made to continue observing for the AlN and BN interface effect reported by Huang¹ when possible. In general, the AlN on sapphire used in Thrust 2 were prepared as described above. However, for samples in which BN was to be deposited at temperatures greater than 1300 °C, the AlN regrowth had to be modified or the substrates would shatter when ramping to deposition temperature and be thrown from the susceptor. Shattering could be completely eliminated by cleaving the initial sputtered AlN on sapphire substrates into 2 equal halves prior to AlN regrowth and increasing the temperatures of the AlN deposition steps (2) and (3) to the highest temperature the substrate would reach during BN deposition. During Thrust 2 layers were deposited with the following range of conditions:



60-480 min, 700-1600 °C, 32-517 $\mu\text{mol}/\text{min}$ of BBr_3 , 3-250 sccm NH_3 , 5-500 Torr, with 20-60 slm of H_2 diluent or mixtures of H_2 and N_2 .

Thrust 3 was based on the work of Subramani² and involved mixing of aluminum, boron, and nitrogen precursors to form alloys and phases containing c-BN. The substrates used for this thrust were sapphire substrates prepared by *in-situ* H_2 etch as described above. Bare sapphire was selected as the substrate because deposition on AlN surfaces resulted in polycrystalline re-nucleation of AlN or its alloys if crystalline films were observed. The precursors selected for this thrust were TMAI, BBr_3 , and NH_3 . This differed from Subramani² which utilized AlCl_3 , BCl_3 , and tert-butylamine ($(\text{CH}_3)_3\text{CNH}_2$). This deviation was required for TMAI to substitute for AlCl_3 , which is a low vapor pressure solid and is not compatible with conventional MOCVD systems. BBr_3 was deemed a closer analog than TEB to substitute for BCl_3 which is a gas at room temperature and would require either the additional hazard of a pressured cylinder of highly toxic and pyrophoric gas or the additional complexity of solvation in liquid for use in a bubbler. NH_3 was chosen for use as it was already proven to react with TMAI and BBr_3 at the desired deposition conditions. During Thrust 3 layers were deposited with the following rage of conditions: 30-240 min, 700-1300 °C, 18-45 $\mu\text{mol}/\text{min}$ of BBr_3 , 10-73 $\mu\text{mol}/\text{min}$ of TMAI 3-25 sccm NH_3 , 5-500 Torr, with 37 slm of H_2 diluent.

RESULTS AND DISCUSSION:

Thrust 1 was intended to study the effects of the AlN-BN interface on the crystalline structure of the BN and was initially focused on reproducing the results of Huang.¹ Direct transfer of the deposition conditions reported by Huang¹ did not produce c-BN detectable by the characteristic (111) diffraction peaks in XRD or the characteristic vibrational mode in FTIR. Expanding the deposition condition to account for “plausible” differences in temperature calibration between the different deposition systems and adjusting gas flows in attempt the yield similar deposition rates was also unsuccessful in producing c-BN. Tool 128 yielded BN deposition rates in excess of 10 times greater than those reported by Huang¹ (1 to 9 nm/hr) for equivalent TEB flow rates (16-87 $\mu\text{mol}/\text{min}$), suggesting the two deposition systems exhibit significant differences in gas handling, severity of gas phase pre-reactions, or both.

Thrust 2 was intended to study the use of BBr_3 as a substitute for the more conventional TEB as a boron precursor. BBr_3 has the notable advantage of being free of carbon, a common impurity in BN, while remaining more reactive at low temperature than BCl_3 or BF_3 .⁵ It was found that producing crystalline BN with the combination of BBr_3 and NH_3 required vastly different deposition condition than the combination of TEB and NH_3 utilized in Thrust 1. In particular, the deposition with gas phase V/III ratios of 1-10 were more successful in producing crystalline films for the combination of BBr_3 and NH_3 , while the combination of TEB and NH_3 commonly require V/III ratios of 100’s or even 1000’s to prevent deposition of discolored, non-

stoichiometric BN.⁶ Attempts to deposit with the combination of BBr_3 and NH_3 at V/III ratios great than 10 yielded increasingly large volumes of fine white powder, presumable BN, that coat the deposition chamber and substrate. A white ceramic-like material also began to coat chamber components at deposition temperatures greater than ~ 1250 °C. This ceramic-like material is thought to be the salt ammonium bromide (NH_4Br), or a closely related compound, based on the physical properties, the high solubility in water, and the release of NH_3 gas when contacted by water. Dust and salt formation could be reduced to manageable levels by reducing the total pressure and increasing the diluent gas flow. The initial portion of Thrust 2 continued to study what, if any, effects the AlN-BN interface played in c-BN formation. However, AlN surfaces did not provide measurably different epitaxial behavior than H_2 etched sapphire surfaces, and the crystalline quality for films deposited by the combination of BBr_3 and NH_3 was consistently poor. Most tested conditions resulted in seemingly amorphous BN, lacking all BN related XRD features. No c-BN was observed by XRD or FTIR in this thrust.

Thrust 3 was intended to study the effects of mixing aluminum, boron, and nitrogen precursors on the crystalline structure of the BN, attempting to emulate the results of Subramani.² No crystalline material was deposited for conditions flowing more BBr_3 than TMAI. Increasing temperature, decreasing pressure, and increasing the flow of TMAI relative to BBr_3 did improve the crystallinity of the films. Increasing temperature, the flow of NH_3 , and the flow of TMAI relative to BBr_3 were found to increase the surface roughness of the deposited films. Deposition on AlN on sapphire substrates was found to produce polycrystalline films while deposition on hydrogen etched sapphire substrates produced epitaxial films with the wurtzite AlBN films [001] aligned to the sapphire [001]. Figure 1 shows representative $2\theta-\omega$ XRD for AlBN films on AlN and sapphire substrates. The wurtzite AlBN (002) peak was shifted to 36.35° in $2\theta-\omega$ for BBr_3/TMAI ratios of 0.25-1. It is unclear why the BBr_3/TMAI ratio has seemingly little impact on the alloy composition. It is unlikely that a solubility limit of boron in AlN was reached as wurtzite AlBN alloys have been demonstrated with up to 20% boron by MOCVD.⁷ Another unexpected behavior of the BBr_3 and TMAI mixture was a synergistic increase in deposition rate of the mixture relative to either precursor used independently. This synergistic effect was the most pronounced at 700 °C, 500 Torr total pressure, and with low NH_3 flows. Figure 2 shows the non-linear behavior of TMAI addition to a fixed flow of BBr_3 and NH_3 . An increase in deposition rate proportional to TMAI flow occurs up to 22 $\mu\text{mol}/\text{min}$. The deposition rate levels off greatly when further increasing TMAI flow. Within the region of proportional behavior, TMAI increases deposition rate 12 times more than BBr_3 on a molar basis. However, under otherwise identical conditions, no deposition occurs in the absence of BBr_3 , regardless of TMAI flow rate. It is unknown what mechanism gives rise to this behavior, but it is likely related to the interaction of gases with BBr_3 or its decomposition products, Br or HBr.

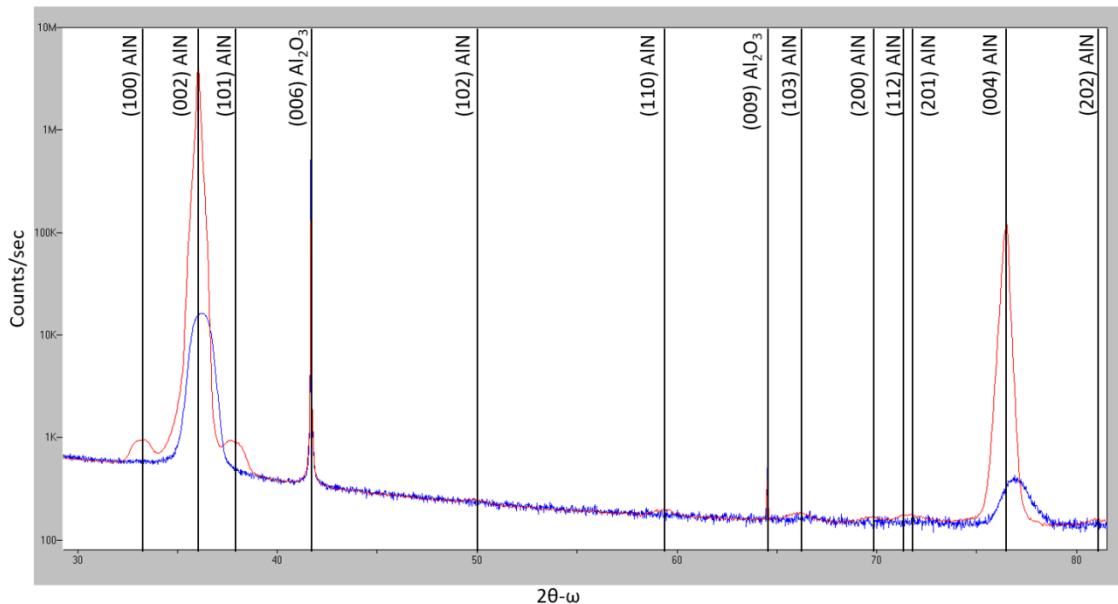


Figure 1: 20- ω XRD of (red) HTA1334 AlN deposition on AlN on sapphire substrate showing numerous asymmetric reflections and (blue) HTA1333 AlN deposition on sapphire showing only the (002) and (004) symmetric reflections. Markers indicate the expected peak positions of polycrystalline wurtzite AlN and single crystalline c-oriented sapphire.

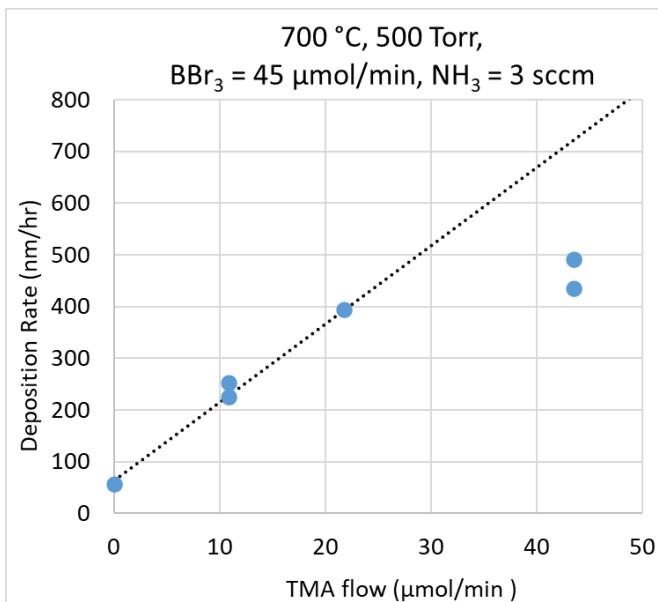


Figure 2: Film deposition rate with TMAI flow with fixed BBr_3 and NH_3 flows. The dashed line is a guide to the eye illustrating the significant deviation from linearity for deposition rate at higher TMAI flows.

ANTICIPATED OUTCOMES AND IMPACTS:

While no c-BN was produced during this project, several important findings were made.

- (1) Simple proximity or mixing of AlN and BN is not sufficient to produce c-BN. With regards to the work of both Huang and Subramani, it appears addition factors must come into play. In the case of Huang, it seems likely that some finite degree of gas phase pre-reaction between TEB and NH₃ is beneficial to nucleation of c-BN on AlN. It is also likely that some aspect of the AlN surface beyond composition and orientation are relevant for the nucleation of c-BN. Possible properties of a surface which are typically unknown during MOCVD include surface stoichiometry, termination, and reconstruction and could all plausibly control nucleation behavior of BN. In the case of Subramani, it is possible that the exact mixture of precursor species is critical and similar, but not identical, precursors simply do not participate in some necessary process of c-BN formation. This could deposition eliminate MOCVD as a potential technique for producing c-BN if AlCl₃ is found to be necessary. However, similarly cost effect and large area chemical vapor deposition techniques, such as hydride vapor phase epitaxy, may remain viable.
- (2) BBr₃ appears especially well suited for the deposition of amorphous BN films. Amorphous BN has recently become a dielectric material of interest with a dielectric constant less than 2 and a critical electrical field of 7 MV/cm.⁸ BBr₃ offers the notably advantages over TEB of being carbon free and depositing stoichiometric BN at temperatures as low as 700 °C with low NH₃. BBr₃ can be supplied in a standard bubbler and would allow low temperature, plasma damage free BN passivation layers to be deposited in virtually all III-nitride MOCVD tools.
- (3) The unusual interaction of BBr₃ with TMAl and NH₃ has wide ranging significance. The initial experimentation suggests the addition of BBr₃ increases the reactivity of NH₃ during the deposition of nitride materials. The direct reaction of BBr₃ and NH₃ would be expected to be a less reactive adduct and would not increase the reactivity of NH₃. Therefore, it is likely that the decomposition species of BBr₃, such as bromine or HBr, are the species responsible for the increased reactivity of NH₃. A chemical additive capable of controlling the reactivity of NH₃ could possibly increase nitrogen incorporation into films and allow for reduced NH₃ partial pressures.

The author is in contact with experts on machine learning at Sandia National Laboratories hoping to utilize the approximately 300 unique deposition conditions tested during this project as a set of training data for future nitride epitaxy surveys. In addition, the large number of FTIR measurements collected for BN films on AlN has improved the sensitivity of the differential

reflectance technique to approximately one monolayer of sp-2 BN on AlN, something previously possible only for BN on sapphire.

CONCLUSION:

We have investigated the use of MOCVD as a technique for c-BN synthesis. The successes of Huang and Subramani were not reproduced. In the case of Huang, some fundamental aspect for how c-BN nucleation occurs on an AlN surface remains unknown. In the case of Subramani, it is possible that an exact reproduction of their precursor mixture may be necessary to produce c-BN. The precursor BBr₃ was identified as having potential applications for low temperature and carbon-free deposition of amorphous BN. The unusual interaction between BBr₃, TMAl, and NH₃ suggest that the addition of bromine or HBr sources may enhance the reactivity of NH₃ during III-nitride deposition and allow greater effective NH₃ partial pressure or lower actual NH₃ partial pressure when desirable.

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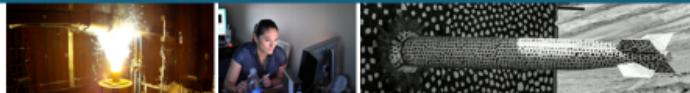
ADDENDUM:



LABORATORY DIRECTED RESEARCH & DEVELOPMENT

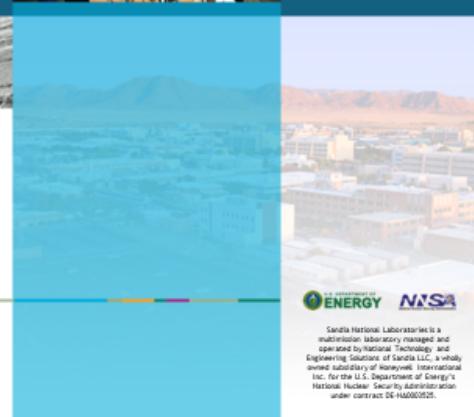
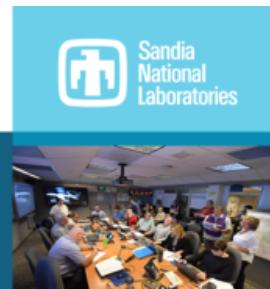
WHERE INNOVATION BEGINS

LDRD Ending Project Review Chemical Vapor Deposition of Cubic Boron Nitride #223219



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PM: Mary Crawford (1800)

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2 PURPOSE, GOALS AND APPROACH



What is the ST&E question that inspired you to do this research?

- “Can cubic boron nitride (c-BN) layers be synthesized by chemical vapor deposition (CVD)?”
 - c-BN offers the smallest, fastest, and most efficient power electronic devices of all known semiconductors.
 - However, c-BN synthesis currently requires either gigapascals of pressure or a non-equilibrium process, such as ion-bombardment. The small crystal size and large cost restrict c-BN to niche uses.
 - A CVD technique would greatly increase the feasibility of c-BN based power electronics and coatings.

How was this different from previous research?

- Combine multiple techniques known to promote c-BN formation: alloying and doping with elements known to modify BN phase stability, use of interfaces known to promote c-BN nucleation, and deposition using precursors that preferentially etch unwanted BN phases.

State-of-the-art c-BN

3

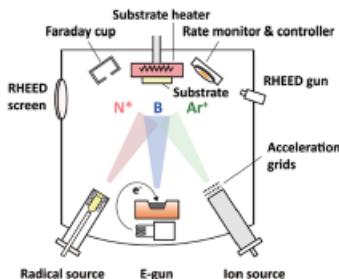
- c-BN has enormous potential for power electronics due to a number of outstanding material properties, such as an ultra-wide bandgap and the ability to readily dope both n-type and p-type, unlike AlN or diamond.
- However, “bulk” c-BN crystals are still ~ 1 mm in diameter and c-BN thin film deposition is complicated by the need for a non-equilibrium energy source to form the cubic phase at low pressure.
- Ion-beam-assisted-molecular-beam-epitaxy is currently the most successful deposition technique for c-BN thin film electronics, but such films are still limited to ~ 100 nm thickness due to residual stress from the ion bombardment.

	c-BN	AlN	Diamond
Bandgap (eV)	6.4	6.0	5.5
Projected critical electric field at 10^{16} cm $^{-3}$ doping (MV cm $^{-1}$)	17.5	15.4	13.0
Electron mobility (cm 2 V $^{-1}$ s $^{-1}$)	825	426	4500
Hole mobility (cm 2 V $^{-1}$ s $^{-1}$)	500	-	3800
Thermal conductivity (W m $^{-1}$ K $^{-1}$)	768	285	2270

Table values taken from Tsao et al., *Adv. Electron. Mater.*, **4**, 1600501 (2018).



c-BN crystals produced at high pressure.
Taniguchi, *Comprehensive Hard Materials*, **3**, 587 (2014).



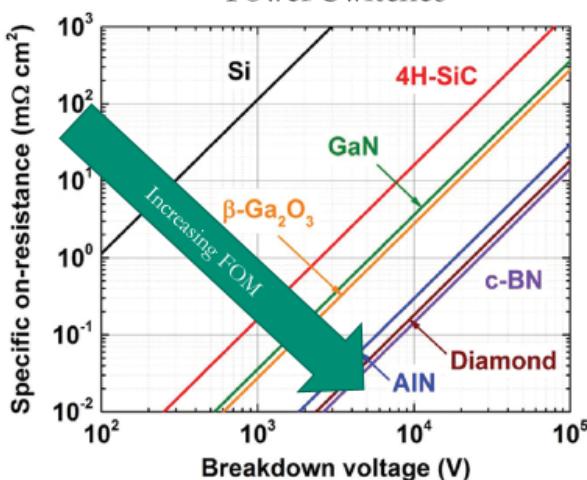
Schematic of ion-beam-assisted-molecular-beam-epitaxy with independent sources.

Hirama et al., *Appl. Phys. Express*, **10**, 035501 (2017).

Power Electronics

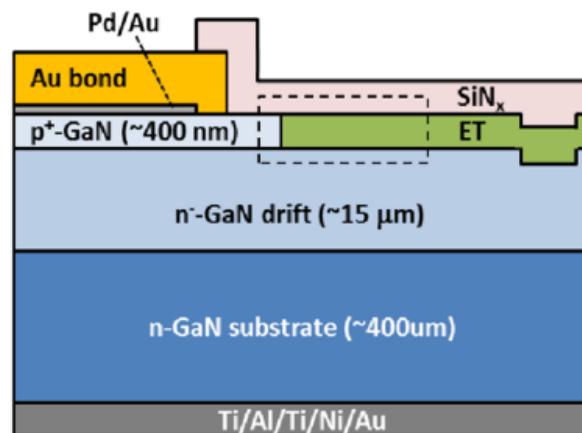
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Figure-of-Merit for Vertical Power Switches



Tsao et al., *Adv. Electron. Mater.*, **4**, 1600501 (2018).

Vertical Power Switch



Dickerson et al., *IEEE Trans. on Electron. Devices*, **63**, 419 (2016).

Background

5

- c-BN does not form at atmospheric pressure without additional non-equilibrium sources of energy such as a plasma or ion beam.
- However, researchers have formed c-BN when BN is synthesized in the presence of aluminum nitride (AlN).
- There does not appear to be strict pressure, temperature, composition, technique, or even state of matter requirements for this phenomenon. The table below shows conditions for 3 reports of c-BN formation:

Researcher	Pressure	Temperature	%Al	Technique	State of precursors
Hirano	5.5 - 7 GPa (>50000 atm)	1000 - 1700 °C	20% AlN 80% BN	Hot press	All solids
Subramani	1 atm	500 °C	Various	CVD	All gases
Huang	0.02 atm	1180 °C	No mixing	CVD	Gases at solid surface

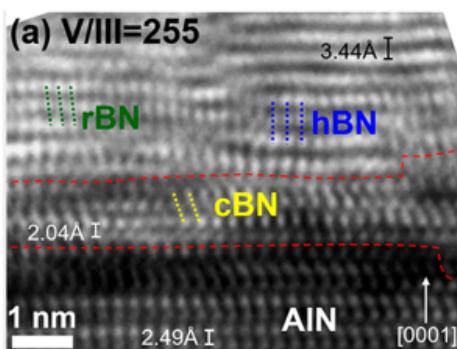
This is a huge process window!

Hirano et al., *J. Am. Ceram. Soc.*, **64**, 734 (1981).
Subramani et al., *Mater. Science-Poland*, **37**, 395 (2019).
Huang et al., *ACS Appl. Nano Mater.*, **3**, 5285 (2020).

Background

6

- Huang et al. recently showed experimentally that ~1 nm of c-BN can be formed at the interface of AlN and BN. Further BN deposition yields non-cubic BN phases.
- Spataru et al. calculated that ~ 1 nm layers of AlN and BN adopt modified phases when in contact.
- It is unknown if this phase modification can be extended beyond a single interface or beyond 1 nm.



High resolution TEM image of BN layers view along the AlN [11-20] zone axis. The region of c-BN is delineated by the red dashed lines.

Huang et al., *ACS Appl. Nano Mater.*, **3**, 5285 (2020).

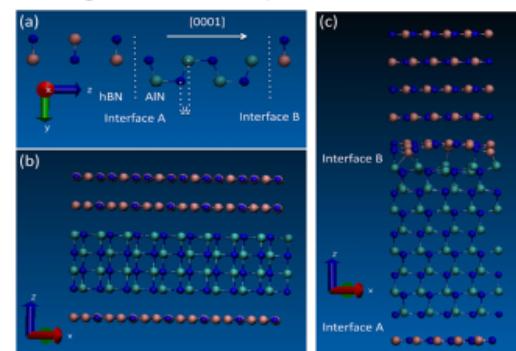


FIG. 1. (a) Illustration of the starting configuration (before optimization) of the $(hBN)_3(AlN)_4$ superlattice. Side view of the optimized supercell geometry of (b) the $6\sqrt{3} \times 6\sqrt{3}/8 \times 8 (hBN)_3(AlN)_4$ SL and (c) the $5 \times 5/4 \times 4 (hBN)_6(AlN)_8$ SL.

Spataru et al., *Appl. Phys. Lett.*, **114**, 011903 (2020).

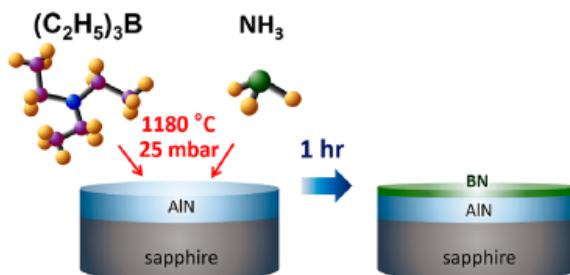
7 | R&D Plan

Research plan divided into 3 thrust, each attempting to exploit different phenomena

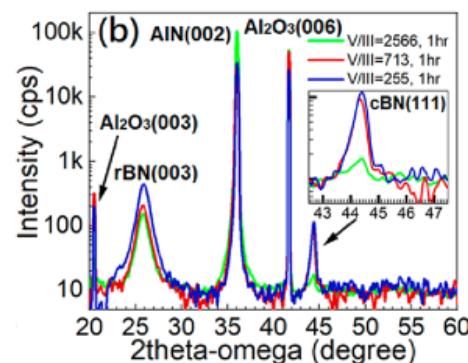
1. Crystal structure transfer between AlN and BN
2. Boron Tribromide (BBr₃)
3. Alloying BN and AlN

8 | Thrust 1: Crystal structure transfer between AlN and BN

- Began with an attempt to reproduce the work of Huang (ie. conventional MOCVD of AlN and BN)
 - Huang demonstrated ~1 nm of c-BN at the interface between AlN and sp2-BN films
- Tested both direct translation of reported conditions and reasonable modifications to conditions to account for differences in systems or calibrations
- No c-BN and only poorly crystalline sp2-BN found by x-ray diffraction (XRD) or Fourier-transform infrared spectroscopy (FTIR)

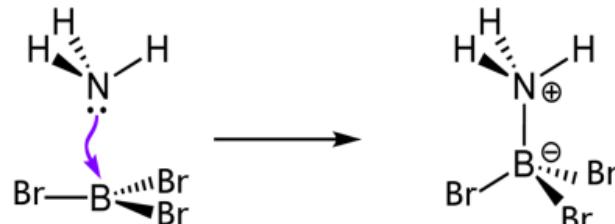


Huang et al., ACS Appl. Nano Mater., 3, 5285 (2020).



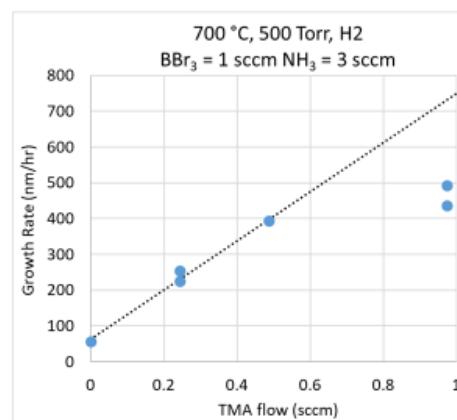
9 Thrust 2: Boron Tribromide

- Boron Tribromide (BBr_3) forms an adduct with ammonia that approximates sp³-hybridized boron and halide acids preferentially etch sp²-BN over c-BN by a factor of ~100 times
- Tested wide range of conditions: 700 to 1600 °C, 5 to 500 Torr, 0.25 to 1000 $\text{NH}_3:\text{BBr}_3$
- In general, BBr_3 allows for ~100 to 1000 times lower NH_3 flows and lower temperature deposition than metalorganic boron precursors
- However, above ~1200 °C begin getting deposits of ammonium bromide or related compounds on chamber components
- Does appear to be a promising pathway for low carbon, low temperature, amorphous BN without a plasma
- No c-BN found by XRD or FTIR



10 Thrust 3: Alloying BN and AlN

- Attempted to emulate the work of Subramani. Could not reproduce all aspects of their process due to their use of aluminum trichloride, Al metal substrates, etc.
 - Low temperature, atmospheric pressure, mixtures of Al and B precursors
- Found some interesting interactions between precursors
 - Conditions existed where trimethylaluminum (TMAI) delivers Al into a growing film ~10 times more efficiently than BBr_3 delivers B, but TMAI deliver no Al if BBr_3 is absent
 - Suggest that BBr_3 or products of its decomposition can increase the reactivity of NH_3
- No c-BN found by XRD





11

PI's PROJECT LEGACY



What will be the impact of your project results, both in your field and in potential applications?

While no c-BN was generated during this study, we have identified possible applications for the novel precursors utilized:

- BBr_3 for low temperature amorphous BN, a dielectric with $k < 2$ and $\sim 7 \text{ MV/cm}$ breakdown field. Could be included on virtually all nitride MOCVD systems
- Addition of Br appears to improve NH_3 reactivity. Could be used to increased effective NH_3 concentrations in situation were greater NH_3 concentration are useful but not possible (GaN power diodes or InN) or when low NH_3 concentrations are useful (AlGaN and AlN)

**What are the key aspects of this research you would want your colleagues to take away?
What are you most proud of? Did anything not work as expected?**

- Approximately 300 unique growth conditions were surveyed
- Can conclude that simple proximity or mixing of AlN and BN is not sufficient to yield c-BN
 - Remains unclear what facet is missing compared to the Huang report in particular

12

CAPABILITIES DEVELOPMENT



- Establishment of Capabilities expected to impact future work
 - MOCVD 128 demonstrated to be compatible with halide chemistries
 - Data collected during FTIR now allows for monolayer thickness resolution for sp₂-BN films on AlN
- Career Development
 - PI and team early career staff
 - PI has greatly improved competence at XRD with tutelage from Stephen Lee



IA/PM PROJECT LEGACY

13



How did this project contribute to LA strategic goals and objectives?

- **Potential mission-relevant Impacts and timeframe:** This short but growth-intensive study revealed the challenges of c-BN and is helping Sandia to re-evaluate future investments of c-BN. It further identified other benefits (amorphous BN, more efficient NH₃ usage in GaN, InN and AlGaN growth) that could impact Sandia's III-N efforts in the near-term.
- **IA metrics:** Early career PI and staff development, expanded Sandia's MOCVD capabilities (reactor 128 to halide chemistries)
- **Summarize any important lessons learned, good or bad – What was learned from any “failure?”:** Proximity or mixing of AlN and BN is not sufficient to yield c-BN. It may be that very particular interface effects, native defects, or impurities are critical for c-BN nucleation. Crystal structure transfer remains a poorly understood effect.

What are the key results from this research that will be useful to other current and future projects?

- c-BN is of great interest to Sandia and the power electronics community. However, practicality of synthesis of thick, device-quality films by manufacturable methods was not known. This short but intensive investigation has demonstrated the complexity and remaining materials challenges that must be overcome.
- During this proposal development and execution, n-type c-BN was demonstrated by MBE using energetic ion-beam exposure during growth (Hirama et al., *Appl. Phys. Lett.*, **116**, 162104 (2020)). This n-type doping is still 5 orders of magnitude worse than bulk c-BN doping concentrations, but it is an important demonstration for the technique. While not nearly as manufacturable a technique as CVD, it points to the importance of non-equilibrium growth conditions and potential interest in pursuing unconventional applications of this in CVD growth techniques (e.g., X-ray excitation in place of ion-beam).

Technology insertion and follow-on funding for potential and realized ROI

- No technology insertion or follow-on funding in place at this time.