Design and development of highly textured boron nitride thin films for electronic devices

Chng, Soon Siang

2021

Chng, S. S. (2021). Design and development of highly textured boron nitride thin films for electronic devices. Doctoral thesis, Nanyang Technological University, Singapore.
<https://hdl.handle.net/10356/152095>

<https://hdl.handle.net/10356/152095>

<https://doi.org/10.32657/10356/152095>

This work is licensed under a Creative Commons Attribution-NonCommercial 4.0 International License (CC BY-NC 4.0).

Downloaded on 26 Apr 2023 13:57:09 SGT

**NANYANG
TECHNOLOGICAL
UNIVERSITY**

SINGAPORE

**Design and Development of Highly
Textured Boron Nitride Thin Films for
Electronic Devices**

CHNG SOON SIANG

School of Electrical and Electronics Engineering

**A thesis submitted to the Nanyang Technological
University in partial fulfillment of the requirement for
the degree of Doctor of Philosophy**

2021

Statement of Originality

I hereby certify that the work embodied in this thesis is the result of original research, is free of plagiarised materials, and has not been submitted for a higher degree to any other University or Institution.

22 Jan 2021

Date

Chng Soon Siang

Supervisor Declaration Statement

I have reviewed the content and presentation style of this thesis and declare it is free of plagiarism and of sufficient grammatical clarity to be examined. To the best of my knowledge, the research and writing are those of the candidate except as acknowledged in the Author Attribution Statement. I confirm that the investigations were conducted in accord with the ethics policies and integrity standards of Nanyang Technological University and that the research data are presented honestly and without prejudice.

22 Jan 2021

Date

Assoc. Prof Edwin Teo Hang Tong

Acknowledgement

I would like to thank Prof Edwin Teo for his immense guidance and countless inspiration and ideas towards my research project, Dr. Zhu Minmin for his practical guidance and creative ideas throughout the years, and Dr. Maziar Shakerzadeh for his advice.

I would also like to thank Ms. Debbie Chia for her excellent administrative work and Mr. Hasman Bin Hassan. All things in the laboratory seem to only work when Hasman is around. His hands-on expertise and experiences with different machines greatly contributed to the completion of my thesis.

Abstract

This thesis focuses on the alignment engineering (i.e. the orientation of the basal plane to the substrate surface) and the isotopic engineering (i.e. the modification of the isotopic composition of the compound) of hexagonal boron nitride (h-BN) thin films for its applications on electronic devices for enhancement thermal and electronic performances. Both alignment engineering and isotopic engineering open up possibilities in the precise manipulation of thermal and electronic properties of the resultant thin films for enhancements in the performances of the eventual devices.

Alignment engineering was shown to be achieved via the precise control of the deposition parameters using the high power impulse magnetron sputtering (HIPIMS) technique. In particular, two strategies were used, namely: control of nitrogen gas flow rate ratio and control of mean power supplied to the target. Depositions were conducted at a certain interval gas flow rate ratio and independently, at a lower mean power supplied to the target yield aligned h-BN.

Isotopic engineering was demonstrated to be achievable using the dual-magnetron HIPIMS technique. Isotopically pure targets were sputtered simultaneously. The resultant h-BN thin films were shown to be isotopically controllable, i.e. the thin films' isotopic concentrations can be controlled, using the precise manipulation of mean power supplied to each target.

Deposited h-BN thin films were applied as encapsulation in InSe-based transistors, with an effective encapsulating effect as it prevents the degradation of InSe transistors upon exposure to ambient conditions. InSe-based h-BN encapsulated transistors retain its semiconducting nature and attain a mobility of $6.3 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ at room temperature.

Isotopically enriched h-BN thin films were shown to have an enhancement in thermal conductivities, on an average of over 200%, as compared to the non-isotopic enriched variants. As evaluated by the performance as a thermal self-dissipative layer on AlGaN/GaN high electron mobility transistor (HEMT), the isotopically enriched layer is capable of reducing thermal self-

heating effects, although the device may not be as well-functioning as it ought to be due to the ion implantation damage done on the 2-dimensional electron gas.

The h-BN thin films were also used as a memory resistive device where oxygen vacancies play a key role in forming the conductive filament in the SET and RESET switching mechanism. The memory resistive mechanism was demonstrated in the h-BN thin films deposited on copper foil and Au/Ti were used as electrodes. The soft-forming step was required, and the breakdown field was measured to be around 10 MV cm^{-1} .

Lastly, future work can be done on manipulating the microstructure of isotopically-enriched h-BN thin films. As the dual-magnetron sputtering setup is dynamic and doubles the deposition parameters due to the magnetron, precise microstructure sculpturing may prove to be a challenging and yet rewarding endeavor. Furthermore, alignment engineering using pure boron targets resulting in a dense microstructure remains elusive.

Authorship Attribution Statement

This thesis contains materials from 2 papers published in the following peer-reviewed journal(s) in which I am listed as an author.

Chapter 5 and Chapter 6 are published in:

- 1) S. S. Chng, M. Zhu, Z. Du, X. Wang, M. Whiteside, Z. K. Ng, M. Shakerzadeh, S. H. Tsang and E. H. T. Teo, *J. Mater. Chem. C*, 2020, 9558–9568.

The contributions of the co-authors are as follows:

- S. S. Chng's contributions were paramount to the research project planning and coordination, the sample preparation, the microstructure characterization (except the TEM, XPS, and thermal measurements that were outsourced), and the editing of the manuscript.
- M. Zhu's contributions were in guiding the research direction.
- Z. Du guided the experimental setup.
- X. Wang contributed to the measurements of thermal conductivities of the thin film using the NanoTR technique.

- M. Whiteside provided the GaN-AlGaIn heterostructures for device fabrication and h-BN thin film depositions.
- Z. K. Ng contributed to providing experimental advice and support in the depositions of the h-BN thin films.
- M. Shakerzadeh guided the manuscript editing.
- S. H. Tsang guided the experimental setup.
- E. H. T. Teo provided supervisory guidance in the research project and direction.

2) S. S. Chng, M. Zhu, J. Wu, X. Wang, Z. K. Ng, K. Zhang, C. Liu, M. Shakerzadeh, S. Tsang and E. H. T. Teo, *J. Mater. Chem. C*, 2020, 8, 4421–4431.

The contributions of the co-authors are as follows:

- S. S. Chng's contributions were paramount to the research project planning and coordination, the samples preparation, the microstructure characterization (except the TEM, XPS, and thermal measurements that were outsourced), and the editing of the manuscript.
- M. Zhu's contribution was in guiding the research direction.
- J. Wu contributed to providing research advice.
- X. Wang contributed to the measurements of thermal conductivities of the thin film using the NanoTR technique.
- Z. K. Ng contributed in providing experimental advice and support in the depositions of the h-BN thin films.
- K. Zhang contributed to providing experimental and technical support.
- C. Liu contributed to providing experimental support and resources.
- M. Shakerzadeh guided the manuscript editing.
- S. H. Tsang guided the experimental setup.
- E. H. T. Teo provided supervisory guidance in the research project and direction.

22 Jan 2021

Date

Chng Soon Siang

Table of Content

Statement of Originality.....	3
Supervisor Declaration Statement.....	4
Acknowledgement	5
Abstract	6
Authorship Attribution Statement.....	7
Table of Content	9
List of Abbreviations	14
1 Introduction.....	15
1.1 Background	15
1.2 Motivation	16
1.2.1 Objectives	17
1.3 Scope Definition.....	18
1.4 Organization of the Thesis	18
1.5 Contributions.....	19
1.5.1 Journal Articles	19
1.6 References	20
2 Literature Review.....	25
2.1 Thin Film Technology.....	25
2.1.1 Magnetron Sputtering Technique	25
2.1.2 Introduction to High Power Impulse Magnetron Sputtering (HIPIMS)	27
2.2 Sputtering of LaB ₆ and Pure Boron Targets using HIPIMS	33
2.2.1 Sputtering with LaB ₆ Target	33

2.2.2	Sputtering with Boron Target	33
2.3	Hexagonal Boron Nitride	39
2.3.1	Anisotropic Nature of h-BN.....	40
2.3.2	Isotope Engineering of h-BN	46
2.3.3	Applications of h-BN Thin Films on Devices	51
2.4	Conclusion.....	58
2.5	References	59
3	Experimental Procedures and Characterization	65
3.1	Experimental Procedures.....	65
3.1.1	Wafer-cleaning Process	65
3.1.2	Electron-beam Physical Vapor Deposition (E-Beam)	65
3.2	Characterization	67
3.2.1	Fourier Transform Infrared Spectrometry (FTIR)	67
3.2.2	Raman Spectrometry.....	69
3.2.3	Transmission Electron Microscopy (TEM)	71
3.2.4	Electron Energy Loss Spectroscopy (EELS)	73
3.2.5	Hall Effect Measurements.....	74
3.3	References	76
4	h-BN Growth using High Power Impulse Magnetron Sputtering (HIPIMS)	79
4.1	h-BN Growth using LaB ₆ Source.....	79
4.1.1	Infrared Spectra of a Typical h-BN Film Deposited using LaB ₆ Source.....	79
4.1.2	Effects of Base Pressure on the Quality of Films Deposited	80
4.1.3	Effect of Base Pressure on Thickness of Thin Films	81
4.1.4	Effect of Base Pressure on the R Value of h-BN Films Deposited	84
4.1.5	Deposition Rate of h-BN Deposition using LaB ₆ as a Source.....	87

4.1.6	Effects of Variation of Peak Current on the FTIR Spectra of Samples	90
4.1.7	Deposition of h-BN on Gallium Nitride Substrates using LaB ₆ as a Source.....	92
4.2	h-BN Growth using Pure Boron Target	95
4.2.1	RF-Assisted Plasma Ignition for the Deposition of h-BN using a Pure Boron Source 95	
4.2.2	Oxidation of h-BN Thin Films Deposited using a Pure Boron Source.....	96
4.2.3	Effects of Substrate Temperature on the Quality of the Deposited h-BN Films ..	101
4.2.4	Effects of Pulse Width on the FTIR and Raman Spectra of Deposited h-BN Films 103	
4.3	Conclusion.....	105
4.4	References	106
5	Control of the Orientation and Isotopic Composition of h-BN Thin Film	110
5.1	h-BN Thin Film Orientation Control using Gas Flow Ratio.....	110
5.1.1	Preparation of the h-BN Thin Films	110
5.1.2	Optical and Bonding Characterizations	111
5.1.3	Surface Morphology and Microstructure of the As-Deposited h-BN Films.....	114
5.1.4	Orientation Control of the As-Deposited h-BN Films and its Associated Thermal Conductivity.....	116
5.2	Orientation Control through the Average Power Supplied to the Target.....	121
5.2.1	Optical and X-Ray Diffraction Characterizations of the h-BN Films	122
5.2.2	Microstructure and Elemental Composition Characterizations of the h-BN Films 126	
5.2.3	Optical Bandgaps and the Thermal Conductivities of the h-BN Films Deposited at Different Average Power Supplied to the Target	131
5.3	Control of Isotopic Composition of h-BN Thin Films	133
5.3.1	Motivation Driving Control of Isotopic Composition	133

5.3.2	Experimental Procedures for the Depositions of Isotopically Enriched h-BN Films	135
5.3.3	Growth of Isotopically Controlled h-BN Thin Films and its Characterizations...	136
5.3.4	Optical Band Gap and Thermal Performances of Isotopically Controlled h-BN Thin Films	142
5.4	Conclusions	145
5.5	References	146
6	Applications of h-BN on Devices for Electronics and Thermal Management	151
6.1	h-BN as a Passivating/Encapsulating Layer for Electronic Devices.....	151
6.1.1	Growth and Characterization of InSe Transistors.....	151
6.1.2	h-BN as Passivation Layer and Long-Term Stability	153
6.1.3	Performances of the Fabricated Device	155
6.2	h-BN Based Resistive Memory Device	156
6.2.1	Operation and Performance of the h-BN Based Resistive Memory Device.....	156
6.2.2	Set/Reset Mechanism of h-BN Based Resistive Memory Device	158
6.3	Isotopically Enriched h-BN Films with Self-Heat Dissipation Effects on GaN and AlGaIn/GaN HEMTs	161
6.3.1	Dielectric Performances of h-BN Thin Films with Different Isotopic Compositions	161
6.3.2	Electrical Performances of h-BN Thin Films with Different Isotopic Compositions	163
6.3.3	Electronic Performances of AlGaIn/GaN High Electron Mobility Transistors (HEMT) with h-BN as Passivating, Heat Self-Dissipating Layer	165
6.4	Conclusions	167
6.5	References	168
7	Conclusions.....	170

7.1	On the Study of Deposition of h-BN using LaB ₆ / pure-Boron Source	170
7.1.1	Deposition using LaB ₆ Source	170
7.1.2	Deposition using Boron Source	171
7.2	On h-BN Thin Films as Encapsulating Layer for InSe Transistors	171
7.3	On h-BN Thin Films as a Novel Memory Resistive Device.....	172
7.4	On Isotopically Enriched h-BN Thin Films as Heat-Dissipative Layer on High-Powered Transistors.....	172
7.5	Future Work	173
7.5.1	On the Deposition using a Pure Boron Source	173
7.5.2	On Encapsulating Layer on InSe Transistors.....	174
7.5.3	On Isotope Engineering of h-BN Thin Films	174
7.5.4	On h-BN as Passivating Layer on AlGaN/GaN HEMTs.....	175
7.6	Final Concluding Remarks.....	175

List of Abbreviations

Abbreviations	What it stands for
BN	Boron Nitride
HIPIMS	High Power Impulse Magnetron Sputtering
LaB₆	Lanthanum Hexaboride
h-BN	Hexagonal Boron Nitride
vo-BN	Vertically ordered BN
TC	Thermal Conductivity
c-BN	Cubic Boron Nitride
HPHT	High Pressure High Temperature
UV	Ultraviolet
CVD	Chemical Vapor Deposition
HRTEM	High Resolution Transmission Electron Microscope (or Microscopy)
t-BN	Turbostratic Boron Nitride
r-BN	Rhombohedral Boron Nitride
w-BN	Wurtzite Boron Nitride
TEM	Transmission Electron Microscope
PVD	Physical Vapor Deposition
DCMS	Direct Current Magnetron Sputtering
RF	Radio Frequency
MFC	Mass Flow Controller
EELS	Electron Energy Loss Spectroscopy
AFM	Atomic Force Microscopy
FTIR	Fourier Transform Infrared Spectroscopy
XRD	X-Ray Diffraction
TDTR	Time Domain Thermoreflectance
FFT	Fast Fourier Transform
IC	Integrated Circuit

1 Introduction

1.1 Background

Human activities can be broadly characterized into the business of outsourcing and the business of sustenance. Activities like the Arts, agriculture, and medicine are mainly for human sustenance, purported a state of normalcy in everyday living. The business of outsourcing comprises the outsourcing of mechanical power and computational power. The development of steam engines and later, induction motors drive the techniques of mass production, effectively providing the mechanical work, otherwise might be performed by humans, that was necessary to bring tremendous progress to humanity. In the 1960s, armed with the understanding of basic solid-state theory, engineers invented the first silicon-based transistors. The invention led to the outsourcing of computational power, the first in human history when humans can outsource their computational needs. Even in the 1960s, supporting America's achievement in landing on the moon was a team of 'human-computers', mathematicians who were employed to calculate the math needed to pull off the feat. Over the years, electronics have performed billions of computations, powering all our devices from personal computers to smartphones. The **integrated circuit** (IC) chips powering these devices are getting smaller by the day, best exemplified in Moore's Law. Fast-forward to today, nano-scale electronics underpin much of our everyday lives, we have outsourced much of our computation needs, and together with machinery, much of our mechanical power needs, these result in the progress that humanity is first witnessing, whereby over 7 billion people enjoy today.

The recent miniaturization to the sub-micron and even to the nanoscale of electronic components has led to a hyped interest in thin-film lamellar materials to exploit the beneficial properties that emerge at the sub-micron scale. Exceptional phenomena have been detected as a result of restricting the material thickness. Properties including heat transport, energy storage, and electronic behaviour can be enhanced from its values of the bulk crystal, a consequence of the high surface area to volume ratio, and the confinement effect of the quasi-particles (electrons and phonons) in the confined setting.

Thin films with a variety of band structures,¹ thermal and mechanical stabilities, optoelectronic responses and other unique properties have been discovered. As examples, a variety of conducting

lamellar materials like graphene, or semiconducting like MoS₂²⁻⁴ and other transition metal dichalcogenides, and insulating like hexagonal boron nitride structures have been studied as a viable material for functional, flexible,^{5,6} and tuneable devices from their heterostructures. There are several problems in material integration especially in heterostructures, such as material compatibility, scalability, product life, and reliability. These issues need to be addressed before the realization of these materials in real-world applications. Furthermore, very often, devices and prototypes are limited by the lack of consistent and robust synthesis techniques which are capable of fabricating complex heterostructures at the industrial scale, beyond a laboratory setting.

1.2 Motivation

Hexagonal boron nitride (h-BN) with its large bandgap ($\sim 5.6 - 6$ eV),⁷⁻⁹ high in-plane thermal conductivity,¹⁰⁻¹⁵ high thermal neutron cross-section,¹⁶⁻²⁰ low dielectric constant coupled with high breakdown field²¹⁻²⁵, room for isotope engineering^{12,15,26,27}, high thermal and chemical stability²⁸⁻³² and low lattice mismatch with other 2-dimensional (2D) material³³⁻³⁵ and have led to it being utilized in thermal neutron detectors, dielectric layers, passivation / encapsulation layer for sensitive transistors, substrates for some 2D materials and in thermal management applications.

On the other hand, high power impulse magnetron sputtering (HIPIMS) is a form of magnetron sputtering characterized by high ionization densities,^{36,37} offers excellent advantages with in adhesion, hardness, and dense morphology.³⁸⁻⁴¹

HIPIMS has become an enabler to the unprecedented widespread use of h-BN thin films at an industrial scale. It offers an opportunity to sputter good quality h-BN thin films with sculptured microstructure, capturing the advantages of HIPIMS in adhesion and dense morphology and the manipulability of deposition parameters points to the many unknown possibilities of controlling the films' resultant properties. Consequently, this thesis dives right into the heart of applying HIPIMS deposited h-BN for industrial applications by studying the properties of h-BN and its influences on the performances of the devices for some applications.

Several materials are limited in their functionalities because of their reactivity upon exposure to the atmosphere. InSe (indium selenide) thin films also suffer from substantial degradation

compared to bulk InSe under exposure to ambient conditions, possibly due to interactions with oxygen and water which are present in the atmosphere.⁴³ To circumvent the problem of limited chemical stability, one should consider encapsulating the as-fabricated InSe transistors with a layer of an h-BN thin film with high chemical stability, for instance, h-BN atomically-thin layers were shown to be inert to oxidation up to 850 °C.⁴⁴ This line of research is pursued in this work.

Metal-oxide-semiconductor structures are typically used to build traditional non-volatile flash memory devices. However, high operating voltage, low endurance and inability to be minimized to a greater extent due to the increasing current leakage at short length-scale are some of the disadvantages that such devices suffer from.⁴⁵ Devices with high speed, scalability, endurance, large capacity, and low power consumption are touted as the defining features of resistive switching random access memory (RRAM), as a candidate for future non-volatile memory.⁴⁶ Little work has been done on hexagonal boron nitride. There have been two reports on the resistive switching effect of h-BN using the CVD method⁴⁷ and a h-BN/polymer nanocomposite.⁴⁸ However, h-BN and its variety of microstructures have the potential as flexible resistive switching devices. This is also pursued in this work.

Due to h-BN exceptional anisotropic in-plane thermal conductivity, its utility as a thermal management mitigation method has been widely explored.^{14,49,50} To further enhance its thermal performances, techniques in isotopic engineering have been utilized to generate isotopically pure h-BN from crystals grown with a metal flux method.¹² However, due to the nature of the method used, wafer-scale applications of isotopically enriched h-BN still prove to be a challenge and might be overcome by the dual-magnetron sputtering method using HIPIMS. The resultant isotopically enriched film can be deposited onto devices directly without any transfer mechanism, enhancing scalability and its enhancement to device thermal performance can be measured. This is pursued in this work.

1.2.1 Objectives

The objectives of this thesis are twofold. To extend the use of HIPIMS as a deposition technique on depositing h-BN using different sources and apply h-BN thin films with a variety of thermal and optoelectronic properties for different applications, namely: as an encapsulating layer, as a

heat-dissipating layer for thermal management and as a resistive memory device. This is achieved through the successful synthesis of vertically orientated h-BN, where the c-axis of the h-BN is orientated **parallel** to the substrate surface, using the HIPIMS deposition technique. Second, to manipulate the isotopic compositions of h-BN thin films to utilize its enhanced optoelectronic and thermal properties to fulfil the requirements as stipulated by the three applications above. This is done by depositing h-BN onto devices and testing and characterise the resulting devices' performances.

1.3 Scope Definition

This thesis focuses on the **refinement** of deposition conditions to deposit h-BN thin films, with variants in microstructures and isotopic compositions to be realized in optoelectronic and thermal management applications. First, the h-BN thin films are deposited with the deposition parameters fine-tuned to allow for control over the microstructures and isotopic compositions. Next, the as-deposited thin films are applied onto electronic devices to fulfil the three stipulated applications as set out in the section on Motivation, namely: as an encapsulating layer on InSe transistors to prevent the transistor from oxidation upon exposure with the atmosphere, with enhanced isotopic composition functioning as a self-heat dissipating layer on high electron mobility transistors (HEMTs) and finally, as a resistive memory device, realized with the formation of conductive filament with oxygen vacancies.

1.4 Organization of the Thesis

This thesis consists of seven chapters, inclusive of both the Introduction and Conclusion chapters. The next chapter is the Literature Review and, in the chapter, the current research on h-BN for various applications and its associated background knowledge from the material science perspective will be introduced. In particular, the discussion will be on the details of the HIPIMS technique and into an in-depth review of the specifics, such as the different effects resulting from the sputtering of a solid target. Chapter 3 will introduce the necessary characterization techniques and experimental procedures for the thesis. It gives the reader an overview of all the various experimental techniques used in this thesis, ranging from experimental procedures to characterization techniques. Chapter 4 covers the study of the anisotropic microstructure of h-BN

and how the various deposition parameters influence the growth of h-BN using the HIPIMS technique and its various refinements. Chapter 5 covers the isotopic engineering of h-BN using various mechanisms and lastly, it covers the discussion on depositing isotopically enriched h-BN thin films. Chapter 6 covers the novel thermal, electronic and encapsulation applications of h-BN, as a self-heat dissipation and encapsulating layer for electronic devices and correspondingly by using isotopically enriched variants of h-BN to achieve similar outcomes. Lastly, the thesis concludes with a Conclusion chapter, outlining the achievements and contributes with an outlook on the future work.

1.5 Contributions

This section summarizes the list of contributions to this field of work in material science and electronics engineering in which I was involved and that contain the results obtained from the work needed to complete this Ph.D. thesis.

1.5.1 Journal Articles

1.5.1.1 First Author

- S. S. Chng, et. al., J. Mater. Chem. C, 2020, 8, 4421–4431.

My contribution was to the research project planning and coordination, the samples preparation, the microstructure characterization (except the TEM, XPS and thermal measurements that were outsourced) and redaction of the manuscript.

- S. S. Chng, et. al., J. Mater. Chem. C, 2020, 9558–9568.

My contribution was to the research project planning and coordination, the samples preparation, the microstructure characterization (except the TEM, XPS and thermal measurements that were outsourced) and redaction of the manuscript.

- [Under review with IOPscience Nanotechnology] Non-volatile resistive memory with thermal self-dissipation based on highly textured hexagonal boron nitride.

My contribution was to the research project planning and coordination, the samples preparation, the microstructure characterization (except the TEM, XPS and thermal measurements that were outsourced) and redaction of the manuscript.

- M. Zhu, et. al., J. Mater. Chem. C, 2018, 6, 12919–12927.

My contribution was to the research project planning and coordination, the samples preparation, the microstructure characterization (except the TEM, XPS and thermal measurements that were outsourced) and edit and comments of the manuscript.

- Zhu, M., Chng, S. S., Cai, W., Liu, C. & Du, Z. Piezoelectric polymer nanofibers for pressure sensors and their applications in human activity monitoring. RSC Adv. 10, 21887–21894 (2020).

My contribution was to the research project planning and coordination, the samples preparation, the microstructure characterization (except the TEM, XPS and thermal measurements that were outsourced) and edit and comments of the manuscript.

- Z. L. Ngoh, F. N. Leong, R. Y. Tay, M. D. Whiteside, S. S. Chng, J. J. Yu, S. H. Tsang, D. Tan, G. I. Ng and E. H. T. Teo, in 2019 IEEE MTT-S International Microwave Workshop Series on Advanced Materials and Processes for RF and THz Applications (IMWS-AMP), 2019, pp. 127–129.

My contribution was on a specific step of the sample preparation, requiring the growth of a thin layer of h-BN onto 3D-C.

- M. Whiteside, S. Arulkumaran, S. S. Chng, M. Shakerzadeh, H. T. E. Teo and G. I. Ng, Appl. Phys. Express, 2020, 13, 065508.

My contribution was limited to the aid in depositions of h-BN onto AlGaIn/GaN HEMTs.

1.6 References

1. Gupta, A., Sakthivel, T. & Seal, S. Recent development in 2D materials beyond graphene. *Prog. Mater. Sci.* **73**, 44–126 (2015).
2. Wang, G. *et al.* Vertically Aligned MoS₂ Nanosheets Patterned on Electrochemically Exfoliated Graphene for High-Performance Lithium and Sodium Storage. *Adv. Energy Mater.* **8**, 1–8 (2018).

3. Liu, J. *et al.* Preparation of MoS₂-polyvinylpyrrolidone nanocomposites for flexible nonvolatile rewritable memory devices with reduced graphene oxide electrodes. *Small* **8**, 3517–3522 (2012).
4. Li, H. *et al.* From bulk to monolayer MoS₂: Evolution of Raman scattering. *Adv. Funct. Mater.* **22**, 1385–1390 (2012).
5. Glavin, N. R. *et al.* Amorphous Boron Nitride: A Universal, Ultrathin Dielectric for 2D Nanoelectronics. *Adv. Funct. Mater.* **26**, 2640–2647 (2016).
6. Wang, J. *et al.* Super-compatible functional boron nitride nanosheets/polymer films with excellent mechanical properties and ultra-high thermal conductivity for thermal management. *J. Mater. Chem. C* **6**, 1363–1369 (2018).
7. Cassabois, G., Valvin, P. & Gil, B. Hexagonal boron nitride is an indirect bandgap semiconductor. **1**, 1–7 (2015).
8. Tsao, J. Y. *et al.* Ultrawide-Bandgap Semiconductors: Research Opportunities and Challenges. *Adv. Electron. Mater.* **4**, 1600501 (2018).
9. Watanabe, K., Taniguchi, T. & Kanda, H. Direct-bandgap properties and evidence for ultraviolet lasing of hexagonal boron nitride single crystal. *Nat. Mater.* **3**, 404–409 (2004).
10. Cai, Q. *et al.* High thermal conductivity of high-quality monolayer boron nitride and its thermal expansion. *Sci. Adv.* **5**, 1–9 (2019).
11. Jiang, P., Qian, X., Yang, R. & Lindsay, L. Anisotropic thermal transport in bulk hexagonal boron nitride. *Phys. Rev. Mater.* **2**, 064005 (2018).
12. Yuan, C. *et al.* Modulating the thermal conductivity in hexagonal boron nitride via controlled boron isotope concentration. *Commun. Phys.* **2**, 1–8 (2019).
13. Lindsay, L., Broido, D. A. & Reinecke, T. L. Thermal Conductivity and Large Isotope Effect in GaN from First Principles. *Phys. Rev. Lett.* **109**, 095901 (2012).
14. Sevik, C., Kinaci, A., Haskins, J. B. & Çağın, T. Characterization of thermal transport in low-dimensional boron nitride nanostructures. *Phys. Rev. B - Condens. Matter Mater. Phys.* **84**, (2011).
15. Lindsay, L. & Broido, D. A. Enhanced thermal conductivity and isotope effect in single-layer hexagonal boron nitride. *Phys. Rev. B* **84**, 155421 (2011).
16. Grenadier, S., Li, J., Lin, J., Jiang, H. & Maity, A. High-efficiency and high-sensitivity thermal neutron detectors based on hexagonal BN epilayers. in *Hard X-Ray, Gamma-Ray*,

- and Neutron Detector Physics XIX* (eds. Fiederle, M., Burger, A., Franks, L., James, R. B. & Payne, S. A.) 20 (SPIE, 2017). doi:10.1117/12.2271556.
17. Maity, A., Grenadier, S. J., Li, J., Lin, J. Y. & Jiang, H. X. Toward achieving flexible and high sensitivity hexagonal boron nitride neutron detectors. *Appl. Phys. Lett.* **111**, 033507 (2017).
 18. Maity, A., Grenadier, S. J., Li, J., Lin, J. Y. & Jiang, H. X. Hexagonal boron nitride neutron detectors with high detection efficiencies. *J. Appl. Phys.* **123**, 044501 (2018).
 19. Maity, A., Grenadier, S. J., Li, J., Lin, J. Y. & Jiang, H. X. High sensitivity hexagonal boron nitride lateral neutron detectors. *Appl. Phys. Lett.* **114**, 222102 (2019).
 20. Maity, A., Doan, T. C., Li, J., Lin, J. Y. & Jiang, H. X. Realization of highly efficient hexagonal boron nitride neutron detectors. *Appl. Phys. Lett.* **109**, 072101 (2016).
 21. Hattori, Y., Taniguchi, T., Watanabe, K. & Nagashio, K. Layer-by-layer dielectric breakdown of hexagonal boron nitride. *ACS Nano* **9**, 916–921 (2015).
 22. Han, Q. *et al.* Boron nitride film as a buffer layer in deposition of dielectrics on graphene. *Small* **10**, 2293–2299 (2014).
 23. Measuring the dielectric and optical response of millimeter-scale amorphous and hexagonal boron nitride films.pdf.
 24. Sutter, P., Lahiri, J., Zahl, P., Wang, B. & Sutter, E. Scalable Synthesis of Uniform Few-Layer Hexagonal Boron Nitride Dielectric Films. (2013) doi:10.1021/nl304080y.
 25. Laturia, A., Van de Put, M. L. & Vandenbergh, W. G. Dielectric properties of hexagonal boron nitride and transition metal dichalcogenides: from monolayer to bulk. *npj 2D Mater. Appl.* **2**, 6 (2018).
 26. Vuong, T. Q. P. *et al.* Isotope engineering of van derWaals interactions in hexagonal boron nitride. *Nat. Mater.* **17**, 152–158 (2018).
 27. Chang, C. W. *et al.* Isotope effect on the thermal conductivity of boron nitride nanotubes. *Phys. Rev. Lett.* **97**, 1–4 (2006).
 28. Sun, X. *et al.* Two-Dimensional Boron Crystals: Structural Stability, Tunable Properties, Fabrications and Applications. *Adv. Funct. Mater.* **27**, (2017).
 29. Kostoglou, N., Polychronopoulou, K. & Rebholz, C. Thermal and chemical stability of hexagonal boron nitride (h-BN) nanoplatelets. *Vacuum* **112**, 42–45 (2015).
 30. Quan, H. *et al.* Stability to moisture of hexagonal boron nitride films deposited on silicon

- by RF magnetron sputtering. *Thin Solid Films* **642**, 90–95 (2017).
31. Yang, X., Ding, Y. & Ni, J. Ab initio prediction of stable boron sheets and boron nanotubes: Structure, stability, and electronic properties. *Phys. Rev. B - Condens. Matter Mater. Phys.* **77**, 2–5 (2008).
 32. Merenkov, I. S. *et al.* Thermal stability of UV light emitting boron nitride nanowalls. *Mater. Des.* **117**, 239–247 (2017).
 33. Camilli, L., Sutter, E. & Sutter, P. Growth of two-dimensional materials on non-catalytic substrates: H-BN/Au(111). *2D Mater.* **1**, (2014).
 34. Müller, F., Hüfner, S., Sachdev, H., Gsell, S. & Schreck, M. Epitaxial growth of hexagonal boron nitride monolayers by a three-step boration-oxidation-nitration process. *Phys. Rev. B - Condens. Matter Mater. Phys.* **82**, 1–11 (2010).
 35. Yin, J. *et al.* Boron Nitride Nanostructures: Fabrication, Functionalization and Applications. *Small* **12**, 2942–2968 (2016).
 36. Kudláček, P., Vlcek, J., Burcalová, K. & Luka, J. Highly ionized fluxes of sputtered titanium atoms in high-power pulsed magnetron discharges. *Plasma Sources Sci. Technol.* **17**, (2008).
 37. Bohlmark, J., Alami, J., Christou, C., Ehiasarian, A. P. & Helmersson, U. Ionization of sputtered metals in high power pulsed magnetron sputtering. *J. Vac. Sci. Technol. A Vacuum, Surfaces, Film.* **23**, 18–22 (2005).
 38. Ehiasarian, A. P. *et al.* Influence of high power impulse magnetron sputtering plasma ionization on the microstructure of TiN thin films. *J. Appl. Phys.* **109**, 104314 (2011).
 39. Lattemann, M., Ehiasarian, A. P., Bohlmark, J., Persson, P. Å. O. & Helmersson, U. Investigation of high power impulse magnetron sputtering pretreated interfaces for adhesion enhancement of hard coatings on steel. *Surf. Coatings Technol.* **200**, 6495–6499 (2006).
 40. Bobzin, K. *et al.* Mechanical properties and oxidation behaviour of (Al,Cr)N and (Al,Cr,Si)N coatings for cutting tools deposited by HPPMS. *Thin Solid Films* **517**, 1251–1256 (2008).
 41. Christie, D. J. Target material pathways model for high power pulsed magnetron sputtering. *J. Vac. Sci. Technol. A Vacuum, Surfaces, Film.* **23**, 330–335 (2005).
 42. Urban, J. M. *et al.* Observation of A1g Raman mode splitting in few layer black phosphorus encapsulated with hexagonal boron nitride. *Nanoscale* **9**, 19298–19303 (2017).

43. Bandurin, D. A. *et al.* High electron mobility, quantum Hall effect and anomalous optical response in atomically thin InSe. *Nat. Nanotechnol.* **12**, 223–227 (2017).
44. Li, L. H., Cervenka, J., Watanabe, K., Taniguchi, T. & Chen, Y. Strong oxidation resistance of atomically thin boron nitride nanosheets. *ACS Nano* **8**, 1457–1462 (2014).
45. Kolar, J., Macak, J. M., Terabe, K. & Wagner, T. Down-scaling of resistive switching to nanoscale using porous anodic alumina membranes. *J. Mater. Chem. C* **2**, 349–355 (2014).
46. Bok, C. H., Wu, C. & Kim, T. W. Operating mechanisms of highly-reproducible write-once-read-many-times memory devices based on graphene quantum dot:poly(methyl silsesquioxane) nanocomposites. *Appl. Phys. Lett.* **110**, 013301 (2017).
47. Qian, K. *et al.* Hexagonal Boron Nitride Thin Film for Flexible Resistive Memory Applications. *Adv. Funct. Mater.* **26**, 2176–2184 (2016).
48. Siddiqui, G. U., Rehman, M. M., Yang, Y.-J. & Choi, K. H. A two-dimensional hexagonal boron nitride/polymer nanocomposite for flexible resistive switching devices. *J. Mater. Chem. C* **5**, 862–871 (2017).
49. Meng, W., Huang, Y., Fu, Y., Wang, Z. & Zhi, C. Polymer composites of boron nitride nanotubes and nanosheets. *J. Mater. Chem. C* **2**, 10049–10061 (2014).
50. Zhu, H. *et al.* Highly thermally conductive papers with percolative layered boron nitride nanosheets. *ACS Nano* **8**, 3606–3613 (2014).

2 Literature Review

In this chapter, the literature survey is presented. The main deposition technique used in **this** work is **high** power impulse magnetron sputtering (HIPIMS), which is fundamentally a form of physical vapor deposition (PVD) (in contrast with chemical vapor deposition (CVD)) and a variant of magnetron sputtering, the usage of a magnetic field to enhance the sputtering phenomenon. There are two main sections to this chapter, first is the section on thin film technology and the sputtering of LaB_6 and pure boron targets using HIPIMS and the second is the section on h-BN. In the first section, recent literature on the sputtering on LaB_6 and pure boron target is presented. This is because, in the depositions of h-BN, these two targets are used. Next, an introduction to h-BN, its thermal, electronic and anisotropic properties, alignment engineering, isotopic engineering and its various applications as thermal management and on electronics is presented. The chapter ends with a conclusion.

2.1 Thin Film Technology

A thin film is defined as a film of a material (elemental or compound) that is deposited on a substrate by chemical decomposition, thermal evaporation, or the evaporation of source materials by the irradiation of energetic species.

Particularly, the need for depositing thin films comes from the fact that atomic growth processes result in unique material properties. Some of these properties are related to the quantum size effects, crystalline orientation and multi-layer aspects. Examples of these properties are mechanical strength, carrier transport, superconductivity, ferroelectricity, magnetic, thermal and optical properties.¹

2.1.1 Magnetron Sputtering Technique

2.1.1.1 Magnetron Sputtering

An important technique that utilizes plasma is the magnetron sputtering technique. Usually, in a deposition, the inert gas atoms (commonly argon) are ionized by the electric and magnetic fields and are accelerated towards the target (negatively biased cathode) as a result of the potential difference between the anode and the cathode. The magnetron comprises of permanent magnets to generate a strong magnetic field to keep the ejected secondary electrons confined within the

peripheral of the target spatially. These electrons are confined in the plasma for a longer duration, ionize sputter-gas atoms to a greater extent, generating higher discharge current and deposition rates of the deposited films.² The inert gas ions impinge on the target causing sputtering of the target atoms and these sputtered species either react with a reactive gas and get deposited on a substrate or are directly deposited onto the substrate. Importantly, these processes do not occur at thermal equilibrium due to kinetic restrictions.

FIG. 1 (a) Side view of a planar magnetron, showing the configuration of the magnetic.³ (b) Schematic of the orbital $E \times B$ drift path of the secondary electrons, together with the configuration of the magnetic field of a planar magnetron.³

Secondary electrons were accelerated in a direction perpendicular to the target surface due to the electron potential generated by the cathode, as illustrated in FIG. 1(a). A Lorentz drift force is derived and acted on the secondary electrons, as the magnetic field lines are aligned in the same direction to the target surface, restricting their movements to cycloidal drift orbits. This results in more collisions and hence, ionization for the sputter-gas atoms is achieved to a greater extent and overall current, the $E \times B$ drift is illustrated in FIG. 1(b).

Table 1 lists some of the advantages of magnetron sputtering over other deposition techniques, the list is not exhaustive and is not in direct comparison with any particular deposition technique. Furthermore, Table 2 lists the goals that are pursued by the research community in the advancement of magnetron sputtering techniques. These goals are in line with some of the novel requirements of deposition of novel compound materials.

Table 1 General Advantages of Magnetron Sputtering⁴

Index	Advantages
1	High discharge currents (ranging from 1 A to 100 A), at voltages of around 500 V, due to low plasma impedance
2	Deposition rates ranging from 1 nm s ⁻¹ to 10 nm s ⁻¹
3	Substrate experiencing low thermal load
4	Coating uniformity in the range of a few percentages even for cathodes which are several meters in length
5	Scalable technology
6	Resulting films are dense and do not delaminate easily
7	Capable of fabricating a large variety of films (nearly all metals and compounds)
8	Film properties are controllable

Table 2 Magnetron Sputtering Goals⁴

Index	Goals
1	Improvement of target utilization
2	Stabilization of the reactive process in the transition regime
3	Achieving a high deposition rate of deposited films which is stable and long term
4	Improved film properties such as hardness, adhesiveness and others.

2.1.2 Introduction to High Power Impulse Magnetron Sputtering (HIPIMS)

It has only been 20 years since this novel physical vapor deposition technique was invented by Kouznetsov et al.⁵ in 1991. The basic working principle of High Power Impulse Magnetron Sputtering, or HIPIMS, is based on direct current magnetron sputtering (DC-MS). It utilizes high power densities to ionize the working gas (typically noble gases like He or Ar) and the reactive gas (depending on the specifics of the deposition, typical reactive gases are N₂ or O₂), the ionized gases, which are positively charged, in turn, are accelerated towards and impinged on the negatively charged target and sputter off the target species. The magnetron is made of permanent magnets which set up a magnetic field that traps the ionized species, forcing them to be confined dynamically, continuously impinging on the target and sputtering off the target species in a cyclotron motion. Sputtered target species may react with the reactive gas in a form of HIPIMS, known as Reactive HIPIMS or R-HIPIMS, thereby forming compound films on the substrate. Reactive sputtering occurs when the sputtering of an elemental target under the presence of a reactive gaseous agent, resulting in a chemical reaction between the target and the gaseous substance.

The yield of secondary electrons from the target upon impingement of elemental species which are ionized on the target is a fundamental parameter of the target in determining the viability of magnetron sputtering using the target. This is because, for targets with a low secondary electron yield, the sputtering process may not be self-sustaining, that is to mean that sustained plasma generation is not possible, hence sputtering is not possible. Secondary electrons are crucial to maintaining the plasma discharge as they can influence the ionization of the working gas and transfer energy to other electrons via collision, enabling a cascade of electronic collisions.⁶ The condition for self-sustaining sputtering is captured in the following equation:⁷

$$\Pi \equiv \alpha\beta\gamma_{ss} = 1 \quad (3.1)$$

Where the probability that a sputtered atom becomes ionized is α , the probability that the newly formed **ion** returns to the target is β , and γ_{ss} is the self-sputtering yield. The concept of self-sustaining sputtering is also illustrated in FIG. 2. Certainly, since $\alpha < 1$ and $\beta < 1$, the condition $\gamma_{ss} > 1$ is a necessary but not sufficient condition for sustained self-sputtering.⁸

The difference between typical DC-MS and HIPIMS is that the latter is coupled with a pulse power supply to control the parameters relating to the pulse, for instance, pulse length, duty cycle and pulse repetition rate. Short pulses in duration for HIPIMS are capable of delivering high instantaneous power to the target results in high ionization and in turn, high ion density which leads to denser films and other desirable properties.⁹ Furthermore, to preserve the structural integrity of the target, the process duty cycle is usually at most a few percent to limit the thermal load on it. The HIPIMS' pulsed power supplies used in this work operate in a 'unipolar' mode, typically ranging from tens of microseconds to milliseconds, the different modes of HIPIMS are illustrated in FIG. 3.¹⁰ As the sputtered target's ionization is known to be correlated to the discharge current, increasing the peak power delivered to the target is a primary objective in a HIPIMS system as it is known that increasing peak power is proportional to increasing peak current in the plasma discharge.¹⁰

FIG. 2 Conditions for self-sputtering runaway, and the onset of stable and sustained self-sputtering.

FIG. 3 Different modes of HIPIMS pulse: (a) unipolar pulse; (b) bipolar pulse; (c) pulse packages/pulse; (d) DC superimposed on unipolar.¹⁰

FIG. 4(a) is the HIPIMS deposition chamber used in this work. FIG. 4(b) illustrates the interior and the structure of the deposition chamber. The pulsed power supplies (Ionautics) deliver the power to the magnetrons and the magnetrons are water-cooled. FIG. 4(c) is an optical image showing an actual deposition that involves only one magnetron. FIG. 4(d) is a schematic of the waveform of a single pulse which is typically obtained through the oscilloscope. The pulse usually

lasts for around tens of microseconds, the voltage applied can be up to 1000 V and the peak discharge current typically reaches 10 A, which is dependent on the material that is being sputtered.

FIG. 4 (a) An optical image of the HIPIMS deposition chamber, resting on a support. The turbomolecular pump is located at the back, with the roughing pump lying on the floor. (b) A schematic showing the interior set-up of the chamber. (c) An optical image depicting a deposition using a LaB_6 target. (d) A schematic illustrating the waveform of a single pulse supplied by the HIPIMS pulsed power supplies to the target.

2.1.2.1 Low Deposition Rates of HIPIMS Deposition

Reduction of the deposition rate of thin films onto substrates is one of the crucial disadvantages of HIPIMS. This is because of the back attraction of the ionized target material towards the target,

which enhances the sustainability of the plasma and the sputtering process but reduces the deposition rate as lesser sputtered target species reach the substrate.¹⁰ This is especially true for nonreactive HIPIMS sputtering, for reactive HIPIMS sputtering, there **is evident** that under certain conditions, the deposition rate may exceed that of DC-MS at the same average power.¹¹

2.1.2.2 Target Poisoning

As most of the films that are needed for applications are compound films, a material with two or more elements chemically bonded, it is crucial for HIPIMS to be able to deposit compound films. Poisoning of the target is defined as the state of the target in which a layer comprised of the reaction compound is formed on the target.¹² This is a problem as it reduces the sputter yield from the target as a whole. As a result, the deposition rate is also reduced. Ultimately, this is because the strengths of the chemical bond of compounds are typically stronger than interatomic bonding. Examples include boron nitride forming on pure boron target or titanium oxide forming on titanium target. The first reason why targets become poisoned is due to the chemical affinity between the target and the reactive gas. Secondly, recoil-implantation of chemisorbed atoms may also form a thick compound layer on the target surface. Lastly, direct implantation of reactive gas ions is also possible.

It has been established that it is good to operate in the transition region between the poisoned and elemental states of the target to obtain both optimal film properties (such as ideal stoichiometric ratio) and high deposition rates. To obtain optimal film properties, such as the ideal stoichiometric ratio of the deposited film, and high deposition rates, it has been established that the deposition ought to be operated within the transition region, during deposition. The transition region is defined to be the state of transition between the poisoned and elemental states of the target. One method of reducing target poisoning is to increase the pump speed of the vacuum pumps, however, this is usually not cost-effective as the pumping speed may be 10 times as high as what is used currently. An alternative would be to set the working pressure of the deposition to a level before hysteresis effects happen. Consequently, reactive gas flow control is still used in many deposition processes as the deposition process can be very stable even while in a poisoned state, although the resultant films' properties may not be optimal.

2.1.2.3 High Plasma Density

High plasma density implies high density of the ionized sputtered target and ionized reactive gas species which then can be manipulated using an electromagnetic field to enhance deposition rate on the substrate. The ionization fraction within the plasma has been observed to be up to 90%.¹³ It also allows for good adhesion of the deposited film, controllable and reproducible microstructure and deposition on complex surfaces. For HIPIMS, the plasma density has been measured to be around the order of 10^{20} m^{-3} and to even higher values within the localized ionization zones.^{6,9}

2.1.2.4 Gas Rarefaction and Sputter Wind

The origin of sputter wind and gas rarefaction comes from collisions between the sputtered and reflected species with the neutral gases in front of the target. As a result of these collisions, the gas is expanded due to the heat generated from this collision, greatly reducing its density. This is an issue as a local reduction in gas density decreases the extent of the sputtering process, it reduces the sputter yield. In a typical DC magnetron sputtering of Cu target, the argon density in front of the target is found to be 25% less due to gas rarefaction at a sputtering power of 3 kW on the 15 cm diameter target. An extrapolation of the data on Cu target is extrapolated to the HIPIMS regime and is shown on FIG. 5.

FIG. 5 Rarefaction of argon density. The gas density was lower in front of the target and it is presented as a function of DC power density in 4 Pa of Argon. The Cu target used is 15 cm in

diameter. Extrapolation to the typical maximum power densities for HIPIMS predicted that rarefaction will occur to a large extent.⁷

2.2 Sputtering of LaB₆ and Pure Boron Targets using HIPIMS

2.2.1 Sputtering with LaB₆ Target

Lanthanum hexaboride, LaB₆, was found to be sputtered with a boron-rich plasma.^{1,2} FIG. 6(a), adapted from REF 14 illustrates the measured plasma composition in the sputtering of the LaB₆ target. The composition of boron species in the plasma can exceed 60% beyond a peak current of around 20 A.

FIG. 6 (a) Time-averaged plasma composition at 0.5 Pa Argon with its dependence on peak current. (b) Time-averaged ion energy distribution functions for ⁴⁰Ar⁺, ¹¹B⁺, and ¹³⁹La⁺, measured for 80A peak current and 20mA superimposed dc current in the range of 0–50eV, the pressure was at 0.5 Pa argon.

2.2.2 Sputtering with Boron Target

On the Periodic Table, Boron has an atomic number of 5 and exists in two isotopes, Boron-10 and Boron-11 with nucleon numbers of 10 and 11, respectively. The natural abundance of Boron-10 and Boron-11 is 19.9% and 80.1%, respectively. It is a dielectric and has an electronic configuration of 1s²2s²2p¹. Boron-10 is well-known as a neutron absorbing material, it has a neutron cross-section of 3840 barns ($3.84 \times 10^{-21} \text{ cm}^2$) and its compounds are some of the most researched materials as candidates for neutron detectors.^{3–6} Table 3 lists some of the common properties of elemental boron.

Table 3 Properties of Elemental Boron

Properties	Value / Units
Atomic Weight	10.81
Mass Density	2.37 / g cm ⁻³
Phase at Room Temperature	Solid
Melting Point	2075 / °C
Boiling Point	4000 / °C
Number of Isotopes	6

As h-BN thin films which are deposited using a LaB₆ source have been shown to contain a low percentage of La (~5%)⁷, the presence of La in h-BN thin films may alter its electronic, thermal and optical properties. Furthermore, the boron atoms in LaB₆ is in natural abundance isotopically, certain applications (such as using h-BN as a neutron-/conversion material in a solid-state semiconductor neutron detector), may require an enriched h-B¹⁰N (the boron in h-BN is mostly boron-10), hence, h-BN deposited by LaB₆ may not fulfil the requirement.

An alternative target for the deposition of h-BN using HIPIMS is sought after. The simplest target consisting of isotopically enriched boron atoms is the elemental target. Deposition of h-BN using a pure boron target (mass purity of 99.9%) via the HIPIMS technique is investigated.

As elemental boron is a dielectric, the predominant sputtering method that was used for the sputtering of boron is the radio-frequency sputtering (RF Sputtering) method. This is because in the sputtering process with a dielectric target powered by a direct-current (DC) power source (for example, DC magnetron sputtering), the dielectric target will behave as a capacitor.⁸ Accumulation of positive ions which plunge onto the surfaces of the dielectric target would not be replenished by the electrons from the power supply, causing the target to be charged up and impingement by more ions is suppressed due to the shielding effect, impeding the sputtering process. There are certain drawbacks to RF sputtering, such as high cost for RF power, low deposition rates and high thermal load to the substrate. For industrial applications, RF sputtering is also a process that is very difficult to scale.⁹ In the literature, many groups have used RF sputtering to sputter a pure boron target.^{10–13} J. Hahn et al. deposited h-BN thin films using a pure boron target via both RF sputtering and DC sputtering at 800 °C.¹² FIG. 7(a) depicts the FTIR spectrum of the h-BN thin films deposited by RF Sputtering and FIG. 7(b) depicts that by DC Sputtering, at different substrate biases from floating up to -400 V. Since the spectra are normalized and superimposed on each

other, a visual inspection on the spectra show that a substrate bias of around -50 V to -100 V gives the highest R value (ratio of the FTIR spectrum intensities of the A_{2u} to E_{1u} peak). The films deposited suffered from oxidation and were delaminated. It was attributed to the expansion of the film due to products from the oxidation reaction.

FIG. 7 (a) FTIR spectra of the BN films deposited under different floating substrate potential (U_F) and DC substrate bias voltage (U_B) with the pressure at 0.2 Pa, 10% N_2 , and the substrate temperature is 350 °C. (a) The target is sputtered under an RF power supply at 500W and (b) under a DC power supply at 200 W.¹²

M. Wakatsuchi et al.¹² applied the reactive sputtering technique on a pure boron target in an electron cyclotron resonance generated plasma environment and the substrate is RF biased. The emission characteristic of the boron target, such as the target temperature and ion current, when sputtered in the electron cyclotron resonance generated plasma environment was investigated in Y. Ito et al. work.¹³ The substrate is RF biased so that the h-BN film deposited can remain conductive and will allow charges to flow freely, preventing the h-BN film from charging up. The purpose of the study was to deposit high quality c-BN thin films. FIG. 8 displays the spectra derived from FTIR of the thin films deposited at numerous substrate biases, each sub-figure corresponds to a different target distance, r_t , from the substrate and target discharge voltage, V_t : (a) $r_t = 0$ mm, $V_t = -620$ V, (b) $r_t = 20$ mm, $V_t = -620$ V and (c) $r_t = 20$ mm, $V_t = -400$ V. One

important conclusion to draw from this study via visual inspection of the FTIR spectra is the likelihood of getting well-aligned h-BN thin films (judging from the intensities of the A_{2u} phonon mode to the E_{1u} phonon mode) is to have the substrate bias to be around -100 V to -150 V. Similar to what was concluded in J. Hahn et al. work.

C. Hu et al.¹¹ used RF magnetron sputtering on a pure boron target to deposit h-BN on $\langle 100 \rangle$ Si substrates. C. Hu et al. work is one of the few that had microstructure analysis of the thin film deposited, beyond the usual FTIR analysis. FIG. 9(a) gives the FTIR spectra of the films deposited, FIG. 9(b) is the HRTEM images of the different regions of the film corresponds to a -150 V substrate bias and finally, FIG. 9(c) is the SAED of that h-BN film. The film which was deposited at a bias of -150 V was chosen to be analyzed for its microstructure as its FTIR showed a small peak at 1050 cm^{-1} which corresponds to a c-BN TO phonon mode. The purpose of the work was to deposit high quality c-BN thin films. Consequently, it was shown that despite the existence of an unpronounced c-BN phonon mode on the FTIR spectrum, the sample was void of c-BN but exists as a mixed-phase BN thin film with w-BN (wurtzite-BN), t-BN (turbostratic-BN) and h-BN. This may demonstrate that although FTIR provides a quick analysis of the local bonding characteristics of a thin film, it is inadequate as an analysis tool in (long-range) phase identification.

E. Oks et al.¹⁴ demonstrated the magnetron sputtering of a pure boron target without using a RF power supply. This is to avoid the associated drawbacks of RF magnetron sputtering. The ignition procedure of the boron target without a RF power source was to apply a pulsed voltage to the target and a DC power source to the substrate simultaneously. It is claimed that once the ignition of the boron target has occurred, the DC power source to the substrate holder can be switched off without affecting the microstructure of the deposited film. This work demonstrated that it may be possible to ignite a boron target using a pulsed power source whose frequency is not at the magnitude of a RF power supply (13.56 MHz), for example, in the work, the maximum frequency of a sustained plasma on the boron target from the pulsed power source is 350 kHz.

It is known that higher base pressure introduces oxygen into the deposition of thin films, as it is in the reduction of corrosion resistance in the case of aluminium⁷ and causes the oxidation of the thin film. Similarly, titanium thin films exhibited significant nitration and are of the amorphous phase when direct-current (DC) sputtered for a high base pressure.⁸ Oxygen contamination in the

deposition process of scandium nitride thin film using DC magnetron sputtering due to high base pressure has resulted in degradation of film crystallinity, a rise in the optical band gap and lower electron concentration.⁹ On the contrary, high base pressure resulted in the lowering of resistivity for indium tin oxide (ITO) thin films using both DC and radio-frequency (RF) sputtering concurrently.¹⁰ As such, the base pressure of the deposition chamber is usually between 10^{-4} to 10^{-7} Torr.

FIG. 8 (a) FTIR spectra of BN films deposited as a function of substrate position from the target, r_t , and the substrate bias, V_t ; (a) $r_t = 0$ mm, $V_t = -620$ V, respectively. (b) $r_t = 20$ mm, $V_t = -620$ V, respectively. (c) $r_t = 20$ mm, $V_t = -400$ V, respectively.¹⁵

FIG. 9 (a) FTIR spectra (transmission) of BN films deposited as a function of substrate bias (b) HRTEM images of BN films deposited at -150 V substrate bias. Left: t-BN area; Right: h-BN and w-BN area. (c) SAED pattern of BN deposited at -150 V substrate bias.¹¹

2.3 Hexagonal Boron Nitride

FIG. 10 (a) Planar view of a h-BN monolayer schematic with its primitive cell shown in a dotted rhombus. The intraplanar lattice constant is shown to be 0.25 nm. (b) Two layers of h-BN are stacked on top of each other and held together by the Van der Waals force. The interplanar distance is shown to be 0.333 nm.

h-BN is a lamellar, otherwise known as layered material, that is non-naturally occurring. In this work, h-BN is synthesized by High Power Impulse Magnetron Sputtering (HIPIMS) technique. h-BN is a large band gap material ($\sim 5 - 6.5$ eV) and the origin of its large band gap is due to the large differences between the electronegativities of boron (2.04, Pauling scale) and nitrogen (3.04).¹⁶ This results in h-BN being electrically insulating, with a large band gap both intra-planar and inter-planar. The large band gap also makes it a viable candidate for optoelectronic applications for its lasing action within the ultraviolet frequency range.^{17,18} As its overall structure and atomic spacing closely resemble that of graphite, the low-dimensional h-BN layer is a superior template and dielectric layer for graphene electronics. The hexagonal structure of h-BN is akin to a honeycomb arrangement comprising alternating nitrogen and boron atoms. Holding the B and N atoms together is the strong covalent bond with partial ionic character due to the large differences between their respective electronegativity. Each layer of h-BN is planar and atomically smooth with no dangling bonds, and each plane is held together to other planes by the weak Van der Waals forces. The origin of the anisotropy of h-BN properties lies in the fact that each h-BN layer is planar and the differences in bonding strength intra-planar and inter-planar. FIG. 10(a) gives a schematic of the planar view of a h-BN monolayer, its primitive cell is shown in a dotted rhombus and the intraplanar lattice constant is shown to be 0.25 nm. FIG. 10(b) gives a schematic of two

layers of h-BN held together by the weak Van der Waals force and with the interplanar distance of 0.33 nm.

2.3.1 Anisotropic Nature of h-BN

2.3.1.1 Origin of Anisotropy

Anisotropy describes a property of a material that is spatial-direction dependent. h-BN is a layered or lamellar material with anisotropic nature, with different properties in different directions of the material, namely, along the c-axis or out-of-plane direction and along the plane consisting of the B-N hexagonal rings or in-plane direction. The anisotropic nature arises from the lamellar (or layered) structure of h-BN. The strong intraplanar B-N covalent bond forms hexagonal B_3N_3 rings which extend 2-dimensionally infinitely theoretically, each such layer is held by weaker Van der Waals forces, arising from the interatomic dipole moments. This dichotomy of strong intraplanar bonds and weak interplanar Van der Waals bonds is the basis for the anisotropic properties of h-BN.

2.3.1.2 Anisotropic Properties of h-BN

Many properties of h-BN are anisotropic, such as the in-plane lifetime-mobility product of monolayer h-BN for both holes and electrons are about 3 orders of magnitude greater than the out-of-plane lifetime-mobility product.²⁶ For electrons and holes, the in-plane mobility–lifetime products, measured by collecting lateral carriers, are $\sim 2.8 \times 10^{-5}$ and $\sim 4.85 \times 10^6 \text{ cm}^2/\text{V}$, whereas from collecting the vertical carriers, the out-of-plane mobility–lifetime products for electrons and holes are measured to be $\sim 5.8 \times 10^{-8}$ and $\sim 6.1 \times 10^{-9} \text{ cm}^2/\text{V}$, respectively.

Similarly, the in-plane thermal conductivity of bulk h-BN crystals is around 2 orders of magnitude higher than the out-of-plane thermal conductivity (out-of-plane thermal conductivity: $k_{\perp} = 4.8 \text{ W m}^{-1} \text{ K}^{-1}$, in-plane thermal conductivity: $k_{\parallel} = 420 \text{ W m}^{-1} \text{ K}^{-1}$, at room temperature) and it is similar even in the case of isotopically-enriched h-BN crystals.^{27,28} FIG. 11(a) shows the in-plane and out-of-plane thermal conductivities of bulk h-BN of isotopically natural abundance, whereas FIG. 11(b) shows the in-plane and out-of-plane thermal conductivities of bulk h-BN of different isotopic compositions.

Anisotropy is also observed in the valence electron loss function of h-BN due to the high inhomogeneity of the excitonic states. Within the hexagonal plane, the electron and hole tend to form a strongly bounded exciton whereas, between the layers, the hole and electron tend to be localized on different layers and form a weakly bounded exciton.²⁹

Furthermore, the dielectric breakdown strength has also been shown to be different in h-BN in different directions, both orthogonal and in the same direction to the c-axis.³⁰ h-BN has also low dielectric constant^{31–33} and exhibited anisotropy in its dielectric constant, that is $\epsilon_r = 3.38$ (in-plane dielectric constant) and $\epsilon_r = 6.61$ (out-of-plane dielectric constant).^{34,35}

FIG. 11 (a) Anisotropic (in-plane and out-of-plane) thermal conductivities of bulk h-BN. The boron in h-BN thin films is isotopically in natural abundance (i.e. 19.9% B^{10} and 80.1% B^{11}).³⁷ (b) Measured in-plane and out-of-plane thermal conductivities of bulk h-BN with the boron in the h-BN being in different isotopic compositions.²⁷

2.3.1.3 Orientation Engineering of h-BN

In this thesis, thermal conductivity anisotropy is of primary concern. Vertically-oriented h-BN has been proposed as a possible solution for the thermal hot-spot problem plaguing nano-scale electron devices operating at high power densities.^{7,39} The strategy is to make use of the high in-plane

thermal conductivity of the hexagonal-boron nitride film to dissipate the heat generated at these thermal hot spots. Together with h-BN, vertically oriented thin films on other surfaces, for instance, carbon nanotubes, graphene, molybdenum disulphide (MoS_2) and zinc oxide, have also been studied for several purposes such as field emission.⁴⁰⁻⁴⁵ In particular, h-BN nanowalls (h-BNNWs), which are layers of vertically orientated h-BN demarcated with voids between each of the walls.^{46,47} Therefore, it is important to study the orientation engineering of thin film to make use of the advantages associated with the anisotropy of h-BN properties. The objective of the orientation engineering (in this case) is to attain control over the direction on the c-axis of the h-BN grown with respect to the substrate surface.

Vertically orientated h-BN films that stick well to Si substrates were grown by J. L. Andújar et al.⁴⁸ With B_2H_6 (1% in H_2) and NH_3 (pure) gases as precursors, the films were synthesized in a radio frequency (13.56 MHz) reactor by glow discharge decomposition of the precursors. A cross-sectional HRTEM image of a BN film grown is presented in FIG. 12. The amorphous interface between the orientated h-BN thin film and the silicon wafer is absent. Despite that, before the deposition, the Si oxide layer was not eliminated. Notably, the microstructure, which is aligned, is permeated throughout the entire film and h-BN lattice fringes are nearly orientated orthogonal to the substrate as shown in the image. The interplanar distance was measured to be 0.35 nm. The SAED pattern of this layer is shown in FIG. 13(a). FIG. 13(a) shows the (002) reflection of h-BN, as two arcs, along with rings indexed (100) and (110) reflections of h-BN. Above this layer, the film shows many crystallites without a preferred orientation and is evidenced by the SAED pattern with the (002) reflection as shown in FIG. 13(b), which shows a full circle instead of arcs.

FIG. 12 A 600 nm thick BN film grown on the cathode as seen by HRTEM showing (a) Si substrate, (b) a-BN interfacial layer, (c) h-BN oriented layer and (d) turbostratic h-BN randomly oriented layer.⁴⁸

FIG. 13 SAED patterns of h-BN regions shown in the previous figure (FIG. 12) near region a and in region b which is far from the interface with substrate.⁴⁸

An indicator of how well-aligned a h-BN thin film with respect to its substrate is the R value. It is a dimensionless number and is given by the following formula:

$$R = \frac{I_{A_{2u}}}{I_{E_{1u}}} \quad (1)$$

Where $I_{A_{2u}}$ is the intensity on the FTIR spectrum corresponding to the A_{2u} phonon mode and $I_{E_{1u}}$ is that corresponding to the E_{1u} phonon mode. An explanation of the various infrared-active

phonon modes of h-BN is given in Chapter 3. It is crucial to note as expounded in Chapter 4, the R value is a number that is dependent on the thickness of the thin film below a certain threshold thickness. Therefore, as an indicator of the degree of alignment of the h-BN thin film, the film must be thicker than a certain threshold thickness, which is around 500 nm.

Cometto et al.⁷ have deposited h-BN thin films using the HIPIMS system. The pulse frequency was 4 kHz and pulse length of 25 μ s, which corresponds to the maximum power density of ~ 60 W cm⁻² in this deposition. The deposition was conducted at a duty cycle of 10%. The base pressure of the depositions was around 5×10^{-6} mbar and it gradually increases up to 8×10^{-3} mbar post-deposition. Lanthanum hexaboride (LaB₆) target (3" diameter) was utilized for the deposition as a source for boron and nitrogen species as it is capable of generating a plasma of high concentration of boron and a high dissociation rate into ions.² The LaB₆ was sputtered in a mixed atmosphere of argon (80%) as the sputtering agent and nitrogen (20%) as a reactive gas. Despite containing around 7.5 at% lanthanum, the measured resistivity of the film remains high. A correlation exists between compressive stress and the films' degree of alignment with respect to the substrate surface was observed experimentally. A major advantage of vertically aligned h-BN thin films is that unlike other dielectric and thermally conductive materials, vertically aligned h-BN thin films can be deposited at room temperature. The thermal conductivity of vertically orientated h-BN is 1 W m⁻¹ K⁻¹.

Overall, the film contains a thin buffer zone, made of 6 nm thick of amorphous BN (a-BN), between the BN film and the substrate, before the film alignment is shown (FIG. 14(a)). This buffer layer is most probably due to the lattice mismatch as the silicon lattice structure and that of the aligned h-BN thin films are of different lattice constants. It is a buffer, thereby reducing film dislocations. The distance between two h-BN planes was measured to be 0.35 nm and the fast-Fourier transform of the aligned h-BN portion of the film exhibits the pattern of two diffraction spots which corresponds to the (0002) plane. To ascertain that the alignment persists throughout the entire thickness of the thin film, FIG. 14(b) shows a HRTEM image above the substrate. It can be ascertained visually by inspecting the planes and with the diffraction arcs shown on the FFT image as the inset that the alignment of h-BN is persistent through the entire film.

FIG. 14 (a) Image of a BN film demonstrating the transition region from the h-BN film to the substrate of the film grown at room temperature as viewed by HRTEM. The FFT of the film shown at the top indicates how the h-BN film is aligned orthogonally to the substrate along the (0002) plane. The distance between two h-BN planes was measured to be 0.35 nm. (b) HRTEM of the taken in the middle region and displaying concentric arcs on its FFT, which indicates the orthogonal orientation of the h-BN planes.⁷

FIG. 15 (a) SAED patterns of TEM bright-field (BF) image. (b) DF image was taken using the (0 0 2) diffraction arc. (c) HRTEM dark field image taken on a h-BN film deposited at 5% H₂ with a thickness of 1.5 μ m. The SAED pattern from a smaller region of the sample. (d) SAED patterns corresponding to regions (1) and (2) as shown in the diagram.⁴⁹

B. BenMoussa et al.⁴⁹ have synthesized vertically aligned h-BN nanowalls using a h-BN target as a boron and nitrogen species source via the technique of reactive RF magnetron sputtering. The addition of hydrogen helps to facilitate the formation of the nanowall with reduced carbon and

oxygen contamination. The RF power sustaining the plasma is set at 75 W and the process pressure ranges from 1.7×10^{-2} mbar to 2.9×10^{-2} mbar. It has been shown, experimentally, that using hydrogen gas as the reactive gas does lead to the formation of hexagonal boron nitride nanowall. Likewise, using RBS, it has shown that the optimal concentration of H_2 for the formation of nanowall is 5%, leading to films that are stoichiometric with enhanced purity.

The cross-sectional TEM image of the thin film grown by B. BenMoussa is shown in FIG. 15(a), as shown on it, the h-BN nanowalls are be observed. The variation of the image intensity is due to a combination of electron diffraction and absorbing contrasts. The preferred orientation of the h-BN planes within the h-BN nanowall structure was revealed in the selected area electron diffraction pattern (SAED) shown in FIG. 15(b). The (0 0 2) plane of the h-BN nanowall has a tilting over the maximum of 20° with respect to the orthogonal direction of the Si plane. Moreover, FIG. 15(b) and FIG. 15(c) reveal an evolution of the microstructures of the thin film: a denser layer is formed near the Si substrate, whereas further away from the substrate, a more porous nanowall structure is formed. A convergent beam electron diffraction (CBED) pattern is obtained and shown in FIG. 15(d). This is done to understand the crystal structure of the nanowalls, made from two typical distinct oriented nanowalls. Often, this implies that the presence of the hexagonal phase. The thickness of the nanowall was worked out to be below 50 nm typically.

Cometto et al. and BenMoussa et al. works have both separately illustrated the use of the magnetron sputtering techniques to grow h-BN thin films with a microstructure that can be described as being orientated to the substrate surface. BenMoussa et al. work further show that the addition of gas into the mixture of the reactive gases may enhance the formation of aligned h-BN whereas Cometto et al. work shows that controlling the parameters of the pulsed power supply may achieve a similar objective.

2.3.2 Isotope Engineering of h-BN

To motivate the purpose of isotope engineering, applications in which isotope engineering is predominantly used are introduced, namely: in thermal neutron detection, in enhancement of phonon-polaritons lifetimes and enhancement of thermal conductivity of h-BN for applications requiring good thermal management.

Boron exists as boron-10 and boron-11 stable isotopes while nitrogen exists as nitrogen-14 and nitrogen-15 stable isotopes. Isotope engineering aims to control the isotopic composition of boron in h-BN, i.e. isotopically enriched h-BN typically means the boron within h-BN is predominantly either boron-11 or boron-10. This is because the natural abundance of nitrogen isotopes is 99.6% for nitrogen-14 and 0.4% for nitrogen-15, the nitrogen isotopic abundance in h-BN is enriched in a typical h-BN compound. The natural abundance of boron isotopes in h-BN is 80.1% boron-11 and 19.9% boron-10. Therefore, there is room for varying the isotopic composition of boron in h-BN.

S. Liu et al.⁵⁰ have successfully synthesized monoisotopic h-BN crystals using a metal flux method. Using a Ni–Cr flux coupled high-purity elemental B¹⁰ and B¹¹ powders via the metal flux method at standard atmospheric pressure, successfully grown the monoisotopic hexagonal boron nitride crystals. The crystals were millimeter-sized and were of high quality. A schematic of the experimental setup, where a 12-in. heating length, the single-zone furnace was used and illustrated in FIG. 16(a). FIG. 16(b) illustrates the growth procedure as a schematic. FIG. 16(c) are the optical images of monoisotopic h-BN crystals grown on the metallic surface of nickel-chromium, illustrating that the crystals are colourless. The extraction of crystals from the metallic surface was accomplished by the peeling of crystals using thermal release tape. It was heated at 150 °C for 10 s to destroy the adhesive effect and enable the transfer of the crystals to a substrate. The extracted crystals measured to be 7 mm across and 10-μm thick are photographed on a glass substrate shown on FIG. 16(d). The largest domain size of a single crystal is roughly 1 mm across.

A. Maity et al. used metal organic chemical vapor deposition (MOCVD) to grow isotopically enriched h-BN epitaxial layers of various thicknesses. Triethylboron (TEB) were used as B and N precursors. The films were grown at 1350 °C using hydrogen as a carrier gas. Before the deposition, an AlN buffer layer (20 nm thick) was deposited on a sapphire substrate at 800 °C. Secondary ion mass spectrometry (SIMS) and X-ray diffraction were used to ascertain the high crystalline quality and ideal stoichiometric ratio of the grown films.^{5,51,52}

FIG. 16 (a) The synthesis setup for monoisotopic h-BN growth shown via a schematic and (b) the procedure of the experiment for h-BN growth. (c) Photographs of monoisotopic h-BN, i.e., h-B¹⁰N and h-B¹¹N, are seen as crystals on top of Ni-Cr metallic surface. (Inset) The h-BN flakes were extracted and isolated from the metal surfaces. (d) Photographs of free-standing hBN crystals on a glass substrate.⁵⁰

2.3.2.1 Enhancement of Phonon-Polaritons Lifetimes

Polaritons are quasiparticles due to the coupling of an oscillating charge with a photon. If the oscillating charge is an ion in a polar lattice, the resultant polaritons are known as phonon-polaritons (PhP). Likewise, if the oscillating charge is plasmon, then the resultant quasiparticle is known as plasmon-polaritons (PP). As the lifetimes of optical phonons are larger than plasmons, the optical losses of PhPs are lower than the PPs. Isotopic engineering is useful in this case as

isotope enrichment results in the shifting of the phonon frequencies (with a dependency of $\sim \mu^{-1/2}$, where μ is the reduced mass) and also in the narrowing of their corresponding linewidths.⁵³ Therefore, in using isotopically pure films, attainment of significant improvement in the propagation of PhP, enabling considerable enhancements in the phonon lifetimes, such as, in waveguides and hyperlenses.^{54–56}

A. Giles et al.⁵⁷ demonstrated through the isotopic enrichment of h-BN, a 3 times increase in bulk phonon lifetimes and an equivalent increment in the propagation length and lifetime of PhPs over hBN crystals with naturally abundant isotopic concentration.

2.3.2.2 Enhancement in Thermal Conductivity

The thermal conductivity of thin films is affected by scattering events, there are three major scattering events, namely: Umklapp scattering, isotopic impurities scattering and grain boundary scattering. The effective scattering rate, τ_{eff}^{-1} can be expressed as the following:

$$\tau_{eff}^{-1} = \tau_{U,p-p}^{-1} + \tau_{bound}^{-1} + \tau_{iso}^{-1}$$

Where $\tau_{U,p-p}^{-1}$ refers to the phonon-phonon Umklapp scattering, τ_{bound}^{-1} refers to the scattering due to grain boundaries and τ_{iso}^{-1} is the scattering rate due to isotopic variation within the films. From the equation, it is straightforward that reducing the scattering rate from isotopic variations does increase thermal conductivity due to enhanced phonon transport.

Phonons transport in crystals containing elements of natural isotopic abundance has higher scattering rates due to the atomic mass variations induced by the isotopes in the lattice, causing a reduction in its thermal conductivity compared to its isotopically-enriched or isotopically-pure variants.⁵⁸ In many compounds, the monoisotopic variants have demonstrated an enhancement in its thermal conductivity, such as in silicon⁵⁹, germanium⁶⁰, gallium arsenide⁶¹, diamond⁶² and graphene⁶³. Successful enhancement in thermal conductivities of these materials gives the first hint that isotopic enrichment in h-BN would affect a clear increment in the thermal conductivity of the film as well.

L. Lindsay et al.⁶⁴ have calculated the thermal conductivity, κ , of both single-layers of h-BN and bulk h-BN by using an exact numerical solution to the phonon Boltzmann transport equation

(BTE). By solving the phonon BTE, the in-plane thermal conductivity, κ_L , of both isotopically natural-abundant and isotopically enriched SLBN, and isotopically enriched h-BN have been calculated. Measured h-BN data agreed well with the theoretical results. FIG. 17(a) shows the calculated thermal conductivity for h-BN (solid red [lower] curve) with its dependence on temperature, T , compared with the experimental data (showed as black diamonds). FIG. 19(b) shows the enhancement in κ_L , $P = (\kappa_{\text{pure}} / \kappa_{\text{nat}} - 1) \times 100\%$, due to isotopic enrichment as a function of T for different values of film thickness, L as percentages. For fixed thickness, the weakening Umklapp scattering causes P to increase as T decreases from 300 K. The isotope scattering is a more crucial factor in limiting κ_L , so its absence is a reason for greater thermal conductivity enhancement. At low temperatures, P drops because most of the phonons available are of low frequency, as there is a strong dependency on the frequency of the isotopic scattering compared to the boundary scattering, this resulted in that the boundary scattering becomes the dominant scattering mechanism as T approaches 0 K. L. Lindsay's work gave the theoretical underpinning that isotopic enrichment would result in a corresponding enrichment of thermal conductivity in the case of h-BN.

FIG. 17 (a) The calculated κ_L of h-BN and its dependence on temperature (solid red (lowest) curve), T , compared with experimentally measured values (black diamonds). The thermal conductivity for isotopically pure h-BN, is shown as the dashed red (lower) curve. The calculated thermal conductivity for naturally occurring SLBN is shown as the solid green (higher) curve, whereas the dashed green (highest) curve shows calculated thermal conductivity for isotopically pure SLBN.⁶⁵ (b) Percent enhancement and its dependence on T for varied values of L of thermal conductivity in isotopically pure SLBN as compared with isotopically naturally-abundant SLBN. Inset compares the percent enhancement for SLBN and h-BN for $L = 2\mu\text{m}$.⁶⁵

C. Yuan et al.²⁷ fabricated isotopically enriched h-BN using a metal flux method⁵⁰ and the in-plane thermal conductivities were experimentally determined to be $k_{\parallel} = 585 \pm 80 \text{ W m}^{-1} \text{ K}^{-1}$ and $550 \pm 75 \text{ W m}^{-1} \text{ K}^{-1}$ at 300 K for the monoisotopic h-B¹⁰N and h-B¹¹N, respectively. These values are the highest thermal conductivity values measured at room temperature in the literature for h-BN. The measured out-of-plane thermal conductivities at 300 K, $k_{\perp}$ are $3.5 \pm 0.8 \text{ W m}^{-1} \text{ K}^{-1}$, $4.5 \pm 1.4 \text{ W m}^{-1} \text{ K}^{-1}$ for the monoisotopic h-B¹⁰N and h-B¹¹N, respectively. Hence, the increment in the thermal conductivity, $k_{\parallel}$, of monoisotopic h-B¹⁰N and h-B¹¹N, with reference to the h-BN in naturally abundant isotopic composition at room temperature is 43% and 35%, respectively. This illustrated that enhancement in thermal conductivity for thermal management applications is indeed attainable through isotope engineering of h-BN. C. Yuan et al. work shows that monoisotopic h-BN crystals growth is not only possible, the enhancement in thermal conductivity of these crystals were indeed experimentally verified.

2.3.3 Applications of h-BN Thin Films on Devices

There are many applications of h-BN thin films on electronic devices. For instance, due to its large bandgap in the deep-UV region, h-BN is touted as an emitter for single photons and a deep-UV laser. In this review, only three of h-BN many applications are elaborated, h-BN as an encapsulating layer, h-BN as a memory resistive device and h-BN as a heat-dissipation layer.

2.3.3.1 Passivation / Encapsulating Layer

Due to the excellent chemical and thermal strengths, h-BN can be touted as a highly desirable encapsulating layer for protection from oxidation at elevated temperatures conditioned on the fact that wide area, high-crystallinity and atomically thin layers could be deposited uniformly on electronics.^{66,67} Depositing BN films on different surfaces such as metallic surfaces or two-dimensional (2D) layers will noticeably improve both the thermal and chemical stabilities of the underlying electronics. Although conducting and semiconducting 2D materials are suitable candidates for advanced 2D electronic devices, their complementary dielectric materials, preferably low thicknesses coupled with high dielectric constant, for transistor gates, memory devices, capacitors and barrier layers for electrical and ambient environment isolation has not matured as a technology.^{68,69} This is a consequence of the difficulty in the synthesis of thin and yet highly resistive materials at lower temperatures ($< 900 \text{ }^{\circ}\text{C}$), a key requirement in direct growth

across large areas.⁷⁰ An ultrathin dielectrics with suitable interfacial properties are highly sought for. Without compromising the unique properties resulted from being 2D, materials deposited using atomic layer deposition of HfO_2 and Al_2O_3 ^{71–73} or CVD-growth of h-BN are some of the recently reported direct-growth methods for the realization of flexible electronic devices.⁶⁶

In the literature, many have used h-BN as an oxidation resistive layer and a dielectric layer for electronics. Z. Liu et al.⁶⁶ demonstrated that direct deposition of the atomically-thin layers of h-BN (5 nm) through their use as non-oxidative, atomically-thin layers on top of the underlying Ni substrate surfaces under high temperature and a highly oxygenated environment. Experiments on Ni samples, both with the presence of h-BN atomic layer coating and without, were conducted to test for h-BN oxidation-resistive property, for 30 min, at 1,100 °C at a pressure of 300 mTorr, filled with oxygen. Annealing of the Ni foils was completed before the oxidation experiments. SEM microscopy was employed to characterize the morphologies of the oxidized Ni foils. Many oxide particles were noticed on the surface of Ni (FIG. 18(a) and (b)), where there was an absence of the h-BN coating. Observation of the ubiquity of the NiO particles on the surfaces was depicted in the inset of FIG. 18(b). With the presence of the h-BN layers, the nickel surface was observed to remain smooth and clean with the presence of nickel grains (FIG. 18 (c) and (d)). The ultrathin h-BN as a dielectric layer will expressively reduce the effects of charging, leading to high clarity of the secondary electron imaging. The experiments were repeated with other metals, such as Cu and further ascertained the good result of using h-BN as an anti-oxidation layer after the transfer process assisted by PMMA. Similarly, h-BN layers can also prevent the surfaces of Cu and stainless steel films from oxidation at 500 °C and 1,100 °C, respectively, lasting for at least 30 min (FIG. 18 (e) – (h)).

Beyond depositing h-BN thin films or atomic layers for oxidation-resistive effects, h-BN was deposited onto AlGaIn-GaN high electron mobility transistors (HEMTs) to enhance its performance.^{74,75} B. Ren et al. demonstrated a successful application of passivating AlGaIn-GaN HEMTs with h-BN resulting in superior electronic performances. Shown in FIG. 19⁷⁴ are the characterized electronics properties of MIS-HEMT, in contrast to the typical Schottky-HEMT. Similarly shown in FIG. 19(a) is the gate leakage current, at drain voltage at 0V. The forward and reverse gate leakage currents of MIS-HEMT suffered at least a significant reduction of more than

3 orders and 6 orders of magnitude, respectively, as compared to regular Schottky-HEMT. Despite the gate voltage of 5V, the forward leakage current is still kept at $\sim 10^{-10}$ A/mm, this is a benefit from h-BN superior insulative property and a high breakdown electric field. The current-voltage characteristics (I_d - V_d) at different gate voltages are illustrated in FIG. 19(b) and FIG. 19(c). It possesses the typical tapering off feature. Due to the self-heating effect, for the Schottky-HEMT, it was experimentally verified that the saturation current is reduced at higher drain voltages. Notably, for MIS-HEMT, the saturated current, despite being continuously increased, could reach around 1230 mA/mm at V_d of 13 V and V_g of 5 V. This output value is significantly larger compared to MIS-HEMT with h-BN deposited by PECVD (~ 490 mA/mm at V_d of 13 V and V_g of 5V). The effective heat-dissipation effect of h-BN causes the self-heating effect in AlGaIn-GaN to be reduced. Calculating from the linear region of the DC output curves, an extremely low on-resistance (R_{on}) is obtained. FIG. 19(d) shows transfer characteristics of the HEMTs at saturated drain current, where the drain voltage, V_d is 8 V.

FIG. 18 (a,b) Pure Ni foils after suffering from oxidation under the same experimental conditions, viewed by SEM. Scale bars, 100 μ m (a), 10 μ m (b) and 1 μ m (b inset). (c,d) The 5 nm h-BN-coated Ni foils after oxidization as viewed by SEM. The oxides of nickel are visible as shown in the inset of (b) while its grains are visible through the transparent h-BN films. Scales bars: (c) 100 μ m and (d) 10 μ m. (e, f) Images of Cu foil after oxidization with and without h-BN coatings as viewed by SEM. Scale bars: (e, f) 5 μ m. (g, h) Images of stainless-steel surface with and without h-BN coatings as viewed by SEM. The straight lines in e and g are from the polish process. Scale bars: (g, h) 40 μ m. Insets in e–h: photos of each sample. Under the presence of the h-BN coating,

the colours of both Cu and stainless steel were retained, otherwise, their colours were altered due to oxidation.⁶⁶

FIG. 19 (a) The gate leakage current and its dependence on the gate voltage, while the drain voltages were maintained at 0 V. The current-voltage characteristics (I_d - V_d) of the output with varied gate voltages for (b) Schottky-HEMT and (c) MIS-HEMT. (d) Gate voltage as a function of output currents (drain currents) and transfer characteristics of Schottky-HEMT and MIS-HEMT.⁷⁴

2.3.3.2 Heat-Dissipating Layer

Circuit density increment and modern electronics miniaturization means that very efficient heat dissipation is becoming increasingly essential for the indispensable operation of electronic devices. Resulting from the rapid and ubiquity use of electronics, battery power consumption is rising faster than before, consequently, generating a great amount of heat and causing electronic failure.⁷⁶ therefore, novel and highly thermally conductive materials are highly sought after for various thermal management applications.⁷⁷ A needed benefit would be if the highly thermally conductive is also electrically insulative for the ease of application onto the electronic circuitry. Unfortunately, insulating materials are usually defined by low thermal conductivity as electronic mobility is a major contribution to heat conduction, this limits many of such materials ability to be efficient heat-spreaders.⁷⁸

Recent research has studied the inclusion of nanomaterials, such as carbon nanotubes, graphene and BN nano-sheets, into polymers, for the enhancement of thermal conductivity.^{79–81} Nevertheless, due to their electrical conductivity and the rapid oxidation of carbon upon exposure to the atmosphere, it is challenging to use CNTs and graphene in many applications for thermal dissipation. Therefore, it is crucial to seek electrical insulators with the desirable property of high thermal conductivities.⁸² In this section, two methods involving h-BN are used to mitigate the thermal hotspot problem are presented.

FIG. 20 (a) The surface of the h-BN laminate is shown as a SEM micrograph. Inset: AFM image of the h-BN laminate (The scale from black to white is 200 nm, giving the statistical mean thickness of the flakes ~ 10 nm). Scale bars: 1 μm . (b) Cross-sectional image of h-BN laminate as viewed by SEM. Scale bar: 10 μm . (c) Thermal conductivity, κ , with its dependence on T measured and as a function of the density, ρ , of the h-BN laminates.⁷⁸

J. Zheng et al. produced h-BN laminates using vacuum filtration of the h-BN solution. The solution was prepared via liquid exfoliation in isopropanol. After the filtration process, the substrate with the deposited h-BN mixture was baked for 1 h in an oven at 100 °C with circulation. Subsequently, the baked film was mechanically peeled from the substrate. A rolling compression procedure was applied to some of the samples, this is done so that the resulting laminates would be of varying densities. FIG. 20(a) and FIG. 20(b) give the SEM image of a typical laminate film. Observations on the cross-section and from the top, are shown in the SEM images of the laminates, showed that the lateral dimensions of such h-BN flakes are around 1 μm and 10 nm thick. There is strong

evidence to indicate the need for h-BN inks to synthesise laminates with desirable thermal conductivity, measuring up to a value of $20 \text{ W m}^{-1} \text{ K}^{-1}$, significantly larger than for the other materials which are currently used in thermal management. Furthermore, the pooled thermal conductivity is adjustable by varying the density of the packing of the laminate.

Q. Cai et al. measured the thermal conductivities of monolayer h-BN (from 1 layer (L) to 3L). The mechanical exfoliation method was used on h-BN single crystals via Scotch tape to obtain monolayer (to 3L) h-BN and these were transferred onto two different substrates which both are silicon substrates, one covered by 90-nm an oxide layer (SiO₂/Si) and another is covered 80-nm gold-coated silicon (Au/Si). Both surfaces have microwells (diameter, 3.8 mm) and connecting trenches (width, 0.2 mm) which are prefabricated. At a temperature close to the room temperature, the thermal conductivities of 1-3L h-BN (12 samples) were measured to be 751 ± 340 , 646 ± 242 , and 602 ± 247 W m⁻¹ K⁻¹, respectively. The thermal conductivity measurements show that atomically thin BN is a very promising material for heat dissipation of flexible electronic devices in the next generation.

FIG. 21 Thermal conductivity of 1-3L BN. (A) Experimentally measured thermal conductivity of the 1-3L BN which is suspended and its dependence on temperature, shown as filled circles. The open rhombus is the theoretical thermal conductivity values at 300 K. (B) Temperature distribution of a 1L BN suspended over 3.8-mm microwells through heating via a laser beam, the layer is heated to 330 K and the heat sink is maintained at 298 K. The dashed circle shows the edge of the suspended BN. (C) A diagram displaying the thermal conductivities of some of the common materials.

2.3.3.3 Electrical Devices

Here, the non-volatile resistive switching memory device of h-BN is presented, amongst the many electrical applications that h-BN is utilized for. The increasing demand for better performances in computing requires novel technologies that ought to be scalable and adaptive. Due to its scalability (could be scaled down to below 10 nm), fast writing/erasing speed, low power consumption and high endurance, non-volatile, resistive switching memories is a potential candidate to replace charged-base memory devices.^{83–85} Many works have been done on the resistive switching effect in numerous 2D materials, namely: graphene⁸⁶ and molybdenum disulfide (MoS₂).⁸⁷ However, few works have studied the resistive switching effect in hexagonal boron nitride (h-BN). For monolayer h-BN, there is only a single work on the resistive switching effect of h-BN developed by the CVD technique⁸⁸. Notably, h-BN and its different nanocomposites leave much potential for flexible resistive switching applications, due to its extremely high flexibility, a tunable bandgap and a myriad of unique electrical and mechanical properties.

K. Qian et al. fabricated a new resistive memory device which is flexible, composed of an ultrathin h-BN (≈ 3 nm) active layer right in between a gold top electrode (TE) and copper foil bottom electrode (BE) on a polyethylene terephthalate (PET) substrate (FIG. 22(a)). The Ag TE/hBN/Cu foil memory device has high write/erase cycling (≈ 550), ON/OFF ratio (≈ 100), retention time ($\approx 3 \times 10^{-3}$ s) and bending endurance (≈ 750 cycles). The memory cell (≈ 3 nm thick) consisting of a h-BN film which is in between Ag TE and Cu foil is shown in the TEM image of FIG. 22(b). . To alter the original resistive memory state into a switching state because the h-BN film was in a highly resistive state and under a compliance current (CC) of 0.1 mA, where the electro-forming process was required. Applied to the Ag TE was a direct current (DC) voltage sweeping (sweep rate 0.01 V s^{-1}) and the Cu foil BE was grounded to ascertain the performance of the device V forming (FIG. 22(c)) is the electroforming process for h-BN memory which is attained by voltage sweep to a particularly high value ($\approx 1.87 \text{ V}$) in which the conductance abruptly increases. Consequently, the repeatable switching current–voltage (I – V) behaviours were obtained under a compliance current of 1 mA after the electroforming process. The h-BN based memory has a hysteresis loop in the I – V curve at forward and reverse voltages (FIG. 22(d)).

FIG. 22 a) Diagram showing the Ag/h-BN/Cu foil on PET substrate device arrays. b) Cross-sectional image of the Ag/h-BN/Cu foil memory cell as viewed by TEM. c) The electroforming process with $V_{\text{forming}} \approx 1.87$ V for h-BN memory device. d) The switching characteristics after the electroforming process for the h-BN memory device.⁸⁸

In this section, three prominent applications of h-BN are presented, they are namely: as an encapsulating / passivation layer, usage in thermal management and as a novel flexible resistive memory device.

2.4 Conclusion

To summarize, to fulfil the objectives of the thesis, which are to fabricate h-BN thin films and its isotopically-enriched variants for thermal management, as passivation layers and as a novel resistive memory device for thermal and electrical applications, the literature survey of topics relevant to these objectives are presented.

The survey begins with an overview and introduction to thin films, its associated advantages and purposes and its enabling deposition techniques, mainly the sputtering technique. The magnetron sputtering technique and the high power impulse magnetron sputtering (HIPIMS) technique were introduced. The most challenging problem of ‘target poisoning’ and other problems related to

reactive-HIPIMS technique were presented. Sputtering of the two targets used in this thesis, lanthanum hexaboride and pure boron targets are introduced and discussed.

The final part of this literature survey introduces hexagonal boron nitride (h-BN). Its thermal, electronic and optical properties are briefly introduced. Isotope engineering of h-BN, its purpose and its current developments are given a thorough introduction. Finally, the chapter ends with just three applications of h-BN (amongst its many possible applications) that this thesis is concerned with. The current developments of these three applications are given a thorough introduction.

2.5 References

- 1 E. M. Oks and A. Anders, *J. Appl. Phys.*, 2012, **112**, 086103.
- 2 R. Franz, C. Clavero, R. Bolat, R. Mendelsberg and A. Anders, *Plasma Sources Sci. Technol.*, 2014, **23**, 035001.
- 3 A. Maity, S. J. Grenadier, J. Li, J. Y. Lin and H. X. Jiang, *Appl. Phys. Lett.*, 2019, **114**, 222102.
- 4 S. Grenadier, J. Li, J. Lin, H. Jiang and A. Maity, in *Hard X-Ray, Gamma-Ray, and Neutron Detector Physics XIX*, eds. M. Fiederle, A. Burger, L. Franks, R. B. James and S. A. Payne, SPIE, 2017, p. 20.
- 5 A. Maity, S. J. Grenadier, J. Li, J. Y. Lin and H. X. Jiang, *Appl. Phys. Lett.*, 2017, **111**, 033507.
- 6 A. Maity, T. C. Doan, J. Li, J. Y. Lin and H. X. Jiang, *Appl. Phys. Lett.*, 2016, **109**, 072101.
- 7 O. Cometto, B. Sun, S. H. Tsang, X. Huang, Y. K. Koh and E. H. T. Teo, *Nanoscale*, 2015, **7**, 18984–18991.
- 8 R. Bandorf, V. Sittinger and G. Bräuer, *Compr. Mater. Process.*, 2014, **4**, 75–99.
- 9 G. Bräuer, in *Comprehensive Materials Processing*, Elsevier, 2014, vol. 4, pp. 57–73.
- 10 D. M. Stewart and R. J. Lad, *Phys. Status Solidi Basic Res.*, 2018, **255**, 1–5.
- 11 C. Hu, S. Kotake, Y. Suzuki and M. Senoo, *Vacuum*, 2000, **59**, 748–754.
- 12 J. Hahn, M. Friedrich, R. Pintaske, M. Schaller, N. Kahl, D. R. T. Zahn and F. Richter, *Diam. Relat. Mater.*, 1996, **5**, 1103–1112.
- 13 Y. Ito, S. Kuriki, M. Saidoh and M. Nishikawa, *Jpn. J. Appl. Phys.*, 1994, **33**, 5959–5966.
- 14 E. Oks, A. Anders, A. Nikolaev and Y. Yushkov, *Rev. Sci. Instrum.*, ,

DOI:10.1063/1.4980149.

- 15 M. Wakatsuchi, Y. Takaba, Y. Ueda and M. Nishikawa, *Proc. Int. Conf. Ion Implant. Technol.*
- 16 G. Cassaboïs, P. Valvin and B. Gil, *Nat. Photonics*, 2016, **10**, 262–266.
- 17 R. Dahal, J. Li, S. Majety, B. N. Pantha, X. K. Cao, J. Y. Lin and H. X. Jiang, *Appl. Phys. Lett.*, 2011, **98**, 211110.
- 18 K. Watanabe, T. Taniguchi and H. Kanda, *Nat. Mater.*, 2004, **3**, 404–409.
- 19 Y. Shi, C. Hamsen, X. Jia, K. K. Kim, A. Reina, M. Hofmann, A. L. Hsu, K. Zhang, H. Li, Z.-Y. Juang, M. S. Dresselhaus, L.-J. Li and J. Kong, *Nano Lett.*, 2010, **10**, 4134–4139.
- 20 L. Song, L. Ci, H. Lu, P. B. Sorokin, C. Jin, J. Ni, A. G. Kvashnin, D. G. Kvashnin, J. Lou, B. I. Yakobson and P. M. Ajayan, *Nano Lett.*, 2010, **10**, 3209–3215.
- 21 X. Blase, A. Rubio, S. G. Louie and M. L. Cohen, *Phys. Rev. B*, 1995, **51**, 6868–6875.
- 22 T. T. Tran, K. Bray, M. J. Ford, M. Toth and I. Aharonovich, *Nat. Nanotechnol.*, 2016, **11**, 37–41.
- 23 A. Aldalbahi and P. Feng, *IEEE Trans. Electron Devices*, 2015, **62**, 1885–1890.
- 24 H. Wang, X. Zhang, H. Liu, Z. Yin, J. Meng, J. Xia, X. M. Meng, J. Wu and J. You, *Adv. Mater.*, 2015, **27**, 8109–8115.
- 25 K. Zhang, Y. Feng, F. Wang, Z. Yang and J. Wang, *J. Mater. Chem. C*, 2017, **5**, 11992–12022.
- 26 R. Dahal, K. Ahmed, J. W. Wu, A. Weltz, J. J.-Q. Lu, Y. Danon and I. B. Bhat, *Appl. Phys. Express*, 2016, **9**, 065801.
- 27 C. Yuan, J. Li, L. Lindsay, D. Cherns, J. W. Pomeroy, S. Liu, J. H. Edgar and M. Kuball, *Commun. Phys.*, 2019, **2**, 43.
- 28 P. Jiang, X. Qian, R. Yang and L. Lindsay, *Phys. Rev. Mater.*, 2018, **2**, 064005.
- 29 S. Galambosi, L. Wirtz, J. A. Soininen, J. Serrano, A. Marini, K. Watanabe, T. Taniguchi, S. Huotari, A. Rubio and K. Hämäläinen, *Phys. Rev. B*, 2011, **83**, 081413.
- 30 Y. Hattori, T. Taniguchi, K. Watanabe and K. Nagashio, *ACS Appl. Mater. Interfaces*, 2016, **8**, 27877–27884.
- 31 C. Pan, K. Kou, Q. Jia, Y. Zhang, G. Wu and T. Ji, *Compos. Part B Eng.*, 2017, **111**, 83–90.
- 32 J. Gu, X. Meng, Y. Tang, Y. Li, Q. Zhuang and J. Kong, *Compos. Part A Appl. Sci. Manuf.*,

- 2017, **92**, 27–32.
- 33 S. Takahashi, Y. Imai, A. Kan, Y. Hotta and H. Ogawa, *J. Alloys Compd.*, 2014, **615**, 141–145.
 - 34 A. Laturia, M. L. Van de Put and W. G. Vandenberghe, *npj 2D Mater. Appl.*, 2018, **2**.
 - 35 N. Ohba, K. Miwa, N. Nagasako and A. Fukumoto, *Phys. Rev. B*, 2001, **63**, 115207.
 - 36 J. Wu, B. Wang, Y. Wei, R. Yang and M. Dresselhaus, *Mater. Res. Lett.*, 2013, **1**, 200–206.
 - 37 P. Jiang, X. Qian, R. Yang and L. Lindsay, *Phys. Rev. Mater.*, 2018, **2**, 064005.
 - 38 X. Duan, M. Wang, D. Jia, N. Jing, Z. Wu, Z. Yang, Z. Tian, S. Wang, P. He, Y. Wang and Y. Zhou, *Mater. Sci. Eng. A*, 2014, **607**, 38–43.
 - 39 O. Cometto, M. K. Samani, B. Liu, S. Sun, S. H. Tsang, J. Liu, K. Zhou and E. H. T. Teo, *ACS Appl. Mater. Interfaces*, 2017, **9**, 7456–7464.
 - 40 A. Wei, X. W. Sun, C. X. Xu, Z. L. Dong, M. B. Yu and W. Huang, *Appl. Phys. Lett.*, 2006, **88**, 24–26.
 - 41 Y. M. Shyu and F. C. N. Hong, *Mater. Chem. Phys.*, 2001, **72**, 223–227.
 - 42 S. H. Jo, J. Y. Lao, Z. F. Ren, R. A. Farrer, T. Baldacchini and J. T. Fourkas, *Appl. Phys. Lett.*, 2003, **83**, 4821–4823.
 - 43 Y. M. Wong, S. Wei, W. P. Kang, J. L. Davidson, W. Hofmeister, J. H. Huang and Y. Cui, *Diam. Relat. Mater.*, 2004, **13**, 2105–2112.
 - 44 K. J. Sankaran, D. Q. Hoang, K. Srinivasu, S. Korneychuk, S. Turner, S. Drikkoningen, P. Pobedinskas, J. Verbeeck, K. C. Leou, I. N. Lin and K. Haenen, *Phys. status solidi*, 2016, **213**, 2654–2661.
 - 45 K. J. Sankaran, D. Q. Hoang, S. Kunuku, S. Korneychuk, S. Turner, P. Pobedinskas, S. Drikkoningen, M. K. Van Bael, J. D’ Haen, J. Verbeeck, K.-C. Leou, I.-N. Lin and K. Haenen, *Sci. Rep.*, 2016, **6**, 29444.
 - 46 K. J. Sankaran, D. Q. Hoang, K. Srinivasu, S. Korneychuk, S. Turner, S. Drikkoningen, P. Pobedinskas, J. Verbeeck, K. C. Leou, I. N. Lin and K. Haenen, *Phys. Status Solidi Appl. Mater. Sci.*, 2016, **213**, 2654–2661.
 - 47 D.-Q. Hoang, S. Korneychuk, K. J. Sankaran, P. Pobedinskas, S. Drikkoningen, S. Turner, M. K. Van Bael, J. Verbeeck, S. S. Nicley and K. Haenen, *Acta Mater.*, 2017, **127**, 17–24.
 - 48 J. L. Andújar, E. Bertran and Y. Maniette, *J. Appl. Phys.*, 1996, **80**, 6553–6555.
 - 49 B. BenMoussa, J. D’Haen, C. Borschel, J. Barjon, A. Soltani, V. Mortet, C. Ronning, M.

- D'Olieslaeger, H.-G. Boyen and K. Haenen, *J. Phys. D. Appl. Phys.*, 2012, **45**, 135302.
- 50 S. Liu, R. He, L. Xue, J. Li, B. Liu and J. H. Edgar, *Chem. Mater.*, 2018, **30**, 6222–6225.
- 51 J. Li, R. Dahal, S. Majety, J. Y. Lin and H. X. Jiang, *Nucl. Instruments Methods Phys. Res. Sect. A Accel. Spectrometers, Detect. Assoc. Equip.*, 2011, **654**, 417–420.
- 52 T. C. Doan, J. Li, J. Y. Lin and H. X. Jiang, *AIP Adv.*, 2016, **6**, 075213.
- 53 M. Cardona and M. L. W. Thewalt, *Rev. Mod. Phys.*, 2005, **77**, 1173–1224.
- 54 S. Dai, Q. Ma, T. Andersen, A. S. Mcleod, Z. Fei, M. K. Liu, M. Wagner, K. Watanabe, T. Taniguchi, M. Thiemens, F. Keilmann, P. Jarillo-Herrero, M. M. Fogler and D. N. Basov, *Nat. Commun.*, 2015, **6**, 6963.
- 55 Z. Liu, H. Lee, Y. Xiong, C. Sun and X. Zhang, *Science (80-.)*, 2007, **315**, 1686.
- 56 Y. Xiong, Z. Liu and X. Zhang, *Appl. Phys. Lett.*, 2009, **94**, 203108.
- 57 A. J. Giles, S. Dai, I. Vurgaftman, T. Hoffman, S. Liu, L. Lindsay, C. T. Ellis, N. Assefa, I. Chatzakis, T. L. Reinecke, J. G. Tischler, M. M. Fogler, J. H. Edgar, D. N. Basov and J. D. Caldwell, *Nat. Mater.*, 2018, **17**, 134–139.
- 58 L. Lindsay, D. A. Broido and T. L. Reinecke, *Phys. Rev. B - Condens. Matter Mater. Phys.*, 2013, **88**, 1–9.
- 59 R. K. Kremer, K. Graf, M. Cardona, G. G. Devyatikh, A. V. Gusev, A. M. Gibin, A. V. Inyushkin, A. N. Taldenkov and H.-J. Pohl, *Solid State Commun.*, 2004, **131**, 499–503.
- 60 M. Asen-Palmer, K. Bartkowski, E. Gmelin, M. Cardona, A. P. Zhernov, A. V. Inyushkin, A. Taldenkov, V. I. Ozhogin, K. M. Itoh and E. E. Haller, *Phys. Rev. B*, 1997, **56**, 9431–9447.
- 61 A. V. Inyushkin, A. N. Taldenkov, A. Y. Yakubovsky, A. V. Markov, L. Moreno-Garsia and B. N. Sharonov, *Semicond. Sci. Technol.*, 2003, **18**, 685–688.
- 62 A. Sparavigna, *Phys. Rev. B*, 2002, **65**, 064305.
- 63 S. Chen, Q. Wu, C. Mishra, J. Kang, H. Zhang, K. Cho, W. Cai, A. A. Balandin and R. S. Ruoff, *Nat. Mater.*, 2012, **11**, 203–207.
- 64 L. Lindsay and D. A. Broido, *Phys. Rev. B - Condens. Matter Mater. Phys.*, 2011, **84**, 155421.
- 65 L. Lindsay and D. A. Broido, *Phys. Rev. B*, 2011, **84**, 155421.
- 66 Z. Liu, Y. Gong, W. Zhou, L. Ma, J. Yu, J. C. Idrobo, J. Jung, A. H. MacDonald, R. Vajtai, J. Lou and P. M. Ajayan, *Nat. Commun.*, 2013, **4**, 2541.

- 67 L. H. Li, J. Cervenka, K. Watanabe, T. Taniguchi and Y. Chen, *ACS Nano*, 2014, **8**, 1457–1462.
- 68 A. K. Geim and I. V. Grigorieva, *Nature*, 2013, **499**, 419–425.
- 69 G. Fiori, F. Bonaccorso, G. Iannaccone, T. Palacios, D. Neumaier, A. Seabaugh, S. K. Banerjee and L. Colombo, *Nat. Nanotechnol.*, 2014, **9**, 768–779.
- 70 N. R. Glavin, C. Muratore, M. L. Jespersen, J. Hu, P. T. Hagerty, A. M. Hilton, A. T. Blake, C. A. Grabowski, M. F. Durstock, M. E. McConney, D. M. Hilgefort, T. S. Fisher and A. A. Voevodin, *Adv. Funct. Mater.*, 2016, **26**, 2640–2647.
- 71 S. Kamiyama, T. Miura and Y. Nara, *Appl. Phys. Lett.*, 2005, **87**, 1–3.
- 72 D. Gu, K. Tapily, P. Shrestha, M. Y. Zhu, G. Celler and H. Baumgart, *J. Electrochem. Soc.*, 2008, **155**, G129.
- 73 S. M. George, *Chem. Rev.*, 2010, **110**, 111–131.
- 74 B. Ren, M. Liao, M. Sumiya, J. Li, L. Wang, X. Liu, Y. Koide and L. Sang, *J. Alloys Compd.*, 2020, **829**, 154542.
- 75 G. H. Lee, A. H. Park, J. H. Lim, C.-H. Lee, D.-W. Jeon, Y.-B. Kim, J. Lee, J. W. Yang, E.-K. Suh and T. H. Seo, *J. Nanosci. Nanotechnol.*, 2020, **20**, 4450–4453.
- 76 H. Zhu, Y. Li, Z. Fang, J. Xu, F. Cao, J. Wan, C. Preston, B. Yang and L. Hu, *ACS Nano*, 2014, **8**, 3606–3613.
- 77 S. V. Garimella, A. S. Fleischer, J. Y. Murthy, A. Keshavarzi, R. Prasher, C. Patel, S. H. Bhavnani, R. Venkatasubramanian, R. Mahajan, Y. Joshi, B. Sammakia, B. A. Myers, L. Chorosinski, M. Baelmans, P. Sathyamurthy and P. E. Raad, *IEEE Trans. Components Packag. Technol.*, 2008, **31**, 801–815.
- 78 J.-C. Zheng, L. Zhang, A. V Kretinin, S. V Morozov, Y. B. Wang, T. Wang, X. Li, F. Ren, J. Zhang, C.-Y. Lu, J.-C. Chen, M. Lu, H.-Q. Wang, A. K. Geim and K. S. Novoselov, *2D Mater.*, 2016, **3**, 011004.
- 79 W. Meng, Y. Huang, Y. Fu, Z. Wang and C. Zhi, *J. Mater. Chem. C*, 2014, **2**, 10049–10061.
- 80 L. Peng, Z. Xu, Z. Liu, Y. Guo, P. Li and C. Gao, *Adv. Mater.*, 2017, **29**, 1700589.
- 81 T. Ramanathan, A. A. Abdala, S. Stankovich, D. A. Dikin, M. Herrera-Alonso, R. D. Piner, D. H. Adamson, H. C. Schniepp, X. Chen, R. S. Ruoff, S. T. Nguyen, I. A. Aksay, R. K. Prud'Homme and L. C. Brinson, *Nat. Nanotechnol.*, 2008, **3**, 327–331.
- 82 Q. Cai, D. Scullion, W. Gan, A. Falin, S. Zhang, K. Watanabe, T. Taniguchi, Y. Chen, E. J.

- G. Santos and L. H. Li, *Sci. Adv.*, 2019, **5**, 1–9.
- 83 J. J. Yang, M. D. Pickett, X. Li, D. A. A. Ohlberg, D. R. Stewart and R. S. Williams, *Nat. Nanotechnol.*, 2008, **3**, 429–433.
- 84 J. J. Yang, D. B. Strukov and D. R. Stewart, *Nat. Nanotechnol.*, 2013, **8**, 13–24.
- 85 R. Waser, R. Dittmann, C. Staikov and K. Szot, *Adv. Mater.*, 2009, **21**, 2632–2663.
- 86 Y. Chen, B. Zhang, G. Liu, X. Zhuang and E. T. Kang, *Chem. Soc. Rev.*, 2012, **41**, 4688–4707.
- 87 J. Liu, Z. Zeng, X. Cao, G. Lu, L. H. Wang, Q. L. Fan, W. Huang and H. Zhang, *Small*, 2012, **8**, 3517–3522.
- 88 K. Qian, R. Y. Tay, V. C. Nguyen, J. Wang, G. Cai, T. Chen, E. H. T. Teo and P. S. Lee, *Adv. Funct. Mater.*, 2016, **26**, 2176–2184.
- 89 G. U. Siddiqui, M. M. Rehman, Y. J. Yang and K. H. Choi, *J. Mater. Chem. C*, 2017, **5**, 862–871.

3 Experimental Procedures and Characterization

This chapter describes most of the experimental tools and techniques (including deposition techniques) that were utilized for thin-film deposition, device fabrication and testing of the electrical, thermal and optical properties and their associated characterizations for h-BN.

3.1 Experimental Procedures

3.1.1 Wafer-cleaning Process

The objective of the wafer-cleaning process is to ensure that the wafer is cleaned thoroughly with little to no residue on its surface, before deposition in the HIPIMS chamber. Contaminants on the surface may interfere with the deposition process, inhibiting the bond and microstructure formation processes, resulting in the deposition of a thin film with less desirable properties.

To abate this issue, the wafer-cleaning process is done in 2 steps:

- 1) Ultrasonication in acetone, followed by 2-propanol and deionized water. The ultrasonication process makes use of the mechanical vibration of water molecules energized by ultrasound to remove most of the contaminants on the surface of the wafer.
- 2) Drying the wafer by blowing nitrogen at high pressure using a nitrogen gun. This step typically removes dirt and dust from the wafer and residual deionized water.

It is ascertained through the quality of the samples grown for the work recorded in this thesis, the cleaning process is sufficient for the purposes required of this work.

3.1.2 Electron-beam Physical Vapor Deposition (E-Beam)

Metallic deposition is a significantly crucial process that is very relevant in the semiconductor industry. It is primarily used to form an integrated circuit and microchip connection. Of the many PVD processes, the E-Beam evaporation technique is useful in depositing metallic elements onto a substrate with high fidelity (accurate spatial deposition) and control. The working principle of a typical E-beam deposition system is as such, first, electron beams are generated using either of these mechanisms: thermionic emission, field electron emission, or the anodic arc emission. Second, high voltage is applied across the electron beam, thereby imparting high kinetic energy. Third, the accelerated electrons impinge onto the evaporation material, such as metallic elements

like gold or titanium. The kinetic energy upon impact on the material residing within a crucible effectively heats up and evaporates the material. The vaporized material rises in the deposition chamber comes into contact with the cooler substrate holder and the substrate solidifies into a thin film deposited onto the substrate. This completes the deposition process.

To ensure high quality deposition occurs, such that the purity of the deposited material is that residing within the crucible, the system must be in a high vacuum state. Typically, the pressure at which the electron gun is switched on is around 5×10^{-6} mbars. FIG. 23(a) illustrates a schematic for the interior set-up of the E-Beam deposition chamber. It is clear from the schematic how the electron beam, which is generated by the electron gun, travels to the crucible and causes the material, such as, gold or aluminium to evaporate and be deposited on the substrate. Precise control of the deposition rate can be controlled through the assistance of the quartz crystal rate sensor. FIG. 23(b) gives the image of the E-Beam deposition machine, Edwards Model FL 400 used in this work.

FIG. 23 (a) A schematic illustrating the interior set-up of the E-Beam deposition chamber, it shows the most important components of the E-Beam system, such as, the electron gun for generation of electron beam and the quartz crystal rate sensor.¹⁶ (b) An image showing the E-Beam machine (Edwards, Model FL 400).

Table 3.4 Relevant Material Properties to the E-Beam Machine

Index	Materials	Density / g cm ⁻³	Z-Value
1	Au	19.3	23.17

2	Ni	8.91	26.26
3	Ti	4.5	14.05
4	Al	2.7	8.17

Several ingots of different materials are placed in the crucible before each E-Beam deposition. Table 3.1 lists all the relevant materials in this work and their properties that are needed to calibrate the E-Beam deposition chamber for a successful deposition. The Z-Value is the acoustic impedance of the deposited material.

3.2 Characterization

In this section, an exposition of the basic material, electrical, thermal and optical characterizations are provided.

3.2.1 Fourier Transform Infrared Spectrometry (FTIR)

3.2.1.1 Infrared Spectrometry

Spectroscopy is defined as the interaction between matter and light. Infrared spectrometry can then be defined as a technique that deals with electromagnetic radiation in the infrared region for the determination of bonding characteristics within a sample for our purposes with thin film growth using physical vapour deposition techniques.

In general, spectroscopy can:

1. determine the quality or purity of a sample.
2. determine the proportion of components in a mixture.

A background spectrum must be measured due to the need to have a relative scale for the absorption intensity. The background scan is usually done with the substrate on which the thin film is grown, e.g. <100> silicon. A comparison of this background spectrum is done with respect to the measured spectrum of the as-deposited thin film on the substrate to determine the percentage transmittance. Consequently, all the spectral features which are derived from the comparison can be due solely to the as-deposited thin film as this process removes any characteristics of the results which are due to the instrument.

3.2.1.2 FTIR of h-BN

From group-theoretic considerations, the zone-center (Γ -point) phonon modes of h-BN are given by the following equation:¹⁸

$$\Gamma = A_{2u} + E_{1u} + E_{2g} + B_{1g} \quad (3.1)$$

Where A_{2u} and E_{1u} are infrared active, E_{2g} is Raman active and B_{1g} is silent. Both the E_{1u} and E_{2g} are doubly degenerate. As h-BN is a partial ionic crystal due to the large difference in the electronegativities of B and N, the effects of the dipole-dipole interactions (Coulomb interactions) resulted in the splitting of the A_{2u} and E_{1u} mode into transverse optical (TO) and longitudinal optical (LO) mode.¹⁸

Schematics of the two infrared active phonon modes are shown in FIG. 24. FIG. 24(a) shows the A_{2u} phonon mode which is the B-N-B out-of-plane bending mode whereas FIG. 24(b) shows the E_{1u} phonon mode which is the B-N in-plane stretching mode. The frequencies of the two modes are, for the E_{1u} phonon mode, $\sim 1380 \text{ cm}^{-1}$ and for the A_{2u} phonon mode, $\sim 780 - 810 \text{ cm}^{-1}$.¹⁹ The FTIR spectra of various h-BN samples is depicted in FIG. 25. FIG. 25 depicts the high purity h-BN power made of $10 \mu\text{m}$ particles as black-lines with symbols. Spectra of HIPIMS grown cubic boron nitride / turbostratic-BN and ordered h-BN thin films are shown in red and green lines with symbols, respectively.

In this work, most of the FTIR transmission spectra were taken at near normal to the sample surface in the range of 400 cm^{-1} to 4000 cm^{-1} , with a resolution of 4 cm^{-1} .

In this regard, a concise introduction to the working principle and operations of FTIR is presented. FTIR spectra of h-BN samples and its associated phonon modes are also presented. In summary, FTIR can be a fast and useful analysis to verify if the as-deposited thin film is h-BN.

FIG. 24 (a) Schematic of A_{2u} phonon mode. (b) Schematic of E_{1u} phonon mode.

FIG. 25 FTIR spectra of BN samples. The cubic boron nitride / turbostratic boron nitride film was synthesised using HIPIMS at a temperature of 500 °C, the substrate biasing is 0 V and the maximum power density is 200 W cm⁻². The vertically orientated h-BN sample was deposited at room temperature and a 60 W cm⁻² peak power density using HIPIMS.²⁰

3.2.2 Raman Spectrometry

3.2.2.1 Classical Raman Effect

According to the electromagnetic theory, an oscillating dipole (under an acceleration) produces electromagnetic (EM) radiation. A laser beam used in Raman spectrometry can be visualised as an oscillating EM wave with electric vector E . Upon interaction with the sample, an electric dipole moment $P = \alpha E$ is induced which deforms molecules. Due to the periodical exchange of energies, the molecules will start to vibrate at the fundamental frequency ν_m . The amplitude modulation of

the dipole moment oscillations by the frequency of the incident radiation's electric field results in the Raman scattering as depicted in FIG. 26(a) - (c). The oscillating dipole then emits EM radiation.

FIG. 26 Graphs representing Rayleigh and Raman scattering. (a) Induced dipole moment of the molecule vibrating at the photon frequency due to energy exchange with the photon. (b) Polarizability, α , alters the amplitude of the dipole moment oscillation. (c) The resultant amplitude modulated dipole moment oscillation. (d) Steady-state vibrations which emit electromagnetic radiation.¹⁷

The three types of EM-radiation emitted by an oscillating dipole in a Raman scattering event are namely, Rayleigh, Raman anti-Stokes and Raman Stokes. These are depicted schematically in FIG. 26(d).

- Rayleigh: A molecule with no quantized vibrational modes will re-emit the radiation with the same frequency ν_0 as the excitation (usually a laser) source as the dominant radiation emitted.
- Raman Stokes: If the molecule has a Raman-active phonon mode, part of the photon energy will be absorbed, and the scattered photon's frequency will become $\nu_0 - \nu_m$. This Raman frequency is called Raman Stokes frequency.
- Raman anti-Stokes: If an excited molecule has a Raman-active phonon mode, it absorbs a photon and will scatter the incident light to frequency $\nu_0 + \nu_m$. This Raman frequency is called Raman Anti-Stokes frequency.
- Only about 0.00001% of the incident radiation produces inelastic Raman scattering with frequencies $\nu_0 \pm \nu_m$.

Raman scattering is contingent on the fact that the molecular vibration causes a variation in the polarizability.

3.2.2.2 Raman Phonon Modes of h-BN

FIG. 27 Schematics of h-BN phonon modes (a) inter-layer shear mode, E_{2g}^{low} (52 cm^{-1}) and (b) intra-layer in-plane anti-symmetric vibration within the hexagonal plane of the B and N atoms pair, E_{2g}^{high} (1367 cm^{-1}).

h-BN has two Raman-active phonon modes, the inter-layer shear mode, E_{2g}^{low} and the intra-layer anti-symmetric vibration of the B and N pair of atoms in the hexagonal plane, E_{2g}^{high} . Their schematics of the two vibration modes are depicted in FIG. 27, the peak positions of these two modes are identified in the h-BN Raman spectra. The h-BN crystals were made under different conditions.²² For the E_{2g}^{low} mode, its peak is of frequency 52 cm^{-1} and for the E_{2g}^{high} mode, its peak is of frequency 1367 cm^{-1} for bulk h-BN.

3.2.3 Transmission Electron Microscopy (TEM)

3.2.3.1 Introduction to Transmission Electron Microscope

In this section, a brief introduction to TEM is presented.

TEM is used to visualise the internal fine structure in solids on the scale of sub-micrometre, i.e. in the range of nanometres to hundreds of nanometres. The internal fine structure of solids is typically known as ‘microstructure’. The amount of the data which can be collected by TEM depends on four factors:

- a) The resolution of the microscope, usually in the range of 0.3 nm.
- b) The bandwidth or resolution of the electron beam, usually in the range of several eV.
- c) The thickness of the specimen, usually less than 100 nm.
- d) The composition and stability of the sample.

As electrons can be focused more easily than x-ray (which can provide more quantitative diffraction patterns than electrons), diffraction patterns can be measured from microscopic regions. Furthermore, the optics of electron microscopes reconfigured to produce images of defects such as dislocations and interfaces, using the variation of electron intensities emerging from the samples, also known as “diffraction contrast”. High-resolution TEM (HRTEM) produces images using the preserved quantum mechanical phase of the electron wave after diffraction and its resultant interference pattern with the phase of the transmitted wave to form images of atoms in high resolutions.

Besides diffraction and spatial imaging, the highly energetic electrons in TEM also cause electronic excitations of the atoms in the sample. There are two types of spectrometry associated with TEM to obtain chemical information from the sample.

The first of such spectrometry is the energy-dispersive x-ray spectrometry (EDS). The characteristic peaks from the chemical elements as seen in the x-ray spectrum obtained from small regions that are illuminated with an electron beam can be used to quantify the concentrations of different elements within a sample.

Another such spectrometry is the electron energy-loss spectrometry (EELS), in which the energy losses of the transmitted electrons through the sample are measured. This spectrometry provides information on local chemistry and structures through the features in the EELS spectra which are caused by plasmon excitations and core electrons excitations.²³

3.2.4 Electron Energy Loss Spectroscopy (EELS)

3.2.4.1 Introduction to EELS

In this section, the usage of EELS as a characterization technique will be briefly explained. The focus of this section will be on the interpretation of core absorption edges of EELS spectra and other related features. As electrons lose energy due to inelastic scattering after interacting with a sample, EELS is the measurement of the loss of energy by these electrons. A variant of EELS in which the incident electrons have a kinetic energy of a few hundred keV and are reflected from the surface of the sample is known as high-resolution EELS (HREELS). EELS is frequently used to study the physics and chemistry of solids due to its capability of providing spectra with an energy resolution down to a few meV, which is sufficient to resolve vibrational and electronic modes of energy loss. EELS is also capable of giving a quantitative account of the atomic composition of a sample.

3.2.4.2 EELS of h-BN

FIG. 28 An EELS spectrum of h-BN grown using atmospheric chemical vapour deposition (AP-CVD).²⁸

FIG. 28 presents a typical EELS spectrum of h-BN. Both the boron-K edge and the nitrogen-K edge are present. The boron-K edge (188 eV) has two components, the first sharp peak at the edge onset is present due to the excitation of the K-shell electrons to the unoccupied π^* antibonding states, it is followed by a broader peak due to excitations to the σ^* antibonding states²⁹.

3.2.5 Hall Effect Measurements

The Hall effect is an important phenomenon that was discovered by E. H. Hall and was named after him. A build-up of charges at the side of a current-carrying conductor will produce a measurable transverse (to the direction of the current) voltage between the two sides of the conductor, this effect is known as the Hall effect. The Hall effect is a result of the magnetic field that is generated by a current flowing through a conductor, this magnetic field acts on the charge carriers and exerts a Lorentz force on them, this Lorentz force caused these charges to move to one side of the conductor. The direction of the Lorentz force is determined by the right-hand rule.

The measurements of the Hall effect can determine both the sign of the majority carriers within a semiconductor and their respective concentrations in a sample. It can also measure the mobility of the majority charge carriers in the sample. As illustrated in FIG. 29, the presence of a magnetic field generated by the current exerts a Lorentz force on the charges. This force gives an acceleration to the moving positive charges in the negative y-direction. Consequently, one side of the conductor will have more positive charges than the other side, this separation of charges generates an electric field and therefore, creates a voltage across the conductor, pointing in the positive y-direction.

Simple analysis invoking Newton's Second Law helps us to determine the magnitude of this electric field.

$$eE_y = ev_x B_z \quad (3.11)$$

FIG. 29 A simple schematic of the van der Pauw-Hall effect.¹⁶

$$E_y = v_x B_z = \frac{J_x}{ep_{p0}} B_z \quad (3.12)$$

Where p_{p0} is the hole concentration in the semiconductor and J_x is the current density in the positive x-direction. To quantify the extent of the Hall effect, the Hall coefficient R_H is defined as the electric field generated by the Hall effect divided by the current density J_x and the magnetic field B_z .

$$R_H = \frac{E_y}{J_x B_z} = \frac{1}{ep_{p0}} \quad (3.13)$$

The concentration of the positive charges (in semiconductors, would be holes) and the majority carrier mobility can be calculated using the following formulae:

$$p_{p0} = \frac{J_x B_z}{e E_y} \quad (3.14)$$

$$\mu_p = \frac{R_H}{\rho} \quad (3.15)$$

Where ρ is the resistivity of the sample.

Certainly, since there is a voltage across the sample, this voltage is known as the Hall voltage, V_H . As such, one can calculate the Hall coefficient from the following formula:

$$R_H = \frac{V_H t L}{W I_x B_z} \quad (3.16)$$

In a laboratory setting, the Hall measurement setup is often used as a dedicated measurement setup that is capable of measuring the magnitude of the magnetic field.

FIG. 30 (a) An optical image of a h-BN sample deposited onto a GaN substrate with the van der Pauw-Hall contacts placed. (b) A schematic showing how the 4 contacts are connected to the ammeter and voltmeter for the Hall measurements.

FIG. 30(a) depicts an optical image of a 1.5 cm^2 h-BN sample deposited on a GaN substrate placed on a grid paper with each square grid denoting 1 cm^2 . The Van der Pauw-Hall contacts are shown on the 4 corners of the sample and its schematic is presented in FIG. 30(b), the direction of the magnetic field, B_z , present in the measurement of the Hall mobility is denoted in the diagram as well.

3.3 References

- 1 K. Wasa, M. Kitabatake and H. Adachi, *Thin Film Materials Technology: Sputtering of Compound Materials*, Elsevier, Norwich, NY, 2004.
- 2 A. H. Simon, in *Handbook of Thin Film Deposition*, Elsevier, 2018, pp. 195–230.
- 3 S. Rossnagel, in *Handbook of Thin Film Deposition Processes and Techniques*, Elsevier, 2001, pp. 319–348.
- 4 G. Bräuer, B. Szyszka, M. Vergöhl and R. Bandorf, *Vacuum*, 2010, **84**, 1354–1359.
- 5 J. M. Schneider, U. Helmersson, V. Kouznetsov, K. Maca and I. Petrov, 1999, **122**, 290–293.
- 6 A. Anders, *J. Appl. Phys.*, DOI:10.1063/1.4978350.

- 7 A. Anders, *Surf. Coatings Technol.*, 2011, **205**, S1–S9.
- 8 A. Anders, J. Andersson and A. Eghasarian, *J. Appl. Phys.*, 2007, **102**, 113303.
- 9 C. Maszl, W. Breilmann, J. Benedikt and A. von Keudell, *J. Phys. D: Appl. Phys.*, 2014, **47**, 224002.
- 10 R. Bandorf, V. Sittinger and G. Bräuer, *Compr. Mater. Process.*, 2014, **4**, 75–99.
- 11 J. Emmerlich, S. Mráz, R. Snyders, K. Jiang and J. M. Schneider, *Vacuum*, 2008, **82**, 867–870.
- 12 W. D. Sproul, D. J. Christie and D. C. Carter, *Thin Solid Films*, 2005, **491**, 1–17.
- 13 P. Kudláček, J. Vlček, K. Burcalová and J. Lukáš, *Plasma Sources Sci. Technol.*, 2008, **17**, 025010.
- 14 K. L. Choy, *Prog. Mater. Sci.*, 2003, **48**, 57–170.
- 15 A. Baptista, F. Silva, J. Porteiro, J. Míguez and G. Pinto, *Coatings*, 2018, **8**, 402.
- 16 T. C. Doan, in *Texas Tech University*, 2016, vol. 9968, p. 99680S.
- 17 P. Larkin, *Infrared and Raman Spectroscopy: Principles and Spectral Interpretation*, Elsevier Inc., 2011.
- 18 N. Ohba, K. Miwa, N. Nagasako and A. Fukumoto, *Phys. Rev. B*, 2001, **63**, 115207.
- 19 R. Geick, C. H. Perry and G. Rupprecht, *Phys. Rev.*, 1966, **146**, 543–547.
- 20 O. Cometto, B. Sun, S. H. Tsang, X. Huang, Y. K. Koh and E. H. T. Teo, *Nanoscale*, 2015, **7**, 18984–18991.
- 21 G. Agostini and C. Lamberti, *Characterization of Semiconductor Heterostructures and Nanostructures*, Elsevier, 2008.
- 22 S. Liu, R. He, Z. Ye, X. Du, J. Lin, H. Jiang, B. Liu and J. H. Edgar, *Cryst. Growth Des.*, 2017, **17**, 4932–4935.
- 23 P. Goodhew, in *Aberration-Corrected Analytical Transmission Electron Microscopy*, John Wiley & Sons, Ltd, Chichester, UK, 2011, pp. 1–19.
- 24 F. Brent and H. James, *Transmission Electron Microscopy and Diffractometry of Materials*, Springer-Verlag Berlin Heidelberg.
- 25 D. B. Williams and C. B. Carter, *Transmission Electron Microscopy*, Springer US, Boston, MA, 2009.
- 26 R. F. Egerton, *Reports Prog. Phys.*, 2009, **72**, 016502.
- 27 R.F. Egerton, *Electron Energy-Loss Spectroscopy in the Electron Microscope*, Springer US,

Year: 2011, Third., 2011.

- 28 K. Kim, A. Hsu, X. Jia, S. M. S. M. M. Kim, Y. Shi, M. Dresselhaus, T. Palacios and J. Kong, *ACS Nano*, 2012, **6**, 8583–8590.
- 29 T. A. Friedmann, P. B. Mirkarimi, D. L. Medlin, K. F. McCarty, E. J. Klaus, D. R. Boehme, H. A. Johnsen, M. J. Mills, D. K. Ottesen and J. C. Barbour, *J. Appl. Phys.*, 1994, **76**, 3088–3101.

4 h-BN Growth using High Power Impulse Magnetron Sputtering (HIPIMS)

4.1 h-BN Growth using LaB₆ Source

4.1.1 Infrared Spectra of a Typical h-BN Film Deposited using LaB₆ Source

FIG. 31 Raman spectra of h-BN thin film deposited using LaB₆ source on a silicon wafer (in red) and of a pure silicon wafer (in black).

FIG. 31 shows a typical Raman spectrum of a h-BN thin film deposited using a LaB₆ source on a silicon wafer (in red) and for comparison purposes, a Raman spectrum of a pure silicon wafer is also shown (in black). Shown on the Raman spectrum coloured in red, there is no discernible peak, except the one located at around 1440 cm⁻¹ which can be attributed to a peak arising from the pure silicon substrate, as evident in the Raman spectrum of the pure silicon wafer. The E_{2g} phonon mode found in h-BN is absent in this case. This is probably because the **small** amount of Lanthanum, approximately 5%,¹ present in the h-BN deposited using LaB₆ source destroys the E_{2g} symmetry. Nitrogen impurities have been shown to affect the intensity, linewidth and energies of ‘D’, ‘2D’ and ‘G’ phonon modes seen by the Raman spectrum of graphene.²⁻⁴ Consequently, from the Raman spectra shown in FIG. 31, it is clear that, regardless of the underlying causes, Raman spectroscopy is unsuitable as a tool for the identification of h-BN thin film deposited on a silicon wafer using LaB₆ target. It is important to note that the h-BN film that is deposited using pure boron target does have the existence of the E_{2g} phonon mode on its Raman spectra. Table 5 lists

the energies of the phonon modes of lanthanum hexaboride and the broadband spectrum at high wavenumbers cannot be attributed to the phonon modes of lanthanum hexaboride.

On the contrary, Fourier Transform Infrared Spectroscopy (FTIR) offers identification of the h-BN thin film readily. FIG. 32 shows the FTIR spectrum of a 1.6 μm thick h-BN thin film deposited using a LaB_6 source. The spectrum clearly shows the existence of both the A_{2u} and E_{1u} phonon modes and their relative intensities with respect to a baseline. As expounded in Chapter 3, the A_{2u} (B-N-B out-of-plane bending mode) phonon mode whereas the E_{1u} fundamental mode relates to the B-N in-plane stretching vibration.

Table 5 Energies of Phonon Modes in Bulk Lanthanum Hexaboride⁵

Phonon Modes	T_{1u}	T_{2g}	E_g	A_{1g}
Wavenumber / cm^{-1}	206	650	1074	1200

FIG. 32 Fourier Transform Infrared Spectrometry (FTIR) typical spectrum of a 1.6 μm h-BN thin film grown on silicon wafer using a LaB_6 source. The baseline and the intensities of the two phonon modes are denoted by the blue dash line and blue two-headed arrows respectively.

4.1.2 Effects of Base Pressure on the Quality of Films Deposited

In sputtering processes, one of the important parameters is the base pressure of the vacuum chamber before the deposition process takes place. Base pressure refers to the pressure at which

the vacuum is before the introduction of any participating gases into the deposition chamber for the deposition process.⁶

As metallic surfaces oxidise easily, it is important to clean its surfaces thoroughly. It only takes around 1 second for a surface to react with oxygen and be oxidised, even at a base pressure in the order of 10^{-6} Torr. Consequently, even if the base pressure is kept as low as 10^{-6} Torr and the deposition has deposition rates of $\sim 5 - 50 \text{ \AA s}^{-1}$, the resultant film will have an oxygen concentration of around 1% or more embedded in it. This shows that in an attempt to deposit high quality films, the base pressure as a deposition parameter is an important factor.¹¹

Therefore, it is important to investigate the effects of base pressure on the quality of the h-BN thin films deposited using the HIPIMS. Two parameters are chosen in this investigation, the thickness of the deposited films and the R value calculated from the Fourier-Transform Infrared Spectrometry (FTIR) spectra obtained of the deposited films. Thickness of the films is chosen as a parameter as it is often necessary to estimate the thickness of the film pre-deposition. This is because the HIPIMS system does not have an in-situ thickness measurement apparatus. The R value is defined as the ratio of the intensities of the A_{2u} mode to that of the E_{1u} mode on the FTIR spectrum of a given sample, as summarized in Equation (4.1) below. The R value gives an estimation of the alignment of the h-BN film.

$$R = \frac{I_{A_{2u}}}{I_{E_{1u}}} \quad (4.1)$$

The intensities of the A_{2u} and E_{1u} phonon modes, $I_{A_{2u}}$ and $I_{E_{1u}}$ respectively, are denoted by the blue two-headed arrows in FIG. 32, the baseline from which the intensities are measured from the spectrum is denoted by the blue dash line.

4.1.3 Effect of Base Pressure on Thickness of Thin Films

Two 4" intrinsic silicon wafers of orientation $\langle 100 \rangle$ were used as substrates for this experiment. The substrates were first ultrasonicated in acetone for 5 minutes, followed by ultrasonication in isopropanol (IPA) for another 5 minutes and finally rinsed in deionized water. The pure lanthanum hexaboride (LaB_6) target (99.99% mass purity) was pre-sputtered for about 10 minutes to sputter off the residue layer on the target. Table 6 lists the deposition conditions for the two depositions

at different base pressures. Each deposition was conducted for 30 minutes. A thin layer of ink was laced on the Si wafer prior to each deposition. After the deposited of h-BN thin films, the layer of ink is cleaned off using acetone and this process reveals the surface of the Si wafer. Using a surface profiler, the thickness of the films was measured. The resulting surface profile measurement reveals a step-like profile, in which the thickness of the h-BN film deposited can be read off. On each wafer, 17 points were laced with such ink and measurements of thickness at these points were taken. The 17 points include the geometric centre of the wafer and the rest of the points are on two perpendicular lines spaced 1 cm apart.

Table 6 Deposition Conditions for Full Wafer Deposition

Sample Name	Base Pressure / mbar	Working Pressure / mbar	Temperature / °C	Pulse Frequency / Hz	Pulse Width / μ s	Gas Ratio / %	Discharge Voltage / V
Low Base Pressure	2.99×10^{-6}	1×10^{-2}	Room temperature	8000	25	25	500
High Base Pressure	5.82×10^{-6}						

FIG. 33(a) is an optical image taken post-deposition of the Si wafer with h-BN (as shown in the FTIR in FIG. 35 (a)) deposited on it. The colours reflect the variation of thickness across the entire wafer. It is clear, from this optical image, that the entire wafer is deposited with h-BN. The optical image also shows the markings by the laced ink which had been cleaned off using acetone. FIG. 33(b) shows the contour plot that is plotted according to the 17 measurements. From FIG. 33(b), the thickness across the wafer range from around 240 nm to 350 nm. That gives a deposition rate of 8 nm min^{-1} to 11.7 nm min^{-1} or equivalently, $1.33 \text{ \AA s}^{-1}$ to $1.95 \text{ \AA s}^{-1}$, respectively. The h-BN film has the highest thickness around the center of the wafer and follows a Gaussian-like distribution across the wafer. This is expected as the line of sight of sputtered particles from the target is incident to the geometric center of the wafer. FIG. 34(a) is the optical image of the h-BN growth done on the Si wafer at high base pressure. As seen in FIG. 34(b), which is a contour plot of the h-BN thickness grown, the h-BN thin film covers the entire wafer. The thickness of the h-BN film deposited at high base pressure across the wafer is around 38% lower than the film deposited at low base pressure. This shows that base pressure does have a significant effect on the thickness of the film grown and in turn, on the deposition rate of film growth. Although one may need to deposit 40% longer in duration for the deposition at high base pressure which more than

compensates the duration needed for the vacuum state of the system to reach an ultrahigh vacuum state of less than 5×10^{-6} mbar, it will be shown that the alignment of the h-BN films deposited deteriorate at high base pressure, defined to be a h-BN structure where there is orthogonal alignment between the basal plane of the deposited h-BN film and the substrate. In both experiments, there is a slight skew of the distribution towards one direction of the wafer. This is because the magnetrons are each inclined at an angle of 60° measured from the horizontal and each magnetron is closer to one side of the wafer than the other.

FIG. 33 (a) An optical image of the Si wafer post-deposition at low base pressure, the colour arising from the variation of thickness of the h-BN thin films on the wafer. (b) A 2-dimension contour plot showing the variation of thickness of the h-BN thin films on the wafer.

FIG. 34 (a) An optical image of the Si wafer post-deposition at high base pressure, the colour arising from the variation of thickness of the h-BN thin films on the wafer. (b) A 2-dimension contour plot showing the variation of thickness of the h-BN thin films on the wafer.

4.1.4 Effect of Base Pressure on the R Value of h-BN Films Deposited

FIG. 35 (a) The FTIR spectra of the h-BN thin films grown at different distances away from the center of the silicon wafer. The h-BN thin film across the wafer was grown at low base pressure. (b) The R value was calculated based on the intensities of the two phonon modes of h-BN shown in (a). (c) The E_{1u} peak position in the FTIR spectra is red-shifted as the distance, of which the h-

BN film is situated on the wafer, from the center of the wafer increases. (d) The A_{2u} peak position in the FTIR spectra remains the same even as the distance, of which the h-BN film is situated on the wafer, from the center of the wafer increases.

To understand the effects of base pressure on the quality of the h-BN films deposited, FTIR was employed as a means, through the calculation of the R value, to quantify the quality. The FTIR spectra of the h-BN film deposited on the silicon wafer at low base pressure are plotted in FIG. 35(a). From the plots, it is evident that both phonon modes are present, the A_{2u} and E_{1u} , this is an indication that h-BN is present in the films. In FIG. 35(b), the R value of the h-BN films against the distances from the center of the wafer on which the h-BN is grown is plotted. The R value is an indication of the alignment of the h-BN film.¹ Away from the center of the wafer, the h-BN grown has a lower degree of alignment. This is to be expected as the thickness of the h-BN film is lower nearer to the edge of the wafer, resulting in a lesser degree of alignment, this is in agreement with the experimental result depicted in FIG. 38(b). The intensity of the A_{2u} phonon mode is stronger (the intensity of the E_{1u} phonon mode is the reference) as the film becomes thicker and thus, the extent of alignment in the direction normal to the substrate plane becomes greater. In FIG. 35(c), it is clear that the E_{1u} phonon mode is red-shifted from positions near the center of the silicon wafer to positions close to the edge of the wafer. This implies that there is a reduction in the phonon energy of the A_{2u} phonon which, in turn, implies a weakening of the extent of the B-N-B bond bending vibration. Similarly, such a shift is due to the thickness of the h-BN film which decreases from the center of the wafer to the edge of the wafer. As seen in FIG. 38(a) as the film thickness increases, the E_{1u} phonon mode gets blue-shifted to around 1380 cm^{-1} which is the frequency of the phonon mode in bulk h-BN. Lastly in FIG. 35(d), the A_{2u} phonon mode remains at 773 cm^{-1} .

At high base pressure, the FTIR spectra of the h-BN film deposited on the silicon wafer are plotted in FIG. 36(a), it can be seen that both the E_{1u} and A_{2u} phonon modes are present. Likewise, as in the case of h-BN films deposited at high base pressure, the R value decreases for h-BN films that are deposited at positions nearer to the edge of the silicon wafer for the depositions conducted at high base pressure. This is shown in FIG. 36(b). The E_{1u} phonon mode red-shifted for h-BN films that are positioned further away from the center of the wafer. Similar to the previous case of h-BN films deposited at low base pressure, in this case, the red-shifting is due to the reduction in

thickness for the h-BN films deposited. Also, the A_{2u} phonon mode frequency is approximately constant.

FIG. 36 (a) The FTIR spectra of the h-BN thin films grown at different distances away from the center of the silicon wafer. The h-BN thin film across the wafer was grown at high base pressure. (b) The R value was calculated based on the intensities of the two phonon modes of h-BN shown in (a). (c) The E_{1u} peak position in the FTIR spectra is red-shifted as the distance, of which the h-BN film is situated on the wafer, from the center of the wafer increases and remains constant beyond 1 cm from the center. (d) The A_{2u} peak position in the FTIR spectra remains approximately the same (within a margin of 2 cm^{-1}) even as the distance, of which the h-BN film is situated on the wafer, from the center of the wafer increases.

In this section, the effects of base pressure on the h-BN films manifest itself as a thickness distribution of h-BN films deposited across the silicon wafer. The h-BN film deposited at both high and low pressures has similar quality as both the E_{1u} and A_{2u} phonon modes are present indicating the presence of h-BN film deposited. Consequently, as thickness influences the extent of alignment within the h-BN thin film, the R value is affected proportionally. This implies that

without taking into consideration the thickness of a h-BN sample, the R value may be a poor indicator of the alignment within the h-BN thin film, alignment may exist within a thinner sample and the absolute magnitude of the R value which is likely to be small may not reflect the existence of the alignment well.

4.1.5 Deposition Rate of h-BN Deposition using LaB₆ as a Source

In Section 4.1.3, the thickness of h-BN films deposited at two different base pressures was investigated. It is shown that base pressure does have a significant effect on the thickness of h-BN films deposited, at high base pressure, the thickness of the h-BN films deposited is reduced by around 38%. It is important as well, to investigate the deposition rate of using the LaB₆ source, as it is an important indication of the flux of ions or neutral species impinged on the substrate surface.

The samples were deposited under the same deposition conditions except they were deposited for different durations. FTIR of the samples was measured to ascertain the presence of h-BN within the films and the spectra are plotted in FIG. 37(a). The spectra show that the E_{1u} and A_{2u} phonon modes are both present, indicating the presence of h-BN. The thickness of each h-BN film deposited at different durations is plotted in FIG. 37(b). The data points are fitted to a linear fit, thickness (nm) = $14.42 \text{ (nm min}^{-1}) \times \text{duration (min)}$, indicating a deposition rate of around $14.42 \text{ nm min}^{-1}$ which is equivalent to 2.403 Å s^{-1} . This rate of reactive sputtering is a reasonable and comparable rate to the non-reactive sputtering of Titanium and Copper.^{12,13}

As shown in FIG. 37(b), the thickness of the h-BN films has a linear dependence on the duration of the deposition. The linear fit was done with the y-intercept to be set at zero as without any deposition, there ought to be no h-BN grown on the substrate. The deposition rate of the h-BN thin film growth across 5 samples deposited at different durations was found to be $14.41 \text{ nm min}^{-1}$.

Table 7 Deposition Conditions of h-BN Thin Films Grown for Different Durations

Sample Name	Base Pressure / mbar	Duration / min	Working Pressure / mbar	Temperature / °C	Pulse Frequency / Hz	Pulse Width / μs	Gas Ratio / %	Discharge Voltage / V
A	3.98×10^{-6}	17	1×10^{-2}	Room temperature	8000	25	25	396

B	2.66×10^{-6}	21	341
C	6.03×10^{-6}	30	343
D	9.55×10^{-6}	60	367
E	5.77×10^{-6}	120	383

FIG. 37 (a) FTIR spectra of the samples grown for different durations, both the E_{1u} and A_{2u} phonon modes are present. (b) Thickness of the h-BN films grown for different durations of depositions. The linear dependence of thickness on deposition duration is drawn as the dashed line. The intercept of the linear dependence is set to be zero. The R coefficient for this linear fit is 0.98998.

FIG. 38 (a) The frequencies of both the A_{2u} and E_{1u} phonon modes of h-BN films deposited for different durations. (b) The R value of the h-BN films deposited for different durations.

The frequencies of the E_{1u} and A_{2u} phonon modes are plotted in FIG. 38(a). From the plot on FIG. 38(a), h-BN films with a low thickness (proportional to the deposition duration) will have its E_{1u}

and A_{2u} phonon modes red-shifted. As the duration for deposition increases, the thickness of the film deposited increases as well, both phonon modes' frequencies increase to that of the bulk h-BN frequency, which is around 1380 cm^{-1} .^{14,15} The asymptotic trend in FIG. 38(a) shows that for h-BN thin film with large thicknesses (approaching bulk properties), the wavenumber of the E_{1u} and A_{2u} phonon modes are 1378 cm^{-1} and 778 cm^{-1} , respectively, comparable to the values of bulk h-BN. This behaviour is to be expected and therefore, a physical model with its asymptotic behaviour trending towards a constant is used. FIG. 38(b) shows the R value against the duration of each deposition. Similarly, there is a positive linear relationship between the extent of alignment indicated by the R value and the duration of the deposition. As the thickness of the films increase, the increase in the intensity of the A_{2u} phonon mode is higher than the increase in the intensity of the E_{1u} phonon mode. This implies that the thicker and aligned h-BN films have greater extent of the A_{2u} phonon, resulting in a stronger indication of the alignment through the R value. The asymptotic behaviour is shown in the light red line on FIG. 38(b), the fitting shows that the asymptotic R value is around 0.634.

The asymptotic relation is used in the fitting of FIG. 38(a) – (b) is of the form:

$$y = a - bc^x \quad (4.2)$$

Where a is the asymptotic value of y as x becomes very large, b and c are fitting parameters describing how rapidly y approaches its asymptotic value.

The table below gives the parameters for each of the trends seen in FIG. 38.

Table 8 Fitting Parameters and its Values for Trends Illustrated in FIG. 38.

Trend	a	b	c
A_{2u}	779.49359	23.5914	0.97508
E_{1u}	1378.16365	112.31685	0.91848
R Value	0.63371	0.70033	0.97309

For both the peak positions of each of the A_{2u} and E_{1u} phonon modes to attain 99.9% of its asymptotic value, it requires the duration of deposition to be 51.75 min and 135.15 min, respectively. Taking 51.75 min as a reference as it corresponds to the 0.1% margin of E_{1u} phonon mode asymptotic value of its peak position and a deposition rate of $14.416 \text{ nm min}^{-1}$, the required

thickness of deposited h-BN thin film such that the effect of thickness on the positions of the infrared phonon modes is negligible, is ~ 750 nm.

From this study, several insights are gleaned.

- 1) The thickness of the film influences the frequency of the phonon modes. Thinner films have red-shifted phonon modes from the bulk h-BN value. The asymptotic wavenumbers of the phonon modes will approach the corresponding values of bulk h-BN at large thicknesses.
- 2) R value may not be of a direct indicator for the alignment of the films but still suffice as a fast (as obtaining FTIR spectra is a fast process) tool to ascertain if further study of a particular film is promising. The asymptotic R value is around 0.63. For the peak positioning of both A_{2u} and E_{1u} phonon modes to be devoid of effects arising from thickness variation, its thickness should be around 750 nm or more, such that other effects arising from stress or crystalline size on the peak positioning can be studied more carefully.

4.1.6 Effects of Variation of Peak Current on the FTIR Spectra of Samples

To investigate how the peak current of the LaB_6 target influences the quality of the h-BN thin films deposited, an experiment was conducted. 3 samples were deposited at different peak currents. The films are deposited at the same duty cycle (Duty Cycle: 10%, Pulse frequency: 4 kHz and pulse width: 25 μ s), the variation in peak current was due to a variation in the process current. Table 9 gives the deposition parameters and the measured properties tabulated according to the peak current of the depositions. Optical spectrometry was used on these samples to characterize them. FIG. 39(a) shows the FTIR spectra obtained for these samples, visually, we can see that the intensity of the A_{2u} peak decreases as the peak current decreases, this translates to a decrease in the R value. FIG. 39(b) gives the Raman spectra, again the La presence in the h-BN thin films may destroy the symmetry of the hexagonal structure of h-BN, resulting in a low manifestation of the E_{2g} phonon. FIG. 40(a) plots the deposition rate and power density as a function of the peak currents, it can be seen that increasing peak current has an enhancing effect on both deposition rate and power density, this is probably because the peak current is adjusted by the process current. FIG. 40(b) gives the R value as a function of the peak currents, and as explained in FIG. 39(a), the peak current affects the R value. A higher peak current may result in higher ion energy,¹⁶ which in

return resulted in greater compressive stress within the h-BN films during deposition, resulting in the film being more vertically orientated using the R value as an indicator.

Table 9 Deposition Parameters and Measured Properties of the h-BN Thin Films Deposited at Different Peak Currents

Sample Name	Peak Current (A)	Power Density (W/cm ²)	Statistical		Deposition Rate / nm min ⁻¹	R Value
			Mean Power to the Target / W	Process Current (mA)		
A	2	10.663	48	150	0.75	0.308
B	5	20.614	94	305	3.77	0.361
C	11	42.982	196	600	6.42	0.457

FIG. 39 (a) FTIR spectra of the h-BN thin films at different peak currents (I_{PEAK}) and (b) the corresponding Raman spectra.

FIG. 40 (a) The deposition rate and power density both as a function of I_{PEAK} . (b) The R value is measured for each film as a function of I_{PEAK} .

4.1.7 Deposition of h-BN on Gallium Nitride Substrates using LaB₆ as a Source

To investigate the effect of substrate on the microstructure of the h-BN deposited using the LaB₆ target as the source, gallium nitride (GaN) was used as the substrate for depositions of h-BN. The GaN that is used in this study is GaN that was deposited on a Si base. This study is important as in the subsequent chapters, particularly Chapters 5 and 6, depositions on GaN-AlGaN high electron mobility transistors are done.

FIG. 41 ascertains that the substrate is indeed GaN on a Si base. The peak at 518.545 cm⁻¹ is assigned to the well-known triple degenerate phonon mode of Si.^{17,18} Similarly, the broadband around 920 cm⁻¹ to 980 cm⁻¹ is due to the Si-OH.¹⁹ The 565.0 cm⁻¹ and 733.5 cm⁻¹ are due to GaN – E₂^{high} and GaN – A₁(LO) phonon modes, respectively.^{20,21} The Raman spectrum as illustrated in FIG. 41 confirms the presence of GaN on a Si base.

FIG. 41 Raman spectrum of GaN on Si base. Each of the phonon modes in the spectrum is assigned.

The h-BN deposited on the GaN substrate at the following deposition conditions tabulated in Table 10.

Table 10 Deposition Conditions of Deposited h-BN on GaN substrate

Sample Name	Base Pressure / mbar	Duration / min	Working Pressure / mbar	Temperature / °C	Pulse Frequency / Hz	Pulse Width / μ s	Gas Ratio / %	Discharge Voltage / V
h-BN on GaN	4.4×10^{-6}	30	8.4×10^{-2}	Room Temperature	8000	25	25	368

FIG. 42 FTIR spectrum of h-BN deposited using LaB₆ target on GaN substrate.

FIG. 42 gives the FTIR spectrum of the as-deposited h-BN thin film on GaN substrate. As seen from the spectrum, both the characteristic phonon modes of h-BN, namely, A_{2u} and E_{1u} phonon modes are present. The R value calculated from the ratio of the intensities of these two phonon modes based on the FTIR spectrum is 0.5385. To study the microstructure of the h-BN film deposited on GaN substrate, HRTEM was employed.

FIG. 43(a) High resolution Transmission Electron Microscopy (HRTEM) image of the thin film on GaN, the GaN substrate, the transition layer which comprises of amorphous BN and the h-BN layer. (b) The microstructure of the h-BN film as viewed by HRTEM, 3 nanoclusters are highlighted. (c) A Fast-Fourier Transform (FFT) of (b) showing the distance in the diffraction arcs is 5.8 nm⁻¹ which translates to an interplanar distance of 0.345 nm (shown schematically in (b)) between the h-BN planes within each nanocluster.

The HRTEM images are shown in FIG. 43 in which (a) is an image on the entire thickness of the film, with which the GaN substrate, h-BN film and a transition layer in between the substrate and the h-BN film are seen. FIG. 43 (b) shows the h-BN layer at high magnification. It can be observed that there are clusters of hexagonal h-BN. In FIG. 43 (c) is the Fast-Fourier Transform (FFT) of FIG. 43 (b), the diameter of the diffraction arcs which correspond to the (0002) planes of h-BN is around 5.8 nm^{-1} , this implies that the calculated interplanar spacing between two (0002) as illustrated in FIG. 43 (b) is 0.345 nm, which is close to that in bulk h-BN. From the diffraction pattern inferred from the FFT, it can be deduced that the h-BN film deposited is generally aligned perpendicular to the substrate surface. In this section, it is demonstrated that h-BN sputtered using HIPIMS onto the GaN substrate under the stipulated conditions results in a polycrystalline, nano-clustered thin film.

4.2 h-BN Growth using Pure Boron Target

4.2.1 RF-Assisted Plasma Ignition for the Deposition of h-BN using a Pure Boron Source

Generation of boron species through physical means has been a longstanding challenge pertaining to deposition of boron compounds.

As boron target is a dielectric target, deposition of h-BN using HIPIMS would be difficult to achieve unless the deposition is done with the substrate temperature at $800 \text{ }^{\circ}\text{C}$, which is a high enough temperature for which the pure boron target would be sufficiently conductive for the ignition of the plasma to occur.^{22,23} As the substrate is around 6 cm away from the target, radiation from the graphite heater heats up the target as well, consequently, the pure boron target becomes sufficiently conductive for the ignition of plasma. To deposit h-BN using a pure boron source at lower temperatures (defined to be $< 200 \text{ }^{\circ}\text{C}$), ignition of the plasma with a pure boron target powered by a HIPIMS power source would be impossible as the target would not be sufficiently conductive for plasma ignition. A method for plasma ignition at any temperature above room temperature is outlined here:

- 1) Ignite the plasma using a RF power source. Depending on the set-up of the deposition chamber, the power required to ignite the plasma on the boron target can range from 50 W to 150 W.
- 2) Once the plasma is ignited, keep the ignition of the plasma ongoing for 10 minutes. The ignition of the plasma activated through the RF power supply changes the conductivity of the boron target from a dielectric material to a conductive material.
- 3) After 10 minutes, terminate the plasma. Despite the termination of the RF power supply, the boron target still retains its conductivity, suitable for ignition of plasma through the re-activation of the power supply.
- 4) Switch the cable connection of the magnetron from the RF power supply to the HIPIMS power supply.
- 5) Ignite the plasma on the boron target by supplying power at a high duty cycle ($> 25\%$) from the HIPIMS power supply.
- 6) Adjust the deposition parameters to the desired values.

An important advantage of this method is it allows for the precise control of the deposition parameters, a feature unique to HIPIMS, on the deposition of the dielectric target. Control of duty cycle and other deposition parameters allow for tuning of deposition conditions for control of properties of the films deposited for a variety of purposes.

At 13.56MHz, the power supply to the dielectric boron target would have made the target sufficiently conductive. Upon termination of the RF power supply, the transient response of the target would be to return to its insulating nature. If the switching of the connecting cables to one connecting the HIPIMS power supply can be completed before a complete return of the target to its insulating nature, then re-ignition of the plasma on the dielectric target powered by a HIPIMS power supply would be achieved.

4.2.2 Oxidation of h-BN Thin Films Deposited using a Pure Boron Source

Table 11 Deposition Conditions of Deposited h-BN using Pure Boron Source

Sample Name	Base Pressure / mbar	Duration / min	Working Pressure / mbar	Temperature / °C	Pulse Frequency / Hz	Pulse Width / μ s	Gas Ratio (Q _{Nitrogen} /Q _{Argon}) / %	Discharge Voltage / V
-------------	----------------------	----------------	-------------------------	------------------	----------------------	-----------------------	--	-----------------------

h-BN	3.2×10^{-6}	30	1.2×10^{-2}	Room Temperature	8000	25	25	781
-------------	----------------------	----	----------------------	---------------------	------	----	----	-----

Table 11 lists the deposition conditions for the deposition of h-BN using a pure boron source at room temperature. The deposition at room temperature was conducted for two reasons: 1) the deposition of h-BN using LaB₆ target was possible at room temperature, it is indeed worthwhile to experiment if similar deposition at room temperature can occur using a pure boron target and 2) for the eventual industrial application, deposition of h-BN at room temperature would result in immense cost saving.

The parameters such as pulse frequency, pulse width and gas flow rate ratio (the ratio of the gas flow rate of nitrogen gas to that of argon gas) are chosen as such because these were the values that resulted in the successful deposition of h-BN using a LaB₆ target.

It is observed that the h-BN films deposited using a pure boron target experience oxidation after some hours of being left exposed to the atmosphere. Tiny crystalline deposits were observed forming on the surface of the samples, these deposits can be easily washed off using deionized water. This can be interpreted as a result of the imperfect stoichiometry of the h-BN film, it may either be due to a deficiency of nitrogen species or overloading of boron species during the deposition. This is supported by the observation that the stoichiometric ratios of B and N in the films deposited have deviated from the ideal ratio of 1, this is explored in subsequent chapters, especially in Chapters 5 and 6. The boron conglomerates deposited on the thin film is oxidised occurring to the following reaction:^{24,25}

When exposed to the moisture present under atmospheric conditions, the following reactions take place, converting boron oxide into boric acid:^{24,25}

To ascertain that exposure to atmospheric conditions is the leading cause of these crystallites, an experiment was conducted. The experiment procedure is illustrated in FIG. 44 and explained below:

1. Two samples are placed on the substrate holder prior to the deposition, they are placed at the center of the substrate holder, with virtually no distance apart.
2. The two samples are deposited with h-BN using a pure boron source.
3. 24 hours after the end of the deposition, one of the samples denoted as Sample B was taken out. Sample A was unavoidably exposed to the atmospheric conditions when the substrate holder was taken out of the chamber for the removal of Sample B.
4. The entire process of taking out Sample B took around 10 minutes. The substrate holder with Sample A on it was placed back into the deposition chamber.
5. The chamber was pumped down to ultrahigh vacuum condition, pressure being less than 10^{-6} Torr and remained in that state for 48 hours.
6. Sample A was then taken out and both samples were characterized with Fourier-Transform Infrared Spectrometry (FTIR).

FIG. 44 Schematic of the experimental procedure to determine the cause of these crystallite deposits / flakes forming on the thin film sample.

FIG. 45 (a) Left: h-BN sample deposited using pure boron target which was taken out first and kept in atmospheric conditions for 48 hours. Right: h-BN sample deposited using pure boron target which was in vacuum for 72 hours. (b) A microscopic (magnification of 5 times) optical image of the h-BN deposited using pure boron target and was taken out first and kept in atmospheric conditions for 48 hours. (c) A microscopic (magnification of 5 times) optical image of the h-BN deposited using pure boron target and was in a vacuum for 72 hours. (d) FTIR spectra for the two h-BN samples.

Optical images of the two h-BN samples deposited using pure boron target are shown in FIG. 45(a). Depicted on the left is Sample B, which was taken out first and kept exposed in atmospheric conditions for 48 hours. On the right is Sample A, which remained in the ultrahigh vacuum deposition chamber for 72 hours. From the optical images, the surface of Sample B was laden with crystallites formation whereas Sample A surface was smooth. A microscope was employed to view these samples at 5 times magnification, clear crystallites were observed on the surface of Sample B (FIG. 45(b)) whilst these are not present in Sample A (FIG. 45(c)).

FIG. 45(d) shows the FTIR spectra of the two samples. The spectrum of Sample B is in red whereas that of Sample A is in black. For the FTIR spectrum of Sample B, the presence of the B-O-H bending mode at around 1200 cm⁻¹ and the O-H stretching mode at around 3200 cm⁻¹ were observed (Table 12 tabulates the different normal vibration modes and its associated infrared wavenumber). This strongly indicates the existence of B(OH)₃ within both samples. It should also be noted that both the characteristic phonon modes of h-BN suffered a reduction in intensities on their FTIR spectra. Again, this is substantiated by J. Hahn et al.²⁶ work on DC and RF sputtering

of pure boron target. It was found in that work that 1 month after deposition, the intensities of the h-BN E_{1u} and A_{2u} phonon modes of the films' FTIR spectra were reduced (FIG. 10 of Reference 26) and the peaks corresponding to O-H stretching mode and N-H bond became pronounced. The result was attributed to a reaction between non-cubic boron nitride material within the samples with the atmosphere. FIG. 45(d) shows that the results presented in FIG. 45(d) are similar to that obtained by J. Hahn et al.²⁶ and Quan et al.²⁷ and the results indicated the formation of $B(OH)_3$ within both samples, Sample A and Sample B.

In conclusion, it is observed that depositions of h-BN thin films using a pure boron target at room temperature resulted in h-BN thin films which oxidized upon exposure in atmospheric condition, forming crystallites of $B(OH)_3$ as evident by the micro-optical images and substantiated by the characterization using FTIR spectrometry.

Therefore, it is important to resolve this issue so that a stable (despite being exposed to atmospheric conditions) h-BN thin film using a pure boron source can be synthesized. The easiest method to prevent oxidation (or at least reduce the extent of oxidation experienced by the thin film) is to conduct the deposition at 800 °C. This is because the enhanced energetics of the boron and nitrogen species within the plasma, which is also continuously supplied into the chamber and sputtered onto the substrate, would favor the formation of B-N than the formation of boron oxide derivatives. Again, this is due to the difference in the enthalpy of formation of H-B-O bond (-210 kJ mol^{-1}) and B-N bond ($560.7 \text{ kJ mol}^{-1}$), an increase in temperature would favor the endothermic formation of the B-N bond. Furthermore, at elevated temperatures, a source of oxygen that comes from the moisture trapped within the chamber walls is baked and expelled through the vacuum system, depleting the source will help with reducing the extent of the formation of boron oxide.

Table 12 Wavenumber Assignments for $B(OH)_3$ Based on C_{3h} Symmetry²⁸

Symmetry Assignment	Description of the normal vibration mode	Assignment	Infrared Wavenumber / cm^{-1}
A' Raman	Symmetric O-H Stretching	ν_1	
	Symmetric B-O-H Bending	ν_2	
	Symmetric B-O Stretching	ν_3	882
E' Infrared Raman	O-H Stretching	ν_4	3200
	B-O Stretching	ν_5	1450
	B-O-H Bending	ν_6	1190

	O-B-O Bending	ν_7	547
A''	O-H Twisting	ν_8	824
Infrared	BO ₃ Bending	ν_9	648
E''	O-H Twisting	ν_{10}	
Raman			

4.2.3 Effects of Substrate Temperature on the Quality of the Deposited h-BN Films

Temperature of the substrate has been known to greatly influence the microstructure and the physical properties of the as-deposited films, especially for the sputtering technique. Higher substrate temperatures during deposition are known to increase adatom mobility, which is a result of increased ion bombardment. Conversely, deposition at lower substrate temperatures is known for mixed phase growth (a-BN, t-BN and c-BN growth).²⁹ As elaborated in the previous section, it was shown that depositing h-BN thin films at low substrate temperatures resulted in the formation of boron oxide within the films due to its interactions with atmospheric moisture. To investigate if substrate temperature plays an important role in this phenomenon, a set of experiments to deposit h-BN at higher substrate temperatures was contrived and conducted.

In this set of experiments, the temperature of the depositions is varied while keeping all other deposition conditions constant. The films are deposited at similar statistical mean power supplied to the boron target. The deposition conditions are tabulated in Table 13. FIG. 46 displays the FTIR spectra of these as-deposited h-BN films. Firstly, it is noted that the characteristic E_{1u} (active in the infrared region) phonon mode assigned to h-BN is present in all spectra, this is an indication of the presence of h-BN.

However, the A_{2u} infrared active phonon mode is absent in all the spectra. The absence could be due to the fact that the films deposited were deposited at a high pulse width, a high duty cycle. High duty cycle translates to lower ion energy which in turn, implies that the extent of ion bombardment on the substrate would be lesser. Consequently, the compressive stress experienced by the film would be reduced and the extent of the films' alignment would also be compromised. As the A_{2u} phonon mode corresponding to the out-of-plane B-N-B bending mode, it is also an indication of the degree of alignment of the film as the infrared rays are incident perpendicularly

to the substrate surface during the FTIR measurements. An absence of the A_{2u} mode can indicate that the majority of h-BN deposited within the films are not aligned with respect to the substrate surface, as a result of high duty cycle deposition.

From the FTIR spectra, for films sputtered at low substrate temperatures, from room temperature to 400 °C, there are indications of the presence of boron oxide. The existence of various peaks which correspond to the boron oxide peaks is clear evidence of its existence. The BO_3 ($\sim 660\text{ cm}^{-1}$), O-B-O bending ($\sim 550\text{ cm}^{-1}$) and B-O-H bending ($\sim 1190\text{ cm}^{-1}$) modes are present in the spectra (see also, Table 12). For depositions conducted at high substrate temperatures, $> 600\text{ °C}$, some indications of the presence of modes related to boron oxide are evident, however, their intensities, as inspected visually, are often reduced to negligible in comparison with the other spectra of h-BN thin films deposited at lower substrate temperatures. The results indicate that depositions conducted at lower substrate temperatures resulted in a by-product, boron oxide.

It is crucial for the deposition of h-BN thin film to yield predominantly h-BN as its content with minimum by-product. For the case of cubic boron nitride (c-BN), a similar endeavor to deposit c-BN with a high yield has not been shown to be successful.^{26,29–32} Consequently, as established from the results, it is desirable to sputtering at temperatures above 600 °C to obtain a higher yield of h-BN.

Table 13 Deposition conditions of h-BN thin films deposited at different temperatures.

Substrate Temperature / °C	Pulse Width / μs	Pulse Frequency / Hz	Working Pressure / mbar	Peak Current / A	Discharge Voltage / V	Mean Power / W	Gas Ratio ($Q_{\text{Nitrogen}}/Q_{\text{Argon}}$) / %
Room Temperature	100	2000	8.3×10^{-3}	2	782	313	25
200			9.9×10^{-3}	1	849	339	
400			9.9×10^{-3}	1	849	339	
600			1.0×10^{-2}	1	817	337	
800			1.0×10^{-2}	1	817	327	
1000			1.0×10^{-2}	1	855	344

FIG. 46 FTIR spectra of the as-deposited h-BN thin films deposited at different temperatures.

4.2.4 Effects of Pulse Width on the FTIR and Raman Spectra of Deposited h-BN Films

It has been known that in the non-reactive sputtering of Titanium, the deposition rate of the as-deposited films increases as the pulse width increase while keeping the mean power constant.¹³ Similar result is obtained in the deposition of Copper.¹²

As deposition rate is less of a concern for the various applications that the deposited h-BN thin films are utilized for, there is a need to investigate instead, the effects of pulse widths on the R value from the FTIR spectra of the deposited h-BN thin while keeping the pulse frequency unchanged. This is to ascertain a range of pulse widths that would be satisfactorily to conduct the subsequent depositions of h-BN thin films using boron targets.

To this aim, 3 values of pulse widths are chosen, 5, 10 and 25 μs . The deposition conditions for the h-BN thin films deposited are tabulated in Table 14. In the previous section, it was established that higher substrate temperatures do result in better quality h-BN thin films as evident from the FTIR spectra of these films, consequently, the substrate temperature during depositions is set at 800 °C. The depositions were conducted for 1 hour each and the depositions were done at similar

average power supplied to the target (~ 350 W) and the average power supplied is kept relatively constant by controlling the process current.

Table 14 Deposition conditions of the h-BN thin films deposited at different pulse widths.

Sample Name	Pulse Width / μs	Average Power / W	Working Pressure / mbar	Temperature / $^{\circ}\text{C}$	Pulse Frequency / Hz	Gas Ratio ($Q_{\text{Nitrogen}}/Q_{\text{Argon}}$) / %	Discharge Voltage / V
h-BN-5	5	362	1.2×10^{-2}				692
h-BN-10	10	362	1.15×10^{-2}				895
h-BN-25	25	344	1.23×10^{-2}	800	8000	25	892
h-BN-40	40	353	9.67×10^{-3}				710
h-BN-55	55	350	8.79×10^{-3}				672

FIG. 47(a) illustrated the FTIR spectra of the as-deposited h-BN thin films at different pulse widths. The A_{2u} and E_{1u} characteristic phonon modes are present. At 25 μs , a small peak indicating the presence of B-O bonding is observed. FIG. 47(b) compiles the Raman spectra of the as-deposited h-BN thin films at different pulse widths. The E_{2g} Raman active phonon mode is present. FIG. 47(c) shows the power density and deposition rate of the h-BN films, at constant average power supplied to the target. Near the similar values of average power supplied to the target, the decrease pulse width resulted in a high deposition rate and this rate correlates with the power density of the deposition process. This result is supported by the general trend seen in the literature where a reduction in pulse width (pulse duration in the literature) is shown to increase the deposition rate.^{12,33} FIG. 47(d) depicts the R value and peak current of the h-BN films deposited. The R value obtains its highest value at 10 μs , corresponds to a duty cycle of 8%. Surprisingly, the R value does not correlate strongly with the peak current, higher peak current does not necessarily imply a larger R value. While higher peak current does correlate with higher ion energy,¹⁶ and higher ion energy distribution during deposition does in general, correlates with greater extent of compressive stress experienced by the thin film due to ion bombardment and thereby inducing alignment. However, the compressive stress model suggests a peak in compressive stress experienced by a thin film and gradually tapered off at higher ion energies.^{34,35} Therefore, the highest peak current

of 18 A during the deposition corresponds to a pulse width of 5 μs does not translate to a greater degree of alignment.

FIG. 47 (a) FTIR spectra of the as-deposited h-BN thin films at different pulse widths. (b) Raman spectra of the as-deposited h-BN thin films at different pulse widths. (c) Measured values of deposition rate and power density of the h-BN thin films. (d) Measured values of R value and peak current of the h-BN thin films.

4.3 Conclusion

For h-BN thin films deposited using a LaB_6 source, the usage of Raman spectrometry to ascertain the presence of h-BN thin film deposited is not viable, possibly due to the disruption to the E_{2g} symmetry, a result of the presence of lanthanum impurity.

The thickness distribution of h-BN thin film deposited is slightly skewed towards the side where it is closer to the magnetron and is Gaussian. At positions further away from the peak of the thickness distribution, the E_{2u} phonon mode gets red-shifted, this red-shifting effect should be due to a thickness effect. Also, the average thickness of the film deposited with an initial low base

pressure is higher than that of the film deposited with an initial high base pressure. It is found that the R value derived from a FTIR spectrum is positively correlated to its thickness, however, beyond a certain critical thickness, the R value would be independent of its film thickness.

A set of experiments was conducted, and the results indicated that higher substrate temperatures during depositions resulted in h-BN thin films that undergo oxidation upon interactions with atmospheric oxygen to a lesser degree. The results indicated 10 μ s – 15 μ s to be a range of pulse widths which will result in a higher degree of alignment of the h-BN thin films as indicated by the R value measured.

Therefore, in subsequent chapters presented in this thesis, the substrate temperature during deposition and the pulse widths of such depositions are often set at 800 °C and 10 μ s, respectively. The thesis will now move to other synthesis methods and controls of deposition parameters that are used in the realization of electronic devices. These are elaborated in both Chapter 5 and Chapter 6.

4.4 References

1. Cometto, O. *et al.* Vertically self-ordered orientation of nanocrystalline hexagonal boron nitride thin films for enhanced thermal characteristics. *Nanoscale* **7**, 18984–18991 (2015).
2. Casiraghi, C. Probing disorder and charged impurities in graphene by Raman spectroscopy. *Phys. Status Solidi - Rapid Res. Lett.* **3**, 175–177 (2009).
3. Kim, S. J. *et al.* Characterization of chemical doping of graphene by in-situ Raman spectroscopy. *Appl. Phys. Lett.* **108**, 203111 (2016).
4. Bruna, M. *et al.* Doping dependence of the Raman spectrum of defected graphene. *ACS Nano* **8**, 7432–7441 (2014).
5. Mattox, T. M., Chockkalingam, S., Roh, I. & Urban, J. J. Evolution of Vibrational Properties in Lanthanum Hexaboride Nanocrystals. *J. Phys. Chem. C* **120**, 5188–5195 (2016).
6. Franz, R., Clavero, C., Bolat, R., Mendelsberg, R. & Anders, A. Observation of multiple charge states and high ion energies in high-power impulse magnetron sputtering (HiPIMS) and burst HiPIMS using a LaB 6 target. *Plasma Sources Sci. Technol.* **23**, 035001 (2014).

7. Frankel, G. S., Chen, X. B., Gupta, R. K., Kandasamy, S. & Birbilis, N. Effect of vacuum system base pressure on corrosion resistance of sputtered Al thin films. *J. Electrochem. Soc.* **161**, C195–C200 (2014).
8. Jeyachandran, Y. L. *et al.* Properties of titanium thin films deposited by dc magnetron sputtering. *Mater. Sci. Eng. A* **431**, 277–284 (2006).
9. Moram, M. A., Barber, Z. H. & Humphreys, C. J. The effect of oxygen incorporation in sputtered scandium nitride films. *Thin Solid Films* **516**, 8569–8572 (2008).
10. Lee, B. H., Kim, I. G., Cho, S. W. & Lee, S. H. Effect of process parameters on the characteristics of indium tin oxide thin film for flat panel display application. *Thin Solid Films* **302**, 25–30 (1997).
11. Simon, A. H. Sputter Processing. in *Handbook of Thin Film Deposition* 195–230 (Elsevier, 2018). doi:10.1016/B978-0-12-812311-9.00007-4
12. Tiron, V., Velicu, I. L., Mihăilă, I. & Popa, G. Deposition rate enhancement in HiPIMS through the control of magnetic field and pulse configuration. *Surf. Coatings Technol.* **337**, 484–491 (2018).
13. Konstantinidis, S., Dauchot, J. P., Ganciu, M., Ricard, A. & Hecq, M. Influence of pulse duration on the plasma characteristics in high-power pulsed magnetron discharges. *J. Appl. Phys.* **99**, 013307 (2006).
14. Geick, R., Perry, C. H. & Rupprecht, G. Normal modes in hexagonal boron nitride. *Phys. Rev.* **146**, 543–547 (1966).
15. Nemanich, R. J., Solin, S. A. & Martin, R. M. Light scattering study of boron nitride microcrystals. *Phys. Rev. B* **23**, 6348–6356 (1981).
16. Hecimovic, A., Burcalova, K. & Ehiasarian, A. P. Origins of ion energy distribution function (IEDF) in high power impulse magnetron sputtering (HIPIMS) plasma discharge. *J. Phys. D: Appl. Phys.* **41**, (2008).
17. Xu, Z. *et al.* Topic Review: Application of Raman Spectroscopy Characterization in Micro/Nano-Machining. *Micromachines* **9**, 361 (2018).
18. Richter, H., Wang, Z. P. & Ley, L. The one phonon Raman spectrum in microcrystalline silicon. *Solid State Commun.* **39**, 625–629 (1981).
19. Xu, J. *et al.* Mechanisms for low-temperature direct bonding of Si/Si and quartz/quartz via VUV/O₃ activation. *RSC Adv.* **8**, 11528–11535 (2018).

20. Bungaro, C., Rapcewicz, K. & Bernholc, J. Ab initio phonon dispersions of wurtzite AlN, GaN, and InN. *Phys. Rev. B* **61**, 6720–6725 (2000).
21. Zhao, D. G., Xu, S. J., Xie, M. H., Tong, S. Y. & Yang, H. Stress and its effect on optical properties of GaN epilayers grown on Si(111), 6H-SiC(0001), and c -plane sapphire. *Appl. Phys. Lett.* **83**, 677–679 (2003).
22. Shaw, W. C., Hudson, D. E. & Danielson, G. C. Electrical Properties of Boron Single Crystals. *Phys. Rev.* **107**, 419–427 (1957).
23. Morita, N. & Yamamoto, A. Optical and Electrical Properties of Boron. *Jpn. J. Appl. Phys.* **14**, 825–832 (1975).
24. Hou, X., Yu, Z., Chen, Z., Chou, K.-C. & Zhao, B. The Reaction Mechanism and Kinetics of α -BN Powder in Wet Air at 1273 K. *J. Am. Ceram. Soc.* **96**, 1877–1882 (2013).
25. Oda, K. & Yoshio, T. Oxidation kinetics of hexagonal boron nitride powder. *J. Mater. Sci.* **28**, 6562–6566 (1993).
26. Hahn, J. *et al.* Cubic boron nitride films by d.c. and r.f. magnetron sputtering: Layer characterization and process diagnostics. *Diam. Relat. Mater.* **5**, 1103–1112 (1996).
27. Quan, H. *et al.* Stability to moisture of hexagonal boron nitride films deposited on silicon by RF magnetron sputtering. *Thin Solid Films* **642**, 90–95 (2017).
28. PARSONS, J. L. & MILBERG, M. E. Vibrational Spectra of Vitreous B₂O₃.xH₂O. *J. Am. Ceram. Soc.* **43**, 326–330 (1960).
29. Kester, D. J., Ailey, K. S., Lichtenwalner, D. J. & Davis, R. F. Growth and characterization of cubic boron nitride thin films. *J. Vac. Sci. Technol. A Vacuum, Surfaces, Film.* **12**, 3074–3081 (1994).
30. Otaño-Rivera, W., Pilione, L. J., Zapien, J. A. & Messier, R. Cubic boron nitride thin film deposition by unbalanced magnetron sputtering and dc pulsed substrate biasing. *J. Vac. Sci. Technol. A Vacuum, Surfaces, Film.* **16**, 1331–1335 (1998).
31. Zhou, W., Ikuhara, Y. & Suzuki, T. Orientational relationship between cubic boron nitride and hexagonal boron nitride in a thin film synthesized by ion plating. *Appl. Phys. Lett.* **67**, 3551–3553 (1995).
32. Shtansky, D. V, Tsuda, O., Ikuhara, Y. & Yoshida, T. CRYSTALLOGRAPHY AND STRUCTURAL EVOLUTION OF CUBIC BORON NITRIDE FILMS DURING BIAS SPUTTER. **48**, 3745–3759 (2000).

33. Anders, A. Deposition rates of high power impulse magnetron sputtering: Physics and economics. *J. Vac. Sci. Technol. A Vacuum, Surfaces, Film.* **28**, 783–790 (2010).
34. Davis, C. A. A simple model for the formation of compressive stress in thin films by ion bombardment. *Thin Solid Films* **226**, 30–34 (1993).
35. Janssen, G. C. A. M. Stress and strain in polycrystalline thin films. *Thin Solid Films* **515**, 6654–6664 (2007).

5 Control of the Orientation and Isotopic Composition of h-BN Thin Film

As the anisotropy of h-BN thin films is a crucial property to be made used of in various applications, control of the orientation of h-BN thin films growth on substrates is of paramount importance. In this chapter, various methods of manipulating the orientation of h-BN thin films and its enhancement to the thermal performances of h-BN are presented in the subsequent sections. Also, isotope engineering of h-BN thin films is explored and its properties are measured and presented.

5.1 h-BN Thin Film Orientation Control using Gas Flow Ratio

It was shown that the control of gas flow ratio (to be defined later) in a HIPIMS reactive sputtering of mixed nitrogen and argon environment can, in turn, control the degree of alignment of the h-BN thin film deposited. Gas flow ratio is defined as the ratio of the gas flow rate of nitrogen gas (measured in units of sccm) to the sum of the gas flow rates of both nitrogen and argon gases (again, measured in units of sccm). This definition is captured in the following equation:

$$\text{Gas Flow Ratio} = \frac{\text{Gas Flow Rate of Nitrogen}}{\text{Gas Flow Rate of Argon} + \text{Gas Flow Rate of Nitrogen}}$$

In a reactive sputtering deposition chamber with any number of gases, the gas flow ratio of any one of the gases is between 0 to 1, equivalently, 0% to 100%. In this work, the gas flow ratio was varied from 5% to 100%.

5.1.1 Preparation of the h-BN Thin Films

Double-sided polished (DSP), 350 μm thick Silicon wafers with an orientation of $\langle 100 \rangle$ were diced and used as the substrate. 6 samples were labelled A-F and deposited. The exact deposition conditions are documented in Table 15. The duration for each deposition is 180 minutes. Prior to the deposition, to ensure high quality of the resultant deposited film, the pressure of the deposition chamber must be evacuated to and was maintained at $\sim 4 \times 10^{-6}$ Torr. Furthermore, to prevent oxidation of the resultant deposited films, the temperature of the substrate holder was set and raised to 800 $^{\circ}\text{C}$ with the mean (average) power supplied to the target ranging from 200W to 280W.

Table 15 Deposition Conditions of the Samples

Sample Name	Gas Flow Ratio of N ₂ /Ar (%)	Base Pressure (Torr)	Working Pressure (Torr)	Power Density (W/cm ²)	Thickness (nm)
A	5	3.96 x 10 ⁻⁶	3.19 x 10 ⁻³	26.13	502.05
B	10	1.99 x 10 ⁻⁶	2.58 x 10 ⁻³	24.30	488.76
C	15	2.76 x 10 ⁻⁶	1.94 x 10 ⁻³	21.56	486.61
D	20	2.72 x 10 ⁻⁶	2.14 x 10 ⁻³	25.22	546.77
E	40	2.83 x 10 ⁻⁶	2.35 x 10 ⁻³	24.77	437.81
F	60	2.54 x 10 ⁻⁶	2.84 x 10 ⁻³	25.78	552.91
G	85	2.70 x 10 ⁻⁶	3.52 x 10 ⁻³	24.12	647.53
H	100	2.07 x 10 ⁻⁶	3.79 x 10 ⁻³	26.22	446.93

5.1.2 Optical and Bonding Characterizations

FIG. 48 (a) Raman and (b) FTIR spectra for the samples.¹

To ascertain the bonding characteristics of the samples, FTIR and Raman spectrometry were employed. As shown in FIG. 48(a), other than Sample A, the other samples contain the E_{2g} phonon mode which is Raman-active. The E_{2g} phonon mode intensity becomes more heightened due to the increase of the gas flow ratio of the samples, indicating a high proportion of the E_{2g} phonon mode, which again signifies a greater proportion of h-BN within the sample. A peak at around 1370 cm⁻¹, which is due to the E_{2g} mode is slightly increased from the characteristic wavenumber

of 1367 cm^{-1} . This blue-shifting possibly indicates the high compressive stress. Furthermore, atomic layer depositions,² chemical vapour deposition³ and by chemical methods⁴ have presented similar peaks observed in h-BN deposited. FIG. 48(b) depicts the FTIR spectra for all the samples, A to F. Both the phonon modes (infrared active A_{2u} and E_{1u}) are present in all the samples. The presence of h-BN in the samples deposited is evidenced by the existent of both the characteristics modes. The peak derived from the A_{2u} mode is around 790 cm^{-1} to 810 cm^{-1} as it gets blue-shifted with increasing gas flow ratios.

To ascertain the presence of h-BN in the samples deposited, XPS is also employed to determine the bonding characteristic of the B-N bond within the samples. As seen in FIG. 49(a), the XPS spectra of all the samples exhibit the B 1s, N 1s and O 1s peaks. In FIG. 49(b), the high resolution XPS of B 1s is shown, the peak position of the B 1s for all the samples is around 189.1 eV. Similarly, as seen in FIG. 49(c), the high resolution XPS of N 1s has its peak position around 396.2 eV. The peak positions of B 1s and N 1s are consistent with previous reported values. The B 1s and N 1s spectra for the samples are also symmetrical about their respective peaks, devoid of any mode mixing arising from other bonds, signifying that the B 1s spectrum is due to the B-N bond in h-BN. Understandably, the numerical difference between XPS peak positions of N 1s and B 1s remains constant, at approximately 207 eV, independent of the gas flow ratio, thereby signifying the existence of h-BN as supported by observations in the literature.⁵

FIG. 49 (a) XPS spectra of the h-BN thin films. High-resolution (b) B 1s, (c) N 1s spectra of the samples obtained from XPS. (d) A plot of the peak binding energies for all the spectra, specifically, B 1s and N 1s peaks.¹

Table 16 Summary of the positions of the peaks of both B 1s and N 1s for the Samples

Sample Name	Gas Flow Ratio of N ₂ /Ar (%)	Peak Identification	Binding Energy (from raw data) / eV	Difference in Binding Energy between B1s and N1s / eV	Binding Energy (fitted Gaussian curves) / eV	Difference in Binding Energy between B1s and N1s (fitted Gaussian curves) / eV
A	5	B 1s	190.5	206.5	190.3	206.8
		N 1s	397		397.1	
B	10	B 1s	189.5	207.3	189.6	207.2
		N 1s	396.8		396.8	
C	15	B 1s	189.6	207.4	189.8	207.1
		N 1s	397		396.9	
D	20	B 1s	189.8	207.2	189.8	207.2
		N 1s	397		397	
E	40	B 1s	189.9	207.3	189.9	207.2

		N 1s	397.16		397.1	
F	60	B 1s	189.7	207.6	189.7	207.5
		N 1s	397.26		397.2	
G	85	B 1s	189.8	207.2	189.8	207.2
		N 1s	397		397	
H	100	B 1s	189.8	207.2	189.8	207.1
		N 1s	397		396.9	

Using the above characterizations, both FTIR and Raman spectrometry, together with XPS, have ascertained that the samples contain predominantly h-BN.

5.1.3 Surface Morphology and Microstructure of the As-Deposited h-BN Films

The surface morphology and microstructure of the as-deposited h-BN thin films were examined. FIG. 50(a) are the Scanning Electron Microscopy (SEM) images on the surface of the h-BN films deposited. The sub-figures correspond to (a) 5%, (b) 20% and (c) 85% gas flow ratios. As the gas flow ratio increases, the domain size of each h-BN crystallites reduces. The cross-sectional image of the h-BN thin film corresponds to the 20% gas flow ratio as viewed by HRTEM is presented in FIG. 51(a). FIG. 51(b) is a magnified HRTEM image of the region that is near to the crossover from the h-BN deposited film to the silicon substrate. There is amorphous boron nitride (a-BN) at the transition region between the substrate and the film, it has a thickness of around 14 nm. It is proposed that this may have provided a microstructural scaffolding on which aligned h-BN is grown on.⁶ FIG. 51(c) shows an EELS spectrum of the sample. It is observed that the 3 absorption edges are present in the spectrum, namely, the boron-K edge, the carbon-K edge and the nitrogen-K edge. The absence of c-BN TO phonon mode in the FTIR spectra, together with the strong π^* peak found in the EELS spectrum, confirms the absence of c-BN.

FIG. 50 Samples corresponding (a) 5%, (b) 20% and (c) 85% gas flow ratios of the deposited h-BN samples as viewed by SEM. Scale bar: 0.5 μm .¹

FIG. 51 (a) Cross-section image of the sample corresponding to 20% gas flow ratio as viewed by TEM, scale bar: 500 nm. (b) Image of the region between the h-BN vertically orientated layer and the silicon substrate as viewed by HRTEM. Scale bar: 10 nm. (c) EELS spectrum of the sample deposited using a pure boron target as the boron source.¹

The EDS analysis confirms the existence of boron and nitrogen. FIG. 52(a) – (c) gives Si, B and N elemental distributions, respectively within the sample. It is observed that boron is less uniformly distributed when compared to the distribution of nitrogen, which is more uniformly distributed due to the use of a pure boron target.

FIG. 52 Elemental map scan of (a) silicon, (b) boron and (c) nitrogen for the sample using EDS corresponding to 20% gas flow ratio.¹

The domain size of the h-BN thin films can be inspected visually and are seen to be decreasing with increase gas flow rate ratio, using the SEM. With TEM, FTIR, Raman, EELS, XPS and EDS, the samples were ascertained to contain h-BN, an a-BN layer was also observed to serve as a plausible microstructural scaffolding for h-BN growth. EELS and EDS are direct evidence for the existence of both boron and nitrogen within the h-BN films, supported by the XPS results. The next sub-section will expound on the orientation of the h-BN thin films deposited.

5.1.4 Orientation Control of the As-Deposited h-BN Films and its Associated Thermal Conductivity

FIG. 53 (a) The peak positions of the A_{2u} and E_{1u} modes of h-BN as a function of the samples' gas ratio. (b) The R value of the deposited film as a function of the samples' gas ratio. A compressive-stress model is used for the fitting. (c) Random and (d) vertically orientated h-BN films as viewed by HRTEM, the films are deposited at 5% and 20% gas ratio, respectively. The insets in (c) and (d) are the respective SAED patterns, ascertaining both the randomly-orientated and vertically-orientated arrangement of BN.¹

As expounded in Chapter 3, the calculation of the R value from the FTIR spectra of the deposited h-BN films is a method to get an approximate of the concentrate of vertically orientated h-BN within the sample. The R value is defined to be the ratio of the intensities of the A_{2u} phonon mode to the intensity assigned to the E_{1u} phonon mode, as illustrated in the equation below:

$$R = \frac{I_{A_{2u}}}{I_{E_{1u}}} \quad (2)$$

where $I_{A_{2u}}$ is the intensity on the FTIR spectrum of the peak of the A_{2u} phonon mode whereas $I_{E_{1u}}$ is the intensity on the FTIR spectrum of the peak of the E_{1u} phonon mode.

The high compressive stress built within the thin film can be explained as the origin of the vertical alignment of the film. Consequently, a model used to account for the compressive stress is used to understand the stress variation within any thin film:⁷⁻⁹

$$\sigma \propto \frac{\sqrt{E}}{\frac{R}{J} + kE^{\frac{5}{3}}} \quad (3)$$

where $k = 0.016\rho E_0^{-5/3}$, J is the ion flux, E is the ion energy and ρ , E_0 and R are material related parameters. The equation has been used as the fitting curve for FIG. 53(b) and FIG. 55(a) to verify the dependence between the degree of how vertically orientated the deposited film will be and the compressive stress built within the film during deposition. It is found that the highest values for R value, thermal conductivity and the compressive stress built within the film fall within the same region of the gas flow rate ratio, at around 25-30% (FIG. 55(a)). These results supported the claim that the alignment is derived from the compressive stress built within the film, consequently, causes the high degree of alignment in the microstructure of the thin film and improves its thermal conductivity.

The fitting parameters in Equation 3 are given in the table below:

Table 17 Parameters Used in the Fitting Curve for FIG. 53(b)

Fitting Parameters	Value
Constant of Proportionality	14.675
R/J	135.212
k	0.17

FIG. 53(a) shows how to peak of both the E_{1u} and A_{2u} phonon mode changes with the gas flow ratio which induces changes in the domain size of h-BN thin film. Shown in FIG. 53(b) is a plot of the R value for each of these samples and as explained earlier, the compressive stress model is fitted to the R value data points. This shows that generally, the degree of alignment of the h-BN films is proportional to the stress, compressive in nature, within the films. Furthermore, HRTEM was deployed to give a visual interpretation of the microstructure of the samples, which

corresponds to 5% and 20% gas flow ratios. This is due to the fact that both samples represent the maximum and minimum R values, respectively. The highly magnified HRTEM images of the two samples are shown in FIG. 53(c) (5% gas flow ratio) and FIG. 53(d) (20% gas flow ratio). Using the Fast-Fourier Transform (FFT) images of the respective HRTEM images, the interplanar distances for the h-BN thin films are calculated to be 0.349 and 0.344 nm, for 5% gas flow ratio and 20% gas flow ratio, respectively. The calculated interplanar distances are similar to the theoretical 0.333 nm in bulk h-BN.¹⁰ The diffraction arcs in the FFT images are found to be originated from the (002), (111) and (010) planes of h-BN.

Thermo-reflectance method, using the NanoTR equipment, was employed to study the thermal properties of the h-BN films and how these properties were influenced by the alignment of the films. Prior to the measurement, a 100 nm layer of aluminium was deposited onto the h-BN thin films as a transducer.

FIG. 54 (a) A schematic highlighting Thermo-reflectance method for the measurement of the thermal conductivities of the samples. (b) The plot of both the raw and fitting signals of the sample corresponding to the 20% gas flow ratio.¹

FIG. 54(a) is a schematic showcasing the thermo-reflectance method. Its measurements comprise of two signals, one is the raw signal and the other is the corresponding fitted signal. Its raw signal from the NanoTR measuring device and the fitting is shown in FIG. 54(b). Furthermore, the measured thermal conductivities of the h-BN thin films are plotted FIG. 55(a), the fitting of the data plot is the compressive stress model as explained previously. The highest thermal conductivity measured is for the sample deposited at 20% gas flow ratio and its value is at 1.5 W m⁻¹ K⁻¹, this

value is 3 times more than the lowest measured thermal conductivity for all of the samples. The conclusion to draw from this is that a small increment in the gas flow ratio, which is also easy and highly controllable, can induce a 300% increase in a sample's thermal conductivity. Another conclusion is that there exists a range of gas flow ratios in which the thermal conductivity of the deposited samples peaks. The last conclusion is that the vertical alignment of the film is a strong predictor of the thermal conductivity of the film. The last conclusion is to be expected given the anisotropy of h-BN thermal properties. FIG. 55(b) shows the dependence on temperatures of the thermal conductivities of two samples, these two samples are deposited at 5% and 20% nitrogen gas flow ratios. It is noted that the thermal conductivities of the films stabilized between 100 °C to 300 °C. The drop in thermal conductivities for both samples from room temperature to 100 °C is around 40 – 42%. Both insights give strong confidence that the thin films would retain its function as a heat-spreader even at elevated temperatures.

The fitting parameters to the curve in FIG. 54(b) is given below:

Table 18 Parameters in the Fitting Curve for FIG. 54(b)

Fitting Parameters	Value
Constant of Proportionality	4.568
R/J	14.88
k	0.01339

FIG. 55 (a) Thermal conductivities of the films, the points are derived using a model describing the compressive stress built within the film. (b) Thermal conductivity of the films synthesised at 5% and 20% nitrogen gas flow ratios as a function of temperature, with its dependence clearly shown.¹

FIG. 56 (a) A schematic illustrating the variation of nitrogen gas flow and how it impacts the microstructures of the resultant film. (b) An image showing how the h-BN film was deposited onto the substrate in the absence of a transition layer between the deposited film and the substrate, as viewed by HRTEM. Two locations are chosen here for discussion and their images are magnified in the panels, the one at the top right shows how the h-BN clusters are randomly orientated while the other shows the interface between h-BN and Si. (c) The transition layer as amorphous boron nitride (a-BN) at the crossover between the Si substrate and the vertically orientated h-BN layer is showed, using the HRTEM. The panel on the top right, again, shows the high degree of alignment of the h-BN film.¹

The growth mechanism of the aligned h-BN thin film is presented in FIG. 56(a). The breaking of chemical bonds within nitrogen molecules as it dissociates into nitrogen species (i.e. ions or atoms) has a lower probability of happening as pure boron target, a dielectric material, has a small secondary electron yield. The deposition at low nitrogen gas flow ratios is depleted with nitrogen species to react with the boron species forming h-BN. This is evidence of the poor stoichiometry

of the resultant film, due to deficit in bond formation. FIG. 56(b) gives direct evidence to this proposed mechanism, the transition layer between the silicon substrate and the h-BN layer is missing. The existence of such a template may be necessary for it to be a microstructure template for which the growth of aligned h-BN may proceed, its absence may then explain the poor extent of vertical alignment of the resultant h-BN thin film. Experimentally, the existence of a polycrystalline film possibly due to the absence of such a transition layer is evident in the importance of such a layer. The compressive stress is induced by the ion bombardment of nitrogen and boron ions, this enabled the formation of the aligned h-BN and justifies the existence of a transition layer may also provide a blueprint for such growth. The polycrystalline film was shown on the top right panel of FIG. 56(b). The optimal gas flow ratio for the deposition of h-BN with the maximal degree of alignment and highest thermal conductivity occurs around 20 – 45%. An increment from low gas flow ratio to values within this interval generally leads to a better alignment and a higher thermal conductivity. The increment in thermal conductivity due to depositing h-BN thin films in this interval can be as high as 300%. FIG. 56(c) displays the h-BN layer growth on a silicon substrate with a transition layer consisting of a-BN, between the film and the silicon substrate. The alignment of the h-BN film is shown on the top right panel of FIG. 56(c). Sputtering of pure boron targets using purely nitrogen gas resulted in poorer alignment and lower thermal conductivity of the resultant films because the bombardment of ions may be blocked by the neutral nitrogen gas due to their increased presence within the plasma mixture. This reduces the free mean path of the sputtered species, enabled lesser of them to arrive at the substrate for reaction and deposition.

5.2 Orientation Control through the Average Power Supplied to the Target

In the previous section, one method of manipulating the alignment of the h-BN films deposited was introduced. It was shown that the control of gas flow ratio does indeed control the degree of vertical alignment of the h-BN thin films. In this section, a second method of controlling how vertically aligned the h-BN film can be is introduced. The microstructure of the films was shown to be impacted by the mean power supplied to the target through the power supplies.

Table 19 Deposition Conditions for Sample A and Sample B.

Deposition Parameters / Units	Sample A	Sample B
Duration / mins	180	240
Gas Ratio / %	20	25
Temperature / °C	800	800
Peak Current / A	7	6
Process Current / mA	650	400
Pulse Width / μ s	10	10
Pulse Frequency / Hz	8000	8000
Average Power / W	600	362
Power Density / W cm^{-2}	161.7	99.23

Table 20 Stress, thickness and R value for Sample A and Sample B.

Parameters	Sample A	Sample B
Compressive Stress / GPa	0.50925	1.0215
Thickness / nm	1272.32	649.8
R-Value	0.458	0.411
Thermal Conductivity / $\text{W m}^{-1} \text{K}^{-1}$	0.4052	1.2319
Deposition Rate / nm min^{-1}	7.0684	4.256

5.2.1 Optical and X-Ray Diffraction Characterizations of the h-BN Films

FIG. 57 (a) XRD 2θ -scans of both Sample A and Sample B. (b) Raman spectra of the as-grown samples using a boron target via the HIPIMS technique. (c) FTIR spectra of the two samples showing two characteristic phonon modes of h-BN: A_{2u} mode (around 811 cm^{-1}) and the E_{1u} mode (around 1379 cm^{-1}).

XRD was employed to quickly identify the identity and the microstructure of the film. Furthermore, FTIR and Raman spectrometry were also conducted on the samples to study the bonding characteristics of the samples. FIG. 57(a) depicts the XRD 2θ scans of both Sample A and Sample B. It shows the existence of a sharp peak at 43.9° which is assigned to the h-BN (101) planes.¹⁰ FIG. 57(b) is the Raman spectra of both Sample A and Sample B. The presence of a single peak at 1372 cm^{-1} in both samples can be assigned to the h-BN E_{2g} phonon mode. The compressive stress within the thin films which was measured to be in the order of 1 GPa as shown in Table 20 resulted in a slight blue-shifting of the E_{2g} phonon mode (of h-BN) shown. Furthermore, the full-width half-maximum (FWHM) of the E_{2g} peak for the two samples, Sample A and Sample B, was measured to be 41 cm^{-1} and 43 cm^{-1} , respectively. The E_{2g} peak location and its associated FWHM extracted were similar to what was obtained from other techniques, such as, chemical vapour deposition,^{3,11} atomic layer deposition² and from a chemical method.⁴ These measured values are larger than that measured in bulk h-BN (6 cm^{-1}) due to the high compressive stress and low crystallization of the film. In these two samples, it is likely that the higher FWHM of the Raman peak is due to the polycrystalline nature of Sample A and the alignment of Sample B, as well as, the stress measured of both samples in the range of hundreds of MPa, tabulated in Table 20. FIG. 57(c) shows the FTIR spectra of the deposited thin films, the two characteristic modes of h-BN are present, namely the A_{2u} mode (811 cm^{-1}) which is assigned to the B-N-B out-of-plane bending of h-BN and the E_{1u} mode (1379 cm^{-1}) which is assigned to the B-N in-plane stretching of the h-BN. Both the N-H bond and O-H bond are not shown in the figures but are present in the spectra, the presence of the two bonds implies the presence of both oxygen and hydrogen interacting with the samples, likely to be due to moisture present under atmospheric conditions.

The significance of the R value in providing an indication to the degree of alignment of h-BN was explained in the previous section. For Sample A, the film attained a R value of 0.458 which is similar to the values for vertically orientated h-BN deposited using LaB_6 as a source. Conversely, the R value for Sample B was measured to be 0.411. A peak, at around 1052 cm^{-1} , as shown in FIG. 57(c), for Sample B, is assigned to be the TO peak in cubic-BN (c-BN). It is likely that c-BN was formed with the aligned h-BN as a growth template, due to their similar lattice spacing between h-BN (002) planes and c-BN (111).¹² Furthermore, the FTIR spectrum of Sample A exhibits the LO mode of the E_{1u} peak, which is commonly understood as the “two-phonon peak”

or the “derivative-like peak”, this peak signifies the presence of vertically orientated h-BN.^{13,14} Such a LO mode of the E_{1u} phonon mode can be attributed to the highly dense microstructure of the h-BN film, thereby, increase in the intensity of the absorption of the LO mode of the E_{1u} phonon. Moreover, by inspection, the two peaks corresponding to both the A_{2u} and E_{1u} phonon modes of Sample B are narrower than that of Sample A, an inference can be made that the crystallinity of Sample B is better than that of Sample A.⁴

FIG. 58 (d) Full XPS survey of both samples, inset is a table detailing the atomic percentages of both boron and nitrogen in the two samples. (e) XPS B 1s and (f) N 1s for both samples.

The presence of the hexagonal B-N bonding is ascertained by the XPS analysis. The XPS survey of both samples is present in FIG. 58(a), the peaks observed were assigned to B 1s, C 1s, N 1s and O 1s for both samples. The atomic concentrations of the elements B and N, as well as, their associated stoichiometric ratio in the h-BN films are presented as an inset in FIG. 58(a). The stoichiometric ratios for both films are near 1:1, signifying good stoichiometry between the B and N elements within the films. However, as XPS is a surface analysis technique, its quantitative analysis of the stoichiometric ratio of the films can at most serve as a guide but not as an absolute reference for the entire film’s depth. The positions for B 1s and N 1s peak positions for both samples are around 398.1 eV (FIG. 58(b)) and 190.5 eV (FIG. 58(c)), which are consistent with the previously reported values for h-BN.¹⁵ The numerical difference between the wavenumbers of the peaks corresponding to both B 1s and N 1s remains constant for each of the two samples at around 207 eV, indicating the presence of h-BN.

FIG. 59 A high-resolution XPS survey of both samples, showing the (a) B 1s peak and (b) N 1s peak with two of its consecutive plasmon peaks, the π and bulk plasmon peaks, for each of these peaks.

5.2.2 Microstructure and Elemental Composition Characterizations of the h-BN Films

FIG. 60 (a) A STEM image depicting the region of interest in which the EELS scan is done on Sample A. (b) An EELS mapping of the region of interest depicted in (a), showing both the presence of boron and nitrogen in Sample A. (c) A High-Loss EELS spectrum of Sample A. The π^* and σ^* edges indicate the presence of sp^2 -bonded h-BN. (d) An EDS spectrum of Sample B, indicating the presence of both boron and nitrogen.

To ascertain the existence of sp^2 bonding, EELS was employed. Furthermore, it is also used to investigate how the elements, boron and nitrogen are varied within the films. FIG. 60(a) gives a STEM image illustrating the region of the sample on which the EELS was employed. FIG. 60(b) then gives the elemental mappings of the elements, namely, boron and nitrogen using EELS. The distributions of these elements are shown to be uniform, according to the intensities shown in each pixel. The intensity of the respective colours indicates the strength of the signal detected by EELS. The EELS spectrum is presented in FIG. 60(c). The EELS collection semi-angle is 50 mrad and the incident probe's convergence semi-angle is 30 mrad. Firstly, the edges for Boron-K, Carbon-

K and Nitrogen-K are all present. The K-shell electrons gained energy and moved into the unoccupied antibonding π^* states is implied in the observed sharp π^* at the boron-K edge, this gives evidence to the sp^2 bonding character of the film.¹⁶ On the contrary, the K-shell electrons also gained energy and moved into the antibonding σ^* was presented as the broader σ^* peak.¹² Importantly, the B:N stoichiometric ratio that is obtained from the EELS spectrum scan is 1.43, this value is larger than the ideal ratio of 1 and is larger than the value obtained for h-BN deposited using LaB₆, which is reported to be 1.15. Since pure boron target was used as the source for the HIPIMS deposition, it can be expected that a greater density of boron species (neutral atoms, charged ions) will be present in the plasma than nitrogen species as nitrogen species preferentially forms nitrogen molecules.¹⁷ On the other hand, higher ionization of N₂ molecules resulting in high densities of nitrogen species in the plasma for the case of deposition using LaB₆ target can be explained by the higher secondary electron yield for LaB₆. Carbon is present due to the contamination from the focused ion beam preparation for the HRTEM imaging. Evidently, the Raman spectrum of Sample A does not show the characteristic ‘D’ and ‘G’ peaks which are found in carbon and B-N-C samples.^{18,19} FIG. 60(d) is the EDS spectrum of Sample B. The spectrum shows the presence of the boron, nitrogen, oxygen and carbon peaks.

The microstructure of the thin films is both Sample A and Sample B show significant differences. HRTEM was used to reveal these differences.

FIG. 61 (a) HRTEM image of Sample B depicting its porous nanostructure with vertically orientated h-BN struts. (b) The cross-section HRTEM image of Sample B in higher magnification, the vertically orientated strut is clearly depicted, the h-BN interplanar distance is shown to be 0.343

nm. The dark contrast elements encapsulating the strut-like h-BN microstructure are platinum from the FIB process during sample preparation. (c) The corresponding FFT pattern of the h-BN thin film in Sample B. The two diffraction arcs are ascertained to be due to the (002) planes of h-BN are clearly shown.

FIG. 61(a) shows the voids that are observed from the electron image of Sample B using HRTEM. These voids are alongside with the h-BN-“struts” which are vertically aligned. The “shadowing effect” on the substrate is likely to be due to the bombardment of the platinum atoms through the porous film on the substrate during the focused ion beam (FIB) process during TEM sample preparation. FIG. 61 (b) then gives a high magnification HRTEM image of the vertically aligned strut-like h-BN being encapsulated by elements with a darker contrast. These elements are the platinum from the FIB process. The interlayer spacing is calculated to be around 0.343 nm as illustrated in FIG. 61 (b), this corresponds to the monolayer of h-BN. The FFT image of FIG. 61 (b) is shown in FIG. 62(c) and the diffraction arcs shown are assigned to be h-BN (002), thereby confirming the presence of vertically aligned h-BN in our as-deposited films.

FIG. 62(a) demonstrates the cross-sectional view of the film of Sample A using HRTEM whereas FIG. 62(b) gives the high magnification HRTEM image of Sample A, it highlights the prominent polycrystalline nature of the thin film. For emphasis, the nanoclusters of h-BN layers (i.e. B_3N_3 layers which are parallel to each other), aligned randomly amongst other clusters are demarcated in white dotted lines shown in the image. It is found that within each nanocluster, the interlayer distance between the B_3N_3 layers is around 0.347 nm.¹⁴ This value is close to the values for turbostratic h-BN (t-BN). The Fast-Fourier Transform (FFT) of the high magnification image in FIG. 62(b) is shown in FIG. 62(c). The polycrystalline nature of the h-BN thin films is evident from the diffraction rings which are assigned to the (002) and (010) reflections. The crystallites of the film each contain h-BN, B_3N_3 rings.²⁰ From the images, it is clear that the Sample A does not have any long-range order, that is to say that the B_3N_3 forms a cluster by stacking itself and the cluster is oriented randomly relative to the substrate normal.

Table 21 tabulates the measured d-spacing with the theoretical d-spacings for the (002), (100) and (110) reflections of h-BN for both samples. The measured d-spacings for (100) and (11) planes are similar to its theoretical values (with only less than 2.5% variation), whereas the measured d-spacing for the (002) reflections are larger than that of typical h-BN samples. This larger values can be explained by the weakening of bonds in polycrystalline h-BN in contrast to the well-ordered and crystalline h-BN. Aita et al.¹² estimated that the d-spacings of turbostratic h-BN is around 0.35 nm to 0.383 nm and this collaborates with the d-spacing findings in this work. Coupled with the previous analyses, we can draw the conclusion that all the samples exhibit similar hexagonal structures, regardless of the power densities supplied to the target.

FIG. 62 (a) HRTEM image of Sample A depicting its dense and polycrystalline nanostructure. It shows clusters of hexagonal BN aligned randomly amongst other clusters. (b) HRTEM of Sample A in high magnification. The clusters of h-BN layers aligned randomly is denoted by white dotted lines. (c) FFT of (b), highlighting the polycrystallinity of the h-BN films through the diffraction rings, indicating the diffraction rings of the (002) planes of h-BN and the corresponding rings arcs.

Table 21 Calculated d-spacings and theoretical d-spacings with its corresponding assigned planes for Sample A and Sample B.

Sample A (600W)				
Diameter (nm ⁻¹)	Interplanar Spacing, d (nm)			Corresponding Plane, (hkl)
	Calculated	Theoretical	Intensity, I/I ₀	
5.72	0.3497	0.336 [‡]	100	(002)

9.434	0.2120	0.21737 [‡]	39	(010)
-------	--------	----------------------	----	-------

Sample B (362W)				
Diameter (nm ⁻¹)	Interplanar Spacing, d (nm)			Corresponding Plane, (hkl)
	Calculated	Theoretical	Intensity, I/I ₀	
5.58	0.3585	0.336 [‡]	100	(002)

[‡]Hexagonal BN, ICDD Reference Code: 98-002-7986

An explanation to the differences observed in the microstructure of the two films is provided. The difference in microstructure can be explained by the difference in the time-averaged power delivered to the target. A higher density of sputtered boron species (atoms and ions) from the boron target was generated in Sample A due to the higher average power that was delivered to the pure boron target. FIG. 61 provided good evidence in the form of HRTEM images, in the differences between the densities shown in the two thin films. Furthermore, the deposition rate of Sample A is nearly double of that of Sample B, even though both films are deposited under similar deposition conditions, except for the difference in the mean power supplied to the target. Consequently, it is deduced that the difference in average power delivered to the boron target resulted in the difference in densities of the sputtered boron species from the target, and therefore, resulted in difference in stress experienced by the thin film, around 0.5 GPa for Sample A and 1.0 GPa for Sample B.

5.2.3 Optical Bandgaps and the Thermal Conductivities of the h-BN Films Deposited at Different Average Power Supplied to the Target

FIG. 63 (a) Absorbance spectrum in the UV-vis range and (b) graphical conversion to Tauc's plot for optical bandgap calculation for both Sample A and Sample B deposited on quartz substrates.

FIG. 63(a) and FIG. 63(b) illustrate the absorbance spectra for both Sample A and Sample B of the h-BN films which were deposited on quartz substrates. The spectra in FIG. 63(a) show a sharp absorption peak at around 210.2 nm and 201.8 nm for Sample A and Sample B, respectively. The conversion of the absorption spectra to Tauc's plot is done using the derived absorption coefficient for an indirect bandgap material, according to the following equation:²¹

$$\alpha = \frac{B(E - E_g)^2}{E} \quad (1)$$

where $\alpha = A/d$ (A is the absorbance that was measured and d is the thickness of the h-BN thin film), B is a constant and E is the excitation photon energy. Calculation of the optical bandgaps of the two samples, $(\alpha E)^2$ were performed and the results were plotted against E , the photon energy, and are shown in FIG. 63(b). Therein, a linear graph is superimposed on the portion of the plot with a positive gradient. The extrapolated linear graph intersects with the x-axis, giving the optical bandgap of the two samples. From FIG. 63(b), the optical bandgap of Sample A and Sample B is 5.33 eV and 5.77 eV, respectively. This is in agreement with the values obtained in the literature.^{22–}

To investigate the heat dissipative effects and its associated stability at high temperatures, the h-BN thin films were deposited onto electronic devices, functioning as both a heat dissipative layer and a passivation layer, consequently, the thermal conductivity of the two samples, Sample A and Sample B, are measured at various temperatures, from room temperature to 300 °C. FIG. 64(a) shows the thermal conductivity of Sample A and Sample B at room temperature. The thermal conductivity of Sample B is approximately 354% higher than that of Sample A. Across the temperature range at which the two samples' thermal conductivities were measured and as illustrated in FIG. 64(b), the thermal conductivity of Sample B is consistently higher than that of Sample A. This is explained by the microstructure of both samples, as the microstructure of the h-BN film of Sample B is vertically aligned, there is a lesser extent of phonon scattering in Sample B, resulting in the higher thermal conductivity. Sample A has a polycrystalline microstructure, resulting in a far greater extent of phonon scattering. Furthermore, Thermal conductivity of Sample B remains relatively constant within a 25% margin from the average value across the temperature range demonstrating its thermal stability. The thermal conductivity of the polycrystalline h-BN film is virtually constant at high temperatures. This shows that Sample B, with its aligned microstructure, may function well as a heat dissipative heater with good stability at high temperatures on electronic devices. Furthermore, Sample A, with its dense, polycrystalline nature, may function as an excellent passivation layer on electronic devices, such as indium selenide transistors which may be sensitive to atmospheric contaminants (e.g. moisture and oxidation).

FIG. 64 (c) Thermal conductivities of both Sample A and Sample B measured at room temperature and (d) measured at temperatures ranging from room temperature to 300 °C.

5.3 Control of Isotopic Composition of h-BN Thin Films

5.3.1 Motivation Driving Control of Isotopic Composition

Enhancement in their thermal conductivities can be attained by replacing certain materials with their monoisotopic variants, especially for the case of insulators and semiconductors. Examples include gallium arsenide, boron carbide²⁵, silicon, germanium, graphene and diamond. The percentage enhancement for thermal conductivities of these monoisotopic variants of several materials at room temperature are reported to be: ~5% for GaAs,²⁶ 10% for BP,²⁷ 7% for Si,^{28,29} 30% for Ge³⁰, ~58% for graphene³¹ and ~50% for diamond³². The transport of acoustic phonons is fundamental to the thermal conductivity in non-conductive materials and semiconductors. Of the parameters influencing the transport, mean free path is a crucial factor, which is a function of the phonon relaxation time. Manipulation of the scattering of the acoustic phonons as it is dependent on the degree of isotopic mass fluctuations, is therefore, possible. This, in turn, generated interest in manipulating thermal conductivity through isotopic enrichment. The equation governing the rate of scattering for phonons with energy ω is given by:³³

$$\tau_{ph}^{-1} = \frac{g_2 V}{4\pi \langle V_{ph} \rangle^3} \omega^4 \quad (1)$$

where V is the volume occupied by the atoms within the sample and the mass fluctuation parameter, g_2 , is given by:

$$g_2 = \frac{\langle M^2 \rangle - \langle M \rangle^2}{\langle M \rangle^2} \quad (2)$$

where $\langle M \rangle$ is the mean isotopic mass of the atom. Hence, enrichment of isotopic composition will directly lead to higher thermal conductivity.

For h-BN, isotopic enrichment is beneficial in the application of thermal neutron detection^{34,35} using solid-state thermal neutron detector owing to the fact of the high thermal neutron cross-section (~3840 barns) of B¹⁰ isotope. Isotopic enrichment of h-BN is proven imperative for reducing optical losses in phonon-polariton devices³⁶ as mean free path of the optical phonons are drastically lengthened within a sample of isotopically pure h-BN. The increment in h-BN thermal conductivity from isotopic enrichment is predicted to be more than 100% at room temperature³⁷ and for multilayer h-BN, such an increment was calculated to be ~ 4 – 10 times.³⁸ Recently, due to advancements in deposition techniques that improved the availability of isotopically pure bulk

h-BN crystals,³⁹ enhancements in in-plane thermal conductivity of h-BN at room temperature for monoisotopic h-B¹⁰N and h-B¹¹N were measured to be 43% and 35% respectively.⁴⁰ Moreover, the value of the in-plane thermal conductivity measured was a record high of $585 \pm 80 \text{ Wm}^{-1}\text{K}^{-1}$. Likewise for sp²-bonded boron nitride nanotubes (BNNT), at 300K, the thermal conductivity enhancement was calculated to be 23%³⁸ and was measured to be ~50%^{41,42}. These experiments illustrated the practical and significant increment to thermal conductivity that can be attained by isotopic enrichment.

However, there is a dearth of studies relating to the understanding and manipulation of thermal properties of isotopically enhanced h-BN. There are only a few studies on few-layers h-BN made using chemical vapour deposition (CVD) or bulk h-BN by conventional techniques which involve high pressure and high temperature.^{43,44} Likewise, few studies have been done on immediate depositing isotopically-pure or enriched h-BN on Si or GaN wafers for large-scale production and industrial applications. Furthermore, what remains unclear is how varying the boron isotopic composition will have an impact on both bandgap and dielectric properties of the resulting h-BN films. As expounded in the earlier chapters, the dielectric dispersion at high frequencies in isotopically-controlled h-BN, such as its dielectric constant, dielectric loss and associating breakdown field, is desired to be studied for multifunctional nanoelectronics and optoelectronic applications.

In this section, how isotopic engineering of h-BN films can be scaled to a larger, industrial scale was investigated. Using pure boron isotopes (B¹⁰ and B¹¹) targets, with high purity, the h-BN thin films were synthesized by controlling the isotopic concentrations of the boron content within h-BN of the resultant h-BN thin films (50% B¹⁰, 60% B¹⁰, 80% B¹⁰ in h-BN) using HIPIMS. Our results illustrate that the films' dielectric loss, dielectric constants and optical band gap have a strong dependence on the isotope compositions of B¹⁰/B¹¹. From frequencies ranging from 0 Hz, up to 10⁷ Hz, the isotopically enhanced h-BN has a low dielectric loss, which is well below 1.3%. Over a broad temperature range, the thermal conductivities of pure h-B¹⁰N and h-B¹¹N are higher than the films with other isotopic compositions. Consequently, these deposited h-BN thin films of varying isotopic compositions coupled with superior dielectrics properties and large bandgap make these films promising as a dielectric layer for self-dissipation of heat on GaN and AlGaIn/GaN

transistors, a step towards the resolution of the thermal hotspot problem. In this section and study, insights on high functioning thermal-adaptive and highly modular electronics at these frequencies are gleaned.

5.3.2 Experimental Procedures for the Depositions of Isotopically Enriched h-BN Films

FIG. 65 (a) A schematic of the dual-sputtering HIPIMS system, with the vacuum pumps shown. (b) A schematic of a typical HIPIMS pulse supplied by the power source. The peak current as shown is around 10A and the voltage supplied to the target is around -1000V.⁴⁵

A dual magnetron sputtering with HIPIMS capabilities was used for the syntheses of these h-BN thin films. A layout of the system is shown in FIG. 65(a). The diagram shows an instance where the two magnetrons are sputtering simultaneously. The targets were isotopically pure boron targets (3-inch in diameter). Double-sided polish Si wafers with $\langle 100 \rangle$ orientation, thickness of 350 μm were used. They were mainly used for characterizations. Furthermore, in one of the depositions, GaN wafers and AlGaIn/GaN heterostructure were also supplemented as substrates. Prior to each deposition, the base pressure of the chamber was maintained at around 3×10^{-6} Torr. Subsequently, the depositions were conducted in the presence of a reactive Ar and N₂ environment, with the total gas flow rate kept constant at 100 sccm, and the gas flow rate ratio kept at 25%. The working pressure for these depositions was $\sim 1.0 - 1.5 \times 10^{-2}$ Torr. The temperature of the substrate holder is held at 800 °C, this temperature is monitored above the graphite heater, using a thermocouple which is placed slightly above it. The graphite heater provides the heat needed for all depositions. The power source for all the depositions are provided by the HIPIMS power supply. It is capable

of delivering a voltage maximally negative 1000 V to the target and is depicted in FIG. 65(b). The pulses were administered to the chamber at 8 kHz and has a width of 10 μ s.¹ The 5 samples were labelled according to the percentage of boron-10 isotope within the film. To understand how the naturally-abundance h-BN thin film will fare in comparison with those of different isotopic concentrations, another h-BN film of naturally-abundant isotopic ratio was deposited under the same conditions but separately. Table 22 gives full details of the deposition conditions.

Table 22 Deposition Parameters for all the samples⁴⁵

Sample Name	Power Density of B ¹⁰ Target / W cm ⁻²	Power Density of B ¹¹ Target / W cm ⁻²	Process Current to B ¹⁰ Target / mA	Process Current to B ¹¹ Target / mA	Peak Current of B ¹⁰ Target / A	Peak Current of B ¹¹ Target / A	Discharge Voltage of B ¹⁰ Target / V	Discharge Voltage of B ¹¹ Target / V
Pure B ¹⁰	79.77	N/A	450	N/A	9	N/A	645	N/A
Pure B ¹¹	N/A	65.79	N/A	400	N/A	9	N/A	600
50% B ¹⁰ 50% B ¹¹	76.48	76.48	363	450	5	5	764	647
60% B ¹⁰ 40% B ¹¹	82.24	54.82	400	330	5	4	751	611
80% B ¹⁰ 20% B ¹¹	109.65	27.96	524	170	11	2	775	607

Sample Name	Power Density of B Target / W cm ⁻²	Process Current to B Target / mA	Peak Current of B Target / A	Discharge Voltage of B Target / V
19.1% B ¹⁰ 80.1% B ¹¹ <i>Target is Pure Boron</i> <i>Target of Natural Abundance</i>	73.58	421	7	784

5.3.3 Growth of Isotopically Controlled h-BN Thin Films and its Characterizations

The Raman spectra of five samples are plotted in FIG. 66(a), for different isotopic (B¹⁰ and B¹¹) concentrations, the E_{2g} phonon has different energies with its $\sim 1/\mu^{1/2}$ dependence as it is of the harmonic oscillator,^{46,47} this shows that it is indeed possible to alter the phonon's energy by manipulating its isotope content. The E_{2g} phonon is the quantum mechanical particle of the vibration of the N and B atoms within the hexagonal plane in antiparallel directions. The phonon

frequency as a function on the reduced mass, μ of the B-N system is illustrated by the plot of the frequency of the E_{2g} phonon against it, as shown in FIG. 66(b). Prediction on the linear relationship between the energies of the E_{2g} phonon mode to the inverse square root of μ is verified here.⁴⁶ Similarly, C. Yuan et al. and S. Liu et al. using the melt flux method, reported on the results (as green and red data points in FIG. 66(b)) of the phonon frequencies with different isotopic compositions.^{39,48} Visually, it is seen that the phonon frequencies of the crystals grown using the melt flux method were higher than those grown in this study. This difference can be account for by the compressive stress within these films due to the highly energetic ion impingement on the substrate surface during the deposition.⁴⁹ One important factor which will increase the phonon energy is the film's crystalline structure at the nano-scale,⁵⁰ which can be experimentally verified by calculating the size of the associated nanocrystals, from the FWHM of the Raman spectra. In this case, the values of the FWHM of these spectra ranged from 40 cm^{-1} to 60 cm^{-1} . These values are consistent with those reported by other researchers using a different deposition technique, such as chemical vapour deposition,^{3,51} chemical method,⁴ RF sputtering,⁵² and atomic layer deposition (ALD)⁵³. The broadening of the Raman peak is associated with a smaller crystalline size and this is governed by the equation: $L_a = [1417/(\text{FWHM})] - 8.7$,⁵⁰. The crystalline sizes range from 14.8 nm to 23.8 nm and Table 23 tabulates this result, together with other results, which are discussed in subsequent sections.

The bonding characteristics of thin films are often one of the important characteristics to investigate and understand in any study of thin films. To this aim, spectrometry is often the technique to consider. In this case, FTIR spectrometry is used as FTIR can be used to differentiate the different phases of BN, such as cubic boron nitride and h-BN.

The plots of the FTIR spectra of all samples with varying isotopic concentrations are contained in FIG. 66(c). Both infrared active E_{1u} (in the range of 1380 cm^{-1} – 1415 cm^{-1}) and A_{2u} (in the range of 800 cm^{-1} – 825 cm^{-1}) characteristic phonon modes of h-BN are present. Similar to the E_{2g} phonon mode, both A_{2u} and E_{1u} phonon modes have an inverse relationship, predicted by VCA, in the form of $\omega \propto \mu^{-1/2}$, with the reduced mass, μ . This is illustrated in FIG. 66(d) in blue dotted lines. One can inspect visually that there is considerable consensus between the experimentally obtained energies of the phonon modes and the dependency on the reduced mass of the h-BN system. This

is a piece of evidence showing the possibility of manipulating the isotopic concentration of the h-BN thin films.

In FIG. 67, the (a) Raman spectrum and (b) FTIR spectrum of the h-B^{NAT}N, are produced, as it is deposited to give a comparison to the other h-BN thin films of different isotopically distributed variants.

FIG. 66 Raman and FTIR spectrometry of h-BN thin films with varying isotopic concentrations. (a) Raman spectra of isotopically varied h-BN thin films. (b) The linear relation between the E_{2g} phonon mode and the reduced mass, μ , of B-N pair. (c) The FTIR spectra of the isotopically varied films. (d) Reduced mass dependency of the frequencies of both the E_{1u} and A_{2u} phonon modes.⁴⁵

Table 23 Reduced mass, crystalline size and relative properties of isotopic h-BN thin films.⁴⁵

	Reduced mass	Crystalline size (nm)	Thermal conductivity (W m ⁻¹ K ⁻¹)	Bandgap (eV)	Dielectric constant	Dielectric loss
B ¹⁰	5.833	22.740	3.901	5.56	5.061	0.016
80% B ¹⁰	6.000	20.529	1.902	5.72	5.462	0.0198
60% B ¹⁰	5.967	14.821	1.361	5.79	6.392	0.0270

50% B¹⁰	5.901	16.107	1.802	5.71	7.112	0.0189
B¹¹	6.160	26.797	3.541	5.54	5.741	0.0137

FIG. 67 (a) Raman and (b) FTIR spectra of h-B^{NATN} thin films.

FIG. 68 HRTEM and XPS analyses of h-BN thin films. (a) The region between the h-BN layer and the silicon substrate as viewed by HRTEM and (b) is the region of the h-BN thin film, far from the substrate. (c) A fast-Fourier transform of the image showed in (b), indicating the presence of two direction arcs, demonstrably belonging to the (002) planes and a diffract ring, derived from the (010) plane. (d) EDS, (e) EELS and (f) XPS spectra of the sample. (g) N 1s and (h) O 1s XPS survey of the sample.⁴⁵

Utilization of HRTEM enabled the study of h-BN thin films, its crystallinity and microstructure. For a start, FIG. 68(a) gives the pictorial representation of the interface between h-BN film and Si substrate a cross-section HRTEM image, the distinction between the two is clear and the interface is has a thin layer of amorphous boron nitride (a-BN). FIG. 68(b) is a high resolution HRTEM image of the sample. Within the films are the nanoclusters which orient itself randomly amongst the other clusters. Calculations done on the FFT shown in FIG. 68(c) reveals that the inter-planar

distance is 0.366 nm from, it is close to the distinctive interplanar distance between each h-BN plane.¹⁰ Each cluster is made of multiple la of h-BN and is separated pictorially by dashed lines on the HRTEM image. Additionally, the concentric diffraction rings are associated with the (010) planes whereas the (002) planes gave rise to the diffraction arcs. The presence of the elements, namely, B, N, C and O, is confirmed by the spectrum derived from the EDS shown in FIG. 68(d). As it is physically unavoidable to avoid contamination due to the mechanical handling of the sample during the observation of the sample using TEM, there is some carbon found in the sample from the EDS analysis. Furthermore, this is corroborated by the absence of the prominent ‘G’ and ‘D’ peaks in the Raman spectra of carbon and B-N-C samples.⁵⁴ Furthermore, in FIG. 68(e), the presence of the representative π^* and σ^* peaks in the EELS spectrum shown, which are near the Nitrogen and Boron K-shells highlight the existence of the sp^2 hybridized bonds. The locations of the peaks corresponding to the π^* and σ^* states (198.3 and 206.2 eV) agree with the values reported in the literature.⁵⁵

The bonding characteristics of thin films are often studied using XPS. The sample with the natural composition in the distribution of its isotopes was selected for this XPS study as it is the sample that was least impacted by the variations in isotopic compositions. FIG. 68(f) plots its XPS spectrum, the existence of all B 1s, N 1s and O 1s peaks corroborates with the EDS analysis (FIG. 68(d)). Imperfect stoichiometry mismatch of B and N in the sample resulted in some oxygen found within it. Excess boron had interacted with oxygen due to unavoidable exposure to the atmosphere. Agreement with the values reported in the literature occurs to the values of the peak positions of both B 1s and N 1s which are located at 189.9 eV and 396.9 eV, respectively. This fact is illustrated in FIG. 68(g) and FIG. 68(h).^{10,44} A single and symmetrical peak was observed in both B 1s and N 1s spectra, giving evidence of the existence of an usual sp^2 -hybridized B-N bonding. The presence of a symmetric B 1s XPS peak, gives evidence that boron and oxygen are not chemically bonded. The estimated B/N stoichiometric ratio is 1.04:1, which is a good evidence that a good 1:1 stoichiometry present for the h-BN film deposited.

5.3.4 Optical Band Gap and Thermal Performances of Isotopically Controlled h-BN Thin Films

The measurement of thermal conductivity for the isotopically pure (i.e. 100% h-B¹⁰N and 100% h-B¹¹N) h-BN thin films is of importance. To that aim, the NanoTR technique is used.⁵⁶ The raw signal was used to measure the thermal conductivity of h-BN films with different isotopic distributions and is shown on FIG. 69(a). The curve that is used for fitting is superimposed on the plot. Shown as an inset in FIG. 69(a), an Al layer with a thickness of 100 nm transducer was deposited on h-BN films for the thermal signal as a transducer, prior to the measurements on thermal conductivity. An enhancement of 231.0% was achieved for the thermal conductivity of h-B¹⁰N whereas the corresponding enhancement for h-B¹¹N is 210.0%, when compared to the isotopically mixed samples. These increments in thermal conductivities for the isotopically enhanced samples are corroborated by the literature.^{21,37} The thermal conductivities of the isotopically disordered samples are consistent, none of them deviates more than 4.68% from the average value of this set of samples. The thermal conductivities for all the samples are summarized on FIG. 69(b). Frequency, it is desirable that electronics devices function well at elevated temperatures. As a result, measurements on the thermal conductivities of the samples were conducted from room temperature to 300 °C and are shown in FIG. 69(c). An increase in the thermal conductivity was measured. For all the samples, the percentage enhancement of the thermal conductivities at 300 °C for is around 8.5% (FIG. 70), the annealing effect can be used to explain this – the fact that increased temperatures resulted in the congregation of the clusters of h-BN. Therefore, this reduced the scattering of the phonons from the boundaries. At elevated temperatures, the stability of the self-heat dissipation effect coupled with its high functional stability makes h-BN a material with desirable thermal properties. Consequently, industrial applications of h-BN, such as depositing it to electron devices to ameliorate the problem of thermal hotspots is possible.

The absorbance spectra of the h-BN samples are plotted in FIG. 69(d). These plots showed a sharp peak at around 200 nm, which is a characteristic peak for the h-BN thin films. Derived from these absorbance spectra of the samples, is the Tauc's plot, to extract the optical bandgap. The formula is presented here as:²¹

$$\alpha = C(E - E_g)^{\frac{1}{2}} \quad (1)$$

Where the absorption coefficient $\alpha = A/d$ (A: absorbance and d: film thickness), E is the phonon energy and C is a constant. The optical bandgap for the samples can be read off from the derived plot. It is the intercept at the x-axis. Consistency between the bandgaps of the two isotopically pure samples are measured to be within a 0.18% margin from their average value. Despite this, the average value of the isotopically pure samples is 3.27% lower than the average optical bandgap value of the isotopically mixed samples. Surprisingly, the optical band gap of the isotopically pure h-BN films (h-B¹⁰N and h-B¹¹N) is lower than that of the isotopically mixed h-BN samples as shown in FIG. 69(e). This difference in the optical bandgap values is probably due to some small differences in both the conditions under which the deposition was done and the microstructures of the films, which resulted in a change in both the way how the atoms are bonded and in turn, the energy dispersion of the as-deposited film. Differences in the values calculated are explained by the small differences in the deposition conditions and that of the microstructures of the sample. This is corroborated with the literature as it was shown that isotopic compositions of thin films have little influence on its optical band gap at 0 K.¹⁶ Variations to the microstructures of the films may alter the bonding characteristics and the band structure of the film. Likewise, Tauc's plots and their corresponding optical bandgaps are shown in FIG. 69(g) - FIG. 69(j). The theoretical value of h-BN was experimentally measured to be around 6.0 eV⁵⁴ which is similar to the bandgap energies obtained in this study, ranging from 5.54 eV to 5.79 eV. Despite the fact that the bandgap of h-BN is less than those of Al₂O₃ (8.8 eV) and SiO₂ (9.0 eV) but it is comparable to those of HfO₂ (6.0 eV), Si₃N₄ (5.3 eV), and ZrO₂ (5.8 eV).⁵⁷

FIG. 69 Thermal performances and bandgap energies of isotopic h-BN. (a) The raw thermal signal from the measurement and its associated fitting curve. The inset is an illustration showing the measurement technique. (b) The experimentally obtained values for the thermal conductivities of the samples. (c) Thermal conductivity of these samples as a function of temperature from room temperature to 300 $^{\circ}\text{C}$. (d) The UV-vis absorption coefficients (e) optical bandgaps of the deposited h-BN films. (f) A compilation of the bandgaps of different materials. (g)-(j) Tauc plots of the isotopically varied samples.⁴⁵

FIG. 70 Percentage increment in thermal conductivities for the isotopically varied h-BN samples at 300 °C as compared to room temperature.⁴⁵

5.4 Conclusions

It was found that the control of orientation using the gas flow rate ratio as a controlling parameter is achievable and its advantage is in its simplicity. Moreover, there is a range of gas flow rate ratios (15% to 30%) in which the orientation of h-BN thin films deposited on substrates would be aligned perpendicularly (the c-axis of h-BN being parallel to the substrate surface). Thermal conductivity of the deposited h-BN films was found to be correlated to the degree of alignment of the h-BN films. This gives a method to synthesize h-BN, to enhance the thermal conductivity of heat-dissipating layer of h-BN deposited on electronics for the mitigation of thermal hotspots problem.

As it was set up in Chapter 1, isotopic enhancement of h-BN thin films is desired for its enhancement in various properties. The Raman and FTIR spectra of the deposited h-BN thin films show a strong dependency on its isotopic compositions, as evidence of the successful manipulation of isotopic composition. The bandgap of the as-deposited h-BN thin films does not have a strong dependency on its isotopic compositions. Furthermore, deposition of h-BN thin films with different isotopic proportions is studied directly on Si and GaN substrates in a mixed argon and nitrogen environment using reactive-HIPIMS. A ~200% improvement for the thermal conductivity of the isotopically pure films was obtained as compared to the mixed composites.

The possibility of one novel memory device based on highly textured hexagonal BN films via high power impulse magnetron sputtering technique using a pure boron source has been realised. Our results reveal that the band gap energies of random and textured h-BN thin films are 5.33 eV and 5.77 eV respectively, although they exhibit the similar hexagonal microstructure. In addition, the thermal conductivity of the oriented h-BN film is approximately 354% that of the random counterpart. Our textured h-BN memory device exhibits reproductive switching endurance and low power consumption. The resistive switching mechanism is related to the formation of a conductive channel, comprising of the oxygen vacancies at interfaces between BN layer and copper substrate.

In Chapter 6, some of the applications which are made possible due to the deposition of h-BN onto electronic devices will be discussed. Having achieved some mastery over the deposition technique of HIPIMS in the synthesis of h-BN thin films, it is important to study its performance in actualised electronic devices.

5.5 References

- 1 S. S. Chng, M. Zhu, J. Wu, X. Wang, Z. K. Ng, K. Zhang, C. Liu, M. Shakerzadeh, S. Tsang and E. H. T. Teo, *J. Mater. Chem. C*, 2020, **8**, 4421–4431.
- 2 M. Snure, Q. Paduano, M. Hamilton, J. Shoaf and J. M. Mann, *Thin Solid Films*, 2014, **571**, 51–55.
- 3 N. Coudurier, M. Chubarov, R. Boichot, F. Mercier, E. Blanquet, R. Reboud, S. Lay, A. Crisci, S. Coindeau, T. Encinas and M. Pons, *Cryst. Res. Technol.*, 2016, **51**, 231–238.
- 4 C. Huang, C. Chen, X. Ye, W. Ye, J. Hu, C. Xu and X. Qiu, *J. Mater. Chem. A*, 2013, **1**, 12192.
- 5 L. Jiang, N. Xiao, B. Wang, E. Grustan-Gutierrez, X. Jing, P. Babor, M. Kolíbal, G. Lu, T. Wu, H. Wang, F. Hui, Y. Shi, B. Song, X. Xie and M. Lanza, *Nano Res.*, 2017, **10**, 2046–2055.
- 6 T. A. Friedmann, P. B. Mirkarimi, D. L. Medlin, K. F. McCarty, E. J. Klaus, D. R. Boehme, H. A. Johnsen, M. J. Mills, D. K. Ottesen and J. C. Barbour, *J. Appl. Phys.*, 1994, **76**, 3088–3101.

- 7 D. R. McKenzie, W. D. McFall, W. G. Sainty, C. a. Davis and R. E. Collins, *Diam. Relat. Mater.*, 1993, **2**, 970–976.
- 8 C. A. Davis, *Thin Solid Films*, 1993, **226**, 30–34.
- 9 D. R. McKenzie, W. D. McFall, S. Reisch, B. W. James, I. S. Falconer, R. W. Boswell, H. Persing, A. J. Perry and A. Durandet, *Surf. Coatings Technol.*, 1996, **78**, 255–262.
- 10 Z. Du, X. Zeng, M. Zhu, A. Kanta, Q. Liu, J. Li and L. B. Kong, *Ceram. Int.*, 2018, **44**, 21461–21469.
- 11 M. H. Khan, H. K. Liu, X. Sun, Y. Yamauchi, Y. Bando, D. Golberg and Z. Huang, *Mater. Today*, 2017, **20**, 611–628.
- 12 T. A. Friedmann, P. B. Mirkarimi, D. L. Medlin, K. F. McCarty, E. J. Klaus, D. R. Boehme, H. A. Johnsen, M. J. Mills, D. K. Ottesen and J. C. Barbour, *J. Appl. Phys.*, 1994, **76**, 3088–3101.
- 13 O. Cometto, B. Sun, S. H. Tsang, X. Huang, Y. K. Koh and E. H. T. Teo, *Nanoscale*, 2015, **7**, 18984–18991.
- 14 T. A. Friedmann, K. F. McCarty, E. J. Klaus, J. C. Barbour, W. M. Clift, H. A. Johnsen, D. L. Medlin, M. J. Mills and D. K. Ottesen, *Thin Solid Films*, 1994, **237**, 48–56.
- 15 K. Zhang, Y. Feng, F. Wang, Z. Yang and J. Wang, *J. Mater. Chem. C*, 2017, **5**, 11992–12022.
- 16 D. L. Medlin, T. A. Friedmann, P. B. Mirkarimi, P. Rez, M. J. Mills and K. F. McCarty, *J. Appl. Phys.*, 1994, **76**, 295–303.
- 17 P. K. Banerjee, B. Chatterjee, J. S. Kim, M. Platek, Y. Zhang and S. S. Mitra, *Phys. Status Solidi a-Applied Res.*, 1993, **140**, 145–161.
- 18 M. Zhu, J. Wu, Z. Du, R. Y. Tay, H. Li, B. Özyilmaz, E. Hang and T. Teo, *Nanoscale*, 2015, **7**, 14730–14737.
- 19 L. Ci, L. Song, C. Jin, D. Jariwala, D. Wu, Y. Li, A. Srivastava, Z. F. Wang, K. Storr, L. Balicas, F. Liu and P. M. Ajayan, *Nat. Mater.*, 2010, **9**, 430–435.
- 20 S. Alkoy, C. Toy, T. Gönül and A. Tekin, *J. Eur. Ceram. Soc.*, 1997, **17**, 1415–1422.
- 21 Z. Zhang, Y. Zhao and M. Zhu, *Appl. Phys. Lett.*, 2006, **88**, 033101.
- 22 G. Cassaboïs, P. Valvin and B. Gil, *Nat. Photonics*, 2016, **10**, 262–266.
- 23 K. Watanabe, T. Taniguchi and H. Kanda, *Nat. Mater.*, 2004, **3**, 404–409.
- 24 X. Z. Du, J. Li, J. Y. Lin and H. X. Jiang, *Appl. Phys. Lett.*, 2017, **111**, 132106.

- 25 Y. NISHI, Y. ARITA, T. MATSUI and T. NAGASAKI, *J. Nucl. Sci. Technol.*, 2002, **39**, 391–394.
- 26 A. V. Inyushkin, A. N. Taldenkov, A. Y. Yakubovsky, A. V. Markov, L. Moreno-Garsia and B. N. Sharonov, *Semicond. Sci. Technol.*, 2003, **18**, 685–688.
- 27 Q. Zheng, S. Li, C. Li, Y. Lv, X. Liu, P. Y. Huang, D. A. Broido, B. Lv and D. G. Cahill, *Adv. Funct. Mater.*, 2018, **28**, 1805116.
- 28 A. V. Inyushkin, A. N. Taldenkov, J. W. Ager, E. E. Haller, H. Riemann, N. V. Abrosimov, H.-J. Pohl and P. Becker, *J. Appl. Phys.*, 2018, **123**, 095112.
- 29 R. K. Kremer, K. Graf, M. Cardona, G. G. Devyatikh, A. V. Gusev, A. M. Gibin, A. V. Inyushkin, A. N. Taldenkov and H.-J. Pohl, *Solid State Commun.*, 2004, **131**, 499–503.
- 30 M. Asen-Palmer, K. Bartkowski, E. Gmelin, M. Cardona, A. P. Zhernov, A. V. Inyushkin, A. Taldenkov, V. I. Ozhogin, K. M. Itoh and E. E. Haller, *Phys. Rev. B*, 1997, **56**, 9431–9447.
- 31 S. Chen, Q. Wu, C. Mishra, J. Kang, H. Zhang, K. Cho, W. Cai, A. A. Balandin and R. S. Ruoff, *Nat. Mater.*, 2012, **11**, 203–207.
- 32 L. Wei, P. K. Kuo, R. L. Thomas, T. R. Anthony and W. F. Banholzer, *Phys. Rev. Lett.*, 1993, **70**, 3764–3767.
- 33 M. Cardona and M. L. W. Thewalt, *Rev. Mod. Phys.*, 2005, **77**, 1173–1224.
- 34 A. Maity, S. J. Grenadier, J. Li, J. Y. Lin and H. X. Jiang, *Appl. Phys. Lett.*, 2019, **114**, 222102.
- 35 A. Maity, S. J. Grenadier, J. Li, J. Y. Lin and H. X. Jiang, *Appl. Phys. Lett.*, 2017, **111**, 033507.
- 36 A. J. Giles, S. Dai, I. Vurgaftman, T. Hoffman, S. Liu, L. Lindsay, C. T. Ellis, N. Assefa, I. Chatzakis, T. L. Reinecke, J. G. Tischler, M. M. Fogler, J. H. Edgar, D. N. Basov and J. D. Caldwell, *Nat. Mater.*, 2018, **17**, 134–139.
- 37 D. T. Morelli, J. P. Heremans and G. A. Slack, *Phys. Rev. B*, 2002, **66**, 195304.
- 38 L. Lindsay and D. A. Broido, *Phys. Rev. B*, 2012, **85**, 035436.
- 39 S. Liu, R. He, L. Xue, J. Li, B. Liu and J. H. Edgar, *Chem. Mater.*, 2018, **30**, 6222–6225.
- 40 C. Yuan, J. Li, L. Lindsay, D. Cherns, J. W. Pomeroy, S. Liu, J. H. Edgar and M. Kuball, *Commun. Phys.*, 2019, **2**, 1–8.
- 41 C. W. Chang, A. M. Fennimore, A. Afanasiev, D. Okawa, T. Ikuno, H. Garcia, D. Li, A.

- Majumdar and A. Zettl, *Phys. Rev. Lett.*, 2006, **97**, 085901.
- 42 D. A. Stewart, I. Savic and N. Mingo, *Nano Lett.*, 2009, **9**, 81–84.
- 43 S. Mateti, K. Yang, X. Liu, S. Huang, J. Wang, L. H. Li, P. Hodgson, M. Zhou, J. He and Y. Chen, *Adv. Funct. Mater.*, 2018, **28**, 1707556.
- 44 J. Lin, R. Y. Tay, H. Li, L. Jing, S. H. Tsang, H. Wang, M. Zhu, D. G. McCulloch and E. H. T. Teo, *Nanoscale*, 2018, **10**, 16243–16251.
- 45 S. S. Chng, M. Zhu, Z. Du, X. Wang, M. Whiteside, Z. K. Ng, M. Shakerzadeh, S. H. Tsang and E. H. T. Teo, *J. Mater. Chem. C*, 2020, **8**, 9558–9568.
- 46 T. Q. P. Vuong, S. Liu, A. Van der Lee, R. Cuscó, L. Artús, T. Michel, P. Valvin, J. H. Edgar, G. Cassabois and B. Gil, *Nat. Mater.*, 2018, **17**, 152–158.
- 47 M. Cardona and M. L. W. Thewalt, *Rev. Mod. Phys.*, 2005, **77**, 1173–1224.
- 48 C. Yuan, J. Li, L. Lindsay, D. Cherns, J. W. Pomeroy, S. Liu, J. H. Edgar and M. Kuball, *Commun. Phys.*, 2019, **2**, 43.
- 49 V. T. Srikar and S. M. Spearing, *Exp. Mech.*, 2003, **43**, 238–247.
- 50 R. J. Nemanich, S. A. Solin and R. M. Martin, *Phys. Rev. B*, 1981, **23**, 6348–6356.
- 51 K. Ahmed, R. Dahal, A. Weltz, J.-Q. Lu, Y. Danon and I. B. Bhat, *Appl. Phys. Lett.*, 2016, **109**, 113501.
- 52 D. Q. Hoang, P. Pobedinskas, S. S. Nicley, S. Turner, S. D. Janssens, M. K. Van Bael, J. D’Haen and K. Haenen, *Cryst. Growth Des.*, 2016, **16**, 3699–3708.
- 53 M. Snure, Q. Paduano, M. Hamilton, J. Shoaf and J. M. Mann, *Thin Solid Films*, 2014, **571**, 51–55.
- 54 R. Y. Tay, H. Li, S. H. Tsang, M. Zhu, M. Loeblein, L. Jing, F. N. Leong and E. H. T. Teo, *Chem. Mater.*, 2016, **28**, 2180–2190.
- 55 Z. Liu, Y. Gong, W. Zhou, L. Ma, J. Yu, J. C. Idrobo, J. Jung, A. H. Macdonald, R. Vajtai, J. Lou and P. M. Ajayan, *Nat. Commun.*, 2013, **4**, 1–8.
- 56 B. Hinterleitner, I. Knapp, M. Poneder, Y. Shi, H. Müller, G. Eguchi, C. Eisenmenger-Sittner, M. Stöger-Pollach, Y. Kakefuda, N. Kawamoto, Q. Guo, T. Baba, T. Mori, S. Ullah, X. Q. Chen and E. Bauer, *Nature*, 2019, **576**, 85–90.
- 57 J. Y. Tsao, S. Chowdhury, M. A. Hollis, D. Jena, N. M. Johnson, K. A. Jones, R. J. Kaplar, S. Rajan, C. G. Van de Walle, E. Bellotti, C. L. Chua, R. Collazo, M. E. Coltrin, J. A. Cooper, K. R. Evans, S. Graham, T. A. Grotjohn, E. R. Heller, M. Higashiwaki, M. S. Islam,

P. W. Juodawlkis, M. A. Khan, A. D. Koehler, J. H. Leach, U. K. Mishra, R. J. Nemanich, R. C. N. Pilawa-Podgurski, J. B. Shealy, Z. Sitar, M. J. Tadjer, A. F. Witulski, M. Wraback and J. A. Simmons, *Adv. Electron. Mater.*, 2018, **4**, 1600501.

6 Applications of h-BN on Devices for Electronics and Thermal Management

6.1 h-BN as a Passivating/Encapsulating Layer for Electronic Devices

Orientation engineering of two-dimensional materials, for energy storage and conversion applications,¹⁻³ has been also utilized on some two-dimensional materials, such as molybdenum disulphide (MoS₂) and graphene. To investigate how orientation engineering can help in enhancing the performance of transistors, h-BN was deposited and used as a passivating/encapsulating layer for InSe transistor.

InSe is an insulative material in the absence of an encapsulating BN layer owing to its sensitivity to moisture under atmospheric conditions, however, the BN-covered device functions as a semiconductor with decent electron mobility at room temperature. Furthermore, such device remains functional even after 2 months and remains thermally stable and functional at elevated temperatures of up to 200 °C.

Microwave assisted chemical vapor transport (MACVD) method was used to synthesize pure InSe.⁴ Pure selenium powders were mixed with indium beads and placed in a quartz tube with only one end. It is a quartz tube with a neck in the middle fabricated, before the tube was evacuated to high vacuum ($\sim 10^{-7}$ torr). The tube was then filled with argon plasma at 37 Torr which was sustained through continuous microwave irradiation at around 750 W. The quartz tube was placed in a microwave plasma system (custom-made) after sealing the neck for the synthesis to keep the temperature of the mixture at 630 °C. Using lithography, electron-beam deposition and lastly, the lift-off process, the InSe transistor was successfully fabricated.

6.1.1 Growth and Characterization of InSe Transistors

FIG. 71(a) and FIG. 71 (b) show the atomic structure of InSe, which is made of In and Se atoms held together by covalent bonds, it is similar to that of h-BN. Raman spectrometry was employed to verify the atomic structure. Three typical the A^1_{1g} , E^1_{2g} , and A^2_{1g} phonon modes were found corresponding to the found Raman peaks, located at 115.7, 177.8 and 227.8 cm^{-1} (FIG. 71(c)).⁵ FIG. 71(d) - FIG. 71(f) was derived using EDS showing both the elemental distributions of In and

Se. The ratio of In and Se is around 1:1 (this is shown in the EDS spectrum in FIG. 72) as indicated by quantitative analysis. This agrees well with the elemental composition of beta InSe.⁶ The electron images of the high quality as-grown InSe crystals were shown in FIG. 71(g) - FIG. 71(h). The lattice constant is about 0.391 nm, denoted as 'd' in FIG. 71(b) and the angle between (100) and (010) planes of the beta InSe is around 120 °C and SAED pattern in the direction of the incident zone axis $\langle 001 \rangle$ is shown in FIG. 71(d), these are consistent values compared with the reported hexagonal structure of beta InSe.⁷ The existence of the six-fold symmetry, together with the above pieces of evidence, ascertain the structure and purity of the InSe films.

FIG. 71 (a) Diagram showing the hexagonal bonding structure of InSe crystals. (b) Diagram showing the interplanar distance, d , of the InSe crystals. (c) Raman spectrum of the InSe crystal. Mapping of the distribution of elements of InSe: (d) the associated electron image, (e) mapping of

Se, (f) mapping of In. (g) Image of InSe, showing the stacking of different layers as viewed by HRTEM. (h) High magnification image and (i) corresponding SAED patterns of InSe sheet synthesized using microwave and as viewed by HRTEM.⁸

FIG. 72 EDS spectrum of InSe crystals.

6.1.2 h-BN as Passivation Layer and Long-Term Stability

FIG. 73 (a) A diagram showing the experimental setup and a representation of the BN encapsulated transistor. (b) I-V characteristic curves for the InSe transistors, one with the encapsulation of BN, the other without. The image of the transistor is shown in the inset. (c) I-V characteristic curves of the InSe transistor with BN encapsulation as a function of time. (d) The V-I characteristic curves of the BN-encapsulated transistor as a function of gate voltage.⁸

FIG. 73(a) is a diagram of the BN-covered InSe field emission transistor (FET) device that is electrically connected. With the bias voltage set at 5 V, the InSe transistor covered by a thin layer of BN film exhibits a typical semiconducting behaviour. Without such a covering, the transistor becomes insulative (FIG. 73(b)). The role of the h-BN layer is to be protective or commonly termed as a passivation layer, to protect and improve the performance of the InSe transistor beneath as the transistor is very sensitive to atmospheric contaminants like moisture. Because of such need, many InSe-based transistors have to be fabricated in an enclosed dry box to protect them from degradation.⁹ Due to the good protective effect, the InSe transistor maintains its semiconducting I-V characteristic, even after 2 months (FIG. 73(c)). Under the application of a gate bias from -70 V to 70 V, the I_{ds} significantly increases as the bias increases, this is shown in FIG. 73(d).

The mobility of the InSe transistor is governed by the following equation:¹⁰

$$\mu = \frac{L}{(WC_{ox}V_{ds})} \times \frac{dI_{ds}}{dV_g} \quad (1)$$

where L and W are the channel length and width, respectively. C_{ox} is the gate capacitance ($1.21 \times 10^{-4} \text{ Fm}^{-2}$), V_{ds} , I_{ds} and V_g are the bias voltage, current, and gate voltage, respectively. The mobility of the InSe transistor is calculated to be $6.3 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ which is higher than those of MoTe_2 ($0.2\text{-}20 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$) and also comparable to MoS_2 transistors ($1\text{-}50 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$).^{11,12} This is shown in the inset of FIG. 74(d).

6.1.3 Performances of the Fabricated Device

FIG. 74 (a) The I_{ds} - V_g curve of InSe transistor as a function of temperature ($^{\circ}\text{C}$). (b) Mobility as a function of temperature ($^{\circ}\text{C}$) for this InSe transistor. (c) The alignment of energy levels at the metal-InSe interface. Φ_m , Φ_{SBH} is the work function of metal and the Schottky barrier height, respectively. (d) Electron mobility of common 2D semiconductor materials, together with InSe transistor in this work for comparison.⁸

The electronics performances of the InSe transistor have to be measured and ascertained. Therefore, measurements were first conducted at room temperature, then from that to 200 $^{\circ}\text{C}$. The transport characteristic and the corresponding mobility of InSe FET are demonstrated in FIG. 9(a) and 9(b), the plots indicated an n-type semiconducting carrier transport. The increase in the electron mobility with temperature increasing from room temperature to 200 $^{\circ}\text{C}$ is more than ten-fold from 11.3 to 71.0 $\text{cm}^2\text{V}^{-1}\text{s}^{-1}$ as seen from the transfer curves. The band structure at the metal-InSe junction is determined to be a Schottky contact as seen in FIG. 9(c). The thermal emission equation describes the drain-source current (I_{ds}) as a function of the Schottky barrier height (Φ_{SBH}) is:¹³

$$I_{ds} = A_{2d}^* T^{\frac{3}{2}} \exp\left(\frac{q\Phi_{SBH}}{K_B T}\right) \left[1 - \exp\left(-\frac{qV_{ds}}{K_B T}\right)\right] \quad (2)$$

where A_{2d}^* is the equivalent Richardson constant, T is the temperature, k_B is the Boltzmann constant, q is the electronic charge, V_{ds} is the drain to source bias.

As the thermal emission current dominates when V_g is bounded by flat-band voltage (V_{FB}), once it exceeds V_{FB} , thermally assisted tunneling current will dominant. Subsequently, as the temperature increases, as shown in FIG 9(a), the current I_{ds} increases. For the ease and convenience of comparison, the bandgaps of many semiconductors are plotted as data points in FIG. 9(d). In general, many semiconductors have bandgap energy from 0.2 to 3 eV, as tabulated. Despite that, the devices exhibit a variety of transport behaviours. One such behaviour is the difference in electron mobility. For instance, the mobility of these semiconductors: PtSe₂, MoTe₂, and WSe₂ are generally below $30 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$,^{11,12,14} whereas that of SnS₂ and MoS₂ is slightly higher at around $\sim 40\text{-}60 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$.^{15,16} One explanation for the carrier transport of InSe is that it is predominantly electron as carriers, thereby possessing higher mobility ($125.8 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ at 200°C). Moreover, this device's performance does not degrade after 2 months and remains functional up to 200°C . This study may highlight some of the ways for easily degradable semiconductors such as InSe to be more deeply employed in the electrical and optoelectronic field. The discharge current can be explained by the equation.

6.2 h-BN Based Resistive Memory Device

6.2.1 Operation and Performance of the h-BN Based Resistive Memory Device

FIG. 75 (a) Schematic diagram and (b) HRTEM image of the Au/BN/CuO/Cu device stack structure.

A novel memory device based on such highly textured h-BN is presented as non-volatile memory device that plays a decisive role in high-speed information processing and high-capacity storage applications. FIG. 6(a) and FIG. 6(b) show a diagram of the Au/BN/CuO/Cu device stack structure and HRTEM image of the active region within the test device, respectively. The presence of the interfacial layer at the BN/Cu bottom electrode interface is indicated in the HRTEM result. The objective of our study is to understand the resistive switching behaviours of our BN-based device, therefore, voltage-sweep measurement under the direct current (DC) was conducted by connecting the top (Au) electrode at room temperature. Meanwhile, a semiconductor parameter analyser (Keithley SCS4200) was contacted at the bottom electrode (Cu) through the Au-coated tungsten probes (FIG. 6(a)). In a typical measurement process, an external voltage was directly applied to the Au electrodes while Cu electrode remained grounded. FIG. 6(c) shows a typical bipolar resistive switching behaviour (positive set/negative reset) of Au/BN/CuO/Cu device adhering to current compliance (CC) of 7 mA. Notably, forming is not needed for resistive switching. In general, the voltage varies from 0 to +0.6 V for the set switching of the device while the range is from 0 to -0.6 V for reset switching. Interestingly, switchable multiple resistance states are obtained by changing the CC level (FIG. 6(d)). This is vital for information storage and potential neuromorphic applications. Additionally, the device also shows the good repeatability of resistance switching, as presented in FIG. 6(d) and FIG. 6(f). The ON and OFF cycles of BN-based memory devices have been exhibited with excellent operation stability after 70 cycles, although some slight fluctuations were observed.

FIG. 76 (a) Current-voltage curves and (b) multiple resistance switching of Au/BN/CuO/Cu memory device under different current compliance (cc). (c) Repeatability resistance switching of the first 20 cycles in the device. (d) Endurance behaviour demonstration of the device.

6.2.2 Set/Reset Mechanism of h-BN Based Resistive Memory Device

FIG. 77 Illustrations of the resistive switching mechanism of Au/BN/CuO/Cu device. (a) application of a positive voltage causes the transport of oxygen anions from the BN layer towards the top electrode, resulting in the formation of conductive filaments consisting of oxygen vacancies (V_o) and (b) a subsequent polarity reversal, i.e. application of a negative voltage sweep pushes the oxygen anions back to the vacancy-rich breakdown path, culminating in a high resistance electrical gap.

The resistive switching phenomenon can be explained by the creation of a conductive channel, comprised of oxygen vacancies, in the CuO and BN layers (FIG. 7(a)). The generation of an oxygen-deprived soft-breakdown path (V_o filament) during the electroforming/set step has been widely reported in the oxide-based resistive memory devices¹⁷. The existence of an oxygen-deprived breakdown path is experimentally verified by the electron-energy loss spectroscopy study at the atomic scale.¹⁸ In the Au/BN/CuO/Cu sandwiched structure, the dissociation of Cu-O bond periodically occurs when the applied external electric field across the device is approaching the breakdown electric field of CuO layer, which is commonly present between the BN film and the Cu substrate. In this case, the oxygen anions dissociated from CuO layer first drift towards the Au electrode under the applied bias, and the simultaneous lateral outward drift occur in order to replenish the oxygen anions, which subsequently brings about a sharp change in current along the V_o -rich breakdown path. Moreover, as the current approach the current compliance (CC) limit, the continued-increasing current is cut-off by the analyser immediately to adhere to the CC limit. At this limit, accompanying with the effect of Joule heating, the minimization of the undesirable structural change of the V_o breakdown path happens. By contrast, as the negative voltage sweep is reversed, the oxygen anions were subsequently actuated back to the conductive path that is comprised of oxygen vacancies. Therefore, a gap is formed in the breakdown path, which may be attributed to part re-oxidization of the conductive path, as shown in FIG. 7(b). This cause the resistance to increase in the breakdown process, thereby causing the transition from low resistance to high resistance (e.g. a reset process). Lastly, as the positive voltage sweep drives the oxygen anions away from the re-oxidized part, thus connecting the conductive path again. This causes a reverse transition from high resistance to low resistance, which also means the set transition (switching back to the FIG. 7(a)).

Based on the above analysis, the presence of oxygen vacancy plays a crucial and essential role in the switching of h-BN memory. HRTEM is used to investigate the interface between the h-BN layer and copper substrate, ascertaining the presence of oxygen between these layers. As shown in FIG. 8(a), BN film and Cu substrate are distinct, whereas the CuO layer remains unclear, mainly owing to the small thickness of the CuO layer. However, the line scanning confirms the existence of oxygen, boron, nitrogen and copper (FIG. 8(b)). Moreover, element mapping also suggests the presence of an ultrathin CuO layer at interfaces (FIG. 8(c)). EDS analysis is further used to

investigate the presence of oxygen elements. FIG. 8(d) shows the elemental distributions of B, N, O, and Cu within the sample. It is noted that an oxide layer occurs at interfaces between h-BN film and Cu substrate. FIG. 8(e)-(f) are the HRTEM images of h-BN and copper zones, indicating the good crystallinity of Cu and h-BN. More importantly, the **FFT pattern** at the interface displays two distinct diffraction patterns at the interface. One is defined to be Cu [101] by indexing pattern, whereas another is found to be CuO [311], which is consistent with that reported in CuO/Cu nanowires¹⁹. Therefore, our h-BN memory device works well throughout by manipulating the oxygen vacancy in the CuO layer, thereby realizing the resistive switching under the positive and negative electric fields. Our textured h-BN memory device exhibits reproductive switching endurance and low power consumption. The resistive switching mechanism is related to the formation of a conductive channel, comprising of the oxygen vacancies at interfaces between the BN layer and copper substrate.

FIG. 78 (a) Cross-section TEM image of h-BN on the copper substrate using the FIB technique. (b) Line scanning and (c) EDS of h-BN on copper substrate. (d) Element mapping of the sample.

HRTEM image of (e) copper zone and (f) h-BN zone. The insets are the corresponding FFT patterns. (g) FFT pattern at interface between h-BN film and copper substrate.⁸

6.3 Isotopically Enriched h-BN Films with Self-Heat Dissipation Effects on GaN and AlGaN/GaN HEMTs

6.3.1 Dielectric Performances of h-BN Thin Films with Different Isotopic Compositions

FIG. 79 Dielectric dispersion and high field response of h-BN. (a) Dielectric constant and dielectric loss. (b) The influence of isotopic composition on dielectric constant and dielectric loss at 40 kHz. (c) Dielectric constant and dielectric loss are dependent on thickness. (d) The value of the breakdown field of h-BN in relation to the other common dielectric materials.²⁰

FIG. 79(a) plots the measured dielectric constant and its loss of h-BN thin films deposited, with its dependence on the applied frequency, which is within the MHz range. Values of the dielectric constant are measured to be around 5 to 7 within this range of frequencies, these values are similar to the values published in the literature.^{21,22} The dielectric constant is kept moderately constant in the MHz range, indicating its fitness in high power density electronic applications. In addition, the dielectric losses of the isotopically varied h-BN films are higher than those of pure hexagonal $B^{10}N$ and $B^{11}N$ samples, reaching the lowest value of 1.3%. FIG. 79(b) portrays, at 40 kHz, both the dielectric constant and loss with its dependence on the isotopic composition. The dielectric

constant corroborates with the values reported in the literature.^{21,22} This is not surprising due to the polycrystalline structure of h-BN. Considering the anisotropy of the dielectric constant of h-BN ($\epsilon_r = 3.38$ in-plane and $\epsilon_r = 6.61$ out-of-plane)²³, one should expect that a polycrystalline h-BN thin film's dielectric constant should be between the two anisotropic dielectric constants. The values are consistent within a 19.6% margin from the average value. The peak of the dielectric loss is measured for the film with isotopic composition of 60% B¹⁰-40% B¹¹. FIG. 79(c) highlights how the film thickness of the h-B¹⁰N thin film affects its dielectric constant. h-BN fulfils most of the criteria as an appropriate passivation layer as it possesses a low dielectric constant despite having a high breakdown field. From the perspective of enhancing electronic **performance**, it is good to note that the small increment of the dielectric constant resulting from the increment of thickness, coupled with a great redundancy in its dielectric loss (below 1.0%) is desirable. This is especially so in the high frequencies' domain. FIG. 79(d) summarizes the different breakdown field values of common dielectric materials, alongside with h-BN. Furthermore, its outstanding thermal performances, presents as a favourable option for heat dissipation in devices. Unfortunately, a common trade-off presented in the microstructure sculpturing of dielectric layer is the dilemma between breakdown field and dielectric constant. Usually, the high value of one would necessitate the lower value of the other, e.g. high breakdown field value is usually associated with lower dielectric constant. This presents a dilemma to an engineer whereby the ideal material as a dielectric layer would be the concurrently high dielectric and breakdown field values. As a dielectric layer, the high breakdown field is a benefit over other materials, yet, this would necessitate deposition a layer with a higher thickness due to the low dielectric constant. Therefore, h-BN films which are deposited using the HIPIMS present as a superior alternative depositing thicker h-BN, achieving both the avoidance of a high dielectric loss and while maintaining the benefit of a high breakdown field.

6.3.2 Electrical Performances of h-BN Thin Films with Different Isotopic Compositions

FIG. 80 Characterization of both the structures and electronic performances of isotopically enriched h-BN-coated GaN wafers. (a) An illustration of the BN/GaN heterostructure. (b) GaN substrate, its associated HRTEM image and corresponding FFT as its inset. (c) Raman spectra of isotopically varied h-BN films on GaN substrate. (d) Hall mobility, (e) sheet resistivity and (f) sheet concentration of BN-encapsulated GaN wafer.²⁰

GaN substrates were used as a substrate to grow these isotopically pure h-BN thin to learn more about the electronic properties. FIG. 80(a) shows a diagram of the BN-GaN heterostructure and similarly, the HRTEM of the GaN substrate is presented in FIG. 80(b), with its inset as the FFT of FIG. 80(b). The diffraction pattern of GaN substrate is presented in the FFT of FIG. 80(b). The value of the inter-planar distance, d , is about 0.512 nm.²⁴ The h-BN films with different isotopic concentrations are deposited on GaN substrate and its associated Raman spectra are presented in FIG. 80(c), distinct and yet expected variations between the energies of the E_{2g} phonon modes are seen. As expected, the film of $\text{h-B}^{10}\text{N}$ has the highest phonon energy/frequency whereas the film of $\text{h-B}^{11}\text{N}$ has the lowest phonon energy/frequency. The related FTIR spectra are plotted in FIG. 81. Prior to and after each deposition, the Hall mobility, sheet concentration and sheet resistivity were measured for these samples and are presented in FIG. 80(d) to FIG. 80(g), respectively. In general, post-deposition sheet resistivity decreases, Hall mobility increases, and the sheet concentration decrease for all the samples, with the exception of the sheet concentration of $\text{h-B}^{10}\text{N}$.

As the dielectric layer sandwiched between the electrodes and the GaN substrate performed well, there is an enhancement in the Hall mobility.²¹ Table 24 documents the percentage changes of these electronic properties after the deposition. The h-BN's low dielectric constant, combined with the high resistivity, enhance it to be an excellent dielectric layer between the interface of the GaN substrate and the Ohmic electrodes. Electric potential from the voltage applied to the gate was enhanced, similar to what was achieved in other transistors.^{25,26} Both the sheet resistivity and concentration showed noteworthy improvements after the deposition, demonstrating the effectiveness of h-BN as an encapsulating layer.

FIG. 81 FTIR spectra of h-B¹⁰N, h-B¹¹N and h-B^{NAT}N on GaN substrate.²⁰

Table 24 Post-deposition percentage change in electronic properties of h-BN thin films deposited on GaN substrates

Sample Label	Post-Deposition Percentage Change in Sheet Resistivity/ %	Post-Deposition Percentage Change in Hall Mobility / %	Post-Deposition Percentage Change in Sheet Concentration / %
h-B ¹⁰ N	-60.662	24.6732	17.34394
h-B ¹¹ N	-68.5439	56.3964	-36.3717
h-B ^{NAT} N	-14.6301	50.6982	-79.626

6.3.3 Electronic Performances of AlGaIn/GaN High Electron Mobility Transistors (HEMT) with h-B¹⁰N as Passivating, Heat Self-Dissipating Layer

FIG. 82 h-B¹⁰N-passivated GaN HEMT devices: Fabrication and electronic performances. (a) GaN/AlGaIn HEMT with h-B¹⁰N as the dielectric-gate layer: A diagram showing each layer of the HEMT. (b) The HEMT device as viewed by the TEM. (c) Elemental mapping of with a view of the cross-section of HEMT device using EDS (d) Illustration of the atomic structure and bonding at the GaN / AlGaIn interface. (e) Image of GaN-AlGaIn/GaN zone as viewed by HRTEM. (f) Line elemental mapping of this region distribution of Ga, N and Al which is periodical and as seen by EDS. (g) The I-V characteristics of the HEMT at room temperature. (h) The DC $I_{DS} - V_{DS}$ characteristic of the h-B¹⁰N-passivated GaN HEMT. (i) The transfer characteristics of the h-B¹⁰N-passivated GaN HEMT.²⁰

As the aim is to mitigate the self-heating thermal hot-spot problem in highly powered HEMT devices, DC performances of h-B¹⁰N as a passivation layer on the AlGaIn/GaN HEMT device was

measured. Furthermore, with h-B¹⁰N having the highest Hall mobility, a low drop in sheet resistivity post-deposition and a small rise in its sheet concentration value, it was deposited onto a HEMT device. FIG. 82(a) is an impression of the HEMT device with its different layers, the topmost layer is the h-B¹⁰N layer and beneath it is the GaN and AlGa_N/GaN heterostructure deposited onto a Si substrate. The different layered layers are shown in FIG. 82(b), shown by a cross-section HRTEM image. The elemental distributions of elements such as Ga, B, N, Al and Si across the thickness of the device (FIG. 82(c)) was illuminated by the line scan of EDS. The differently shaded regions are used to demarcate the different layers are, starting with the h-BN layer, continued by the GaN layer, followed by the AlGa_N/GaN heterostructure, then with a thin buffer layer of AlN between the AlGa_N/GaN heterostructure and finally, the Si substrate.

As AlGa_N and GaN inadvertently form a two-dimensional electron gas (2DEG) layer due to the formation of a potential well induced by the bandgap, a schematic showing the bonding and the atomic structures of GaN and AlGa_N is presented in FIG. 82(d). The highly magnified HRTEM image at the transition region between the AlGa_N and GaN layers is shown in FIG. 82(e) and the EDS line scan which confirms the highly lamellar structure of the 2DEG AlGa_N/GaN heterostructure is shown in FIG. 82(f).

Under standard operating conditions, HEMT device's I-V characteristics is shown on FIG. 82(g) to be linear, highlighting the ohmic behavior of the HEMT device. The DC performance of the GaN/h-B¹⁰N HEMT was measured) up to $V_D = 20$ V, as a function of gate voltage (from 0 V to 5 V) mainly so that dielectric breakdown can be avoided), is shown in FIG. 82(h). As shown in FIG. 82(h), as a result of self-heating effect, I_D falls below the maximum current density (I_{Dmax}). For the drain current density (I_{Dmax}), the highest value attained was 150.2 mA mm^{-1} However, the decline is only about 5.3%, much lower than the ~ 10% and ~ 27% of GaN/Diamond and GaN/SiC HEMTs, respectively.^{27,28} The measured transfer characteristics (FIG. 82(i)) provided a means to measure both transconductance ($g_{m \text{ max}}$) and drain current density (at $V_G = 0$ V), I_{DRM} . The highest extrinsic transconductance ($g_{m \text{ max}}$) was measured to be 33.82 mS mm^{-1} and the highest I_{DRM} of 171.1 mA mm^{-1} was attained. For different values of V_D , the change in $g_{m \text{ max}}$ at is minimal, which is in the range of 2.3% while I_{DRM} improves with increase in V_D . A small decline in effective mobility might have been indicated by a lower $g_{m \text{ max}}$ reduction which ascertains the lower degree of self-

heating effect plaguing the HEMT. This is primarily due to the enhanced heat spreading effect by the passivation layer. As a result, it is to be expected that the HEMT can operate with small power output at a high V_D and without facing a dilemma for current density and transconductance, which are both desired properties for GaN-based HEMT devices.

6.4 Conclusions

As it was set out in Chapter 1, Chapter 6 focuses on the applications of as-deposited h-BN thin films, with both controls in its degree of alignment and isotopic compositions. BN-passivated InSe transistor is functional even after 2 months and can function even at high temperatures, with moderately high mobility of up to $71.0 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$. It paves the way for h-BN to be used as an encapsulation layer for sensitive semiconductors in electronics. Using HIPIMS, not only can depositions be done at lower temperatures ($\sim 800 \text{ }^\circ\text{C}$) as compared to those arising from CVD methods ($> 1000 \text{ }^\circ\text{C}$) which would better preserve the integrity of the devices, micro-sculpturing of the films is possible as well.

The as-deposited h-BN memory device exhibits reproductive switching endurance and low power consumption. The mechanism behind the resistive switching phenomenon is proposed to be related to the formation of a conductive channel which is comprised of oxygen vacancies at interfaces between BN layer and copper substrate.

Finally, isotopically enriched electronic devices were discussed. Besides the fact that the device exhibits good thermal response, the dielectric dispersion of the isotopically varied films also has is dependent on the isotopic distribution of boron (B^{10} and B^{11}). The as-deposited h-BN films' dielectric constant ranges from 5 to 7, while the dielectric loss is less than 1.3%. Analysis of the hall mobility, and both the sheet resistivity and concentration of the films on GaN substrates were done, showing that h-BN does perform well as a dielectric layer, as exemplified by the DC performances and transfer characteristics of the h-BN encapsulated AlGaN/GaN HEMT. Owing to the lower self-heating effect of the HEMT due to the greater extent of heat dissipation via the h-BN encapsulation layer, a lower $g_{m \text{ max}}$ reduction of the HEMT device was achieved. This shows that the effective electron mobility of the HEMT was reduced slightly.

6.5 References

- 1 Z. Y. Zhang, C. S. Lee and W. J. Zhang, *Adv. Energy Mater.*, 2017, **7**, 1–20.
- 2 G. Wang, J. Zhang, S. Yang, F. Wang, X. Zhuang, K. Müllen and X. Feng, *Adv. Energy Mater.*, 2018, **8**, 1–8.
- 3 P. Zhang, J. Li, L. Lv, Y. Zhao and L. Qu, *ACS Nano*, 2017, **11**, 5087–5093.
- 4 A. Chaturvedi, A. Slabon, P. Hu, S. Feng, K. ke Zhang, R. R. Prabhakar and C. Kloc, *J. Cryst. Growth*, 2016, **450**, 140–147.
- 5 Z. Yang, W. Jie, C. H. Mak, S. Lin, H. Lin, X. Yang, F. Yan, S. P. Lau and J. Hao, *ACS Nano*, 2017, **11**, 4225–4236.
- 6 G. Han, Z. G. Chen, J. Drennan and J. Zou, *Small*, 2014, **10**, 2747–2765.
- 7 M. Li, C.-Y. Lin, S.-H. Yang, Y.-M. Chang, J.-K. Chang, F.-S. Yang, C. Zhong, W.-B. Jian, C.-H. Lien, C.-H. Ho, H.-J. Liu, R. Huang, W. Li, Y.-F. Lin and J. Chu, *Adv. Mater.*, 2018, **30**, 1803690.
- 8 S. S. Chng, M. Zhu, J. Wu, X. Wang, Z. K. Ng, K. Zhang, C. Liu, M. Shakerzadeh, S. Tsang and E. H. T. Teo, *J. Mater. Chem. C*, 2020, **8**, 4421–4431.
- 9 D. A. Bandurin, A. V. Tyurnina, G. L. Yu, A. Mishchenko, V. Zólyomi, S. V. Morozov, R. K. Kumar, R. V. Gorbachev, Z. R. Kudrynskyi, S. Pezzini, Z. D. Kovalyuk, U. Zeitler, K. S. Novoselov, A. Patané, L. Eaves, I. V. Grigorieva, V. I. Fal’Ko, A. K. Geim and Y. Cao, *Nat. Nanotechnol.*, 2017, **12**, 223–227.
- 10 M. Zhu, J. Wu, Z. Du, S. Tsang and E. H. T. Teo, *J. Appl. Phys.*, 2018, **124**, 215302.
- 11 B. Sirota, N. Glavin, S. Krylyuk, A. V. Davydov and A. A. Voevodin, *Sci. Rep.*, 2018, **8**, 1–8.
- 12 W. L. Chow, P. Yu, F. Liu, J. Hong, X. Wang, Q. Zeng, C. H. Hsu, C. Zhu, J. Zhou, X. Wang, J. Xia, J. Yan, Y. Chen, D. Wu, T. Yu, Z. Shen, H. Lin, C. Jin, B. K. Tay and Z. Liu, *Adv. Mater.*, 2017, **29**, 1–8.
- 13 J. Wang, Q. Yao, C. W. Huang, X. Zou, L. Liao, S. Chen, Z. Fan, K. Zhang, W. Wu, X. Xiao, C. Jiang and W. W. Wu, *Adv. Mater.*, 2016, **28**, 8302–8308.
- 14 M. A. Stoeckel, M. Gobbi, T. Leydecker, Y. Wang, M. Eredia, S. Bonacchi, R. Verucchi, M. Timpel, M. V. Nardi, E. Orgiu and P. Samorì, *ACS Nano*, 2019, **13**, 11613–11622.
- 15 H. S. Song, S. L. Li, L. Gao, Y. Xu, K. Ueno, J. Tang, Y. B. Cheng and K. Tsukagoshi, *Nanoscale*, 2013, **5**, 9666–9670.

- 16 M. M. Perera, M. W. Lin, H. J. Chuang, B. P. Chamlagain, C. Wang, X. Tan, M. M. C. Cheng, D. Tománek and Z. Zhou, *ACS Nano*, 2013, **7**, 4449–4458.
- 17 H. Zhang, X. Ju, Y. Zhou, C. Gu, J. Pan and D. S. Ang, *ACS Appl. Mater. Interfaces*, 2019, **11**, 41490–41496.
- 18 H. Zhang, X. Ju, K. S. Yew and D. S. Ang, *ACS Appl. Mater. Interfaces*, 2019, **12**, 1036–1045.
- 19 B. Zhang, B. Chen, J. Wu, S. Hao, G. Yang, X. Cao, L. Jing, M. Zhu, S. H. Tsang, E. H. T. Teo and Y. Huang, *Small*, 2017, **13**, 1603411.
- 20 S. S. Chng, M. Zhu, Z. Du, X. Wang, M. Whiteside, Z. K. Ng, M. Shakerzadeh, S. H. Tsang and E. H. T. Teo, *J. Mater. Chem. C*, 2020, **8**, 9558–9568.
- 21 N. R. Glavin, C. Muratore, M. L. Jespersen, J. Hu, P. T. Hagerty, A. M. Hilton, A. T. Blake, C. A. Grabowski, M. F. Durstock, M. E. McConney, D. M. Hilgefort, T. S. Fisher and A. A. Voevodin, *Adv. Funct. Mater.*, 2016, **26**, 2640–2647.
- 22 Y. Hattori, T. Taniguchi, K. Watanabe and K. Nagashio, *ACS Appl. Mater. Interfaces*, 2016, **8**, 27877–27884.
- 23 N. Ohba, K. Miwa, N. Nagasako and A. Fukumoto, *Phys. Rev. B*, 2001, **63**, 115207.
- 24 J. Lee, Y. Park, C. Yang, H. Kim, K. Kim, K. Kang, T. Kang, S. Park and J. Lee, *J. Cryst. Growth*, 2000, **213**, 33–39.
- 25 N. Petrone, T. Chari, I. Meric, L. Wang, K. L. Shepard and J. Hone, *ACS Nano*, 2015, **9**, 8953–8959.
- 26 Y. Kobayashi, K. Kumakura, T. Akasaka and T. Makimoto, *Nature*, 2012, **484**, 223–227.
- 27 K. Ranjan, S. Arulkumaran, G. I. Ng and A. Sandupatla, *IEEE J. Electron Devices Soc.*, 2019, **7**, 1264–1269.
- 28 K. Takagi, S. Takatsuka, Y. Kashiwabara, S. Teramoto, K. Matsushita, H. Sakurai, K. Onodera, H. Kawasaki, Y. Takada and K. Tsuda, in *2009 IEEE MTT-S International Microwave Symposium Digest*, IEEE, 2009, pp. 457–460.

7 Conclusions

This chapter will summarize the contributions made by the author towards the realization of applications utilizing aligned h-BN deposited with HIPIMS, as stated in the Objectives in the Introduction chapter.

7.1 On the Study of Deposition of h-BN using LaB₆ / pure-Boron Source

On the study of the depositions of h-BN thin films using LaB₆ or pure boron source, the following conclusions are made:

7.1.1 Deposition using LaB₆ Source

A simple experiment was conducted to ascertain how the thicknesses of the thin film growth are distributed on the wafer. The thickness distribution of h-BN on a 4" wafer taped to the substrate holder as it is in a typical experimental set-up follows a Gaussian-like distribution. The peak of the thickness distribution nearly coincides with the geometric centre of the wafer. The thickness of the h-BN films causes a shift in the energies of the E_{1u} and A_{2u} phonon modes. At low thicknesses, a redshift is observed in both modes. At higher thicknesses, ~ 2 μm or more, the energies of the phonons approach those observed in bulk h-BN. Interestingly, the R value, a measure of the degree of alignment of h-BN with respect to the substrate, is dependent on the thin film thickness. There is a direct relationship between the R value of a thin film and its thickness. There is a direct relationship between the R value of a thin film and both the peak current and power density of the deposition.

The method of calculating the proportion of the intensity of a FTIR vibrational mode with respect to that of another mode is well-known as a pseudo-quantification technique that is used to establish the presence and its relative abundance in the sample for a species. This method has been used to justify the efficacy of deposition techniques for the synthesis of c-BN and subsequently h-BN. For instance, c-BN TO mode increment is used as evidence showing a deposition parameter is positively correlated to the relative abundance of the c-BN phase within a BN sample. However, this thesis found that thickness of the thin film sample strongly correlates with the ratio, i.e. the ratio of the A_{2u} vibrational mode with respect to the E_{1u} vibrational mode is dependent on both the

alignment of the sample and the thickness of the sample. Without accounting for its dependence on the thickness of the samples grown, the comparison of R value between different samples of different thicknesses is unjustified. This result highlights the need to have thickness of the sample accounted for when evaluating its R value.

Deposition on GaN results in polycrystalline structure of h-BN with some degree of overall alignment. This is a preliminary exploration of deposition of h-BN onto GaN substrates as many devices use III-V semiconductors as its substrate.

7.1.2 Deposition using Boron Source

A method to deposit pure boron using HIPIMS is explored. Oxidation of h-BN thin films due to imperfect stoichiometry was studied. Oxidation of the films was found to be due to exposure to the atmospheric environment. Temperature and Pulse Length were two parameters chosen to be studied. It was found that sputtering at 800 °C and with a pulse length of 25 μ s resulted in better quality h-BN thin films that oxidise to a much lesser extent upon exposure to atmospheric conditions. It is important that deposited films remain stable in standard atmospheric conditions. In order to fully take advantage of h-BN interesting opto-electronic and thermal properties, it needs to first be able to function under standard atmospheric conditions. The oxidation of h-BN under standard atmospheric conditions poses a problem for its use in electronic devices. Depositing the films at an elevated temperature, determined empirically to be around 800 °C greatly alleviates the problem but does not fully resolve it. Films deposited at 800 °C on <100> silicon substrates show slight signs of oxidation or degradation due to atmospheric contact after months of storage in a dry box. While complete eradication of the problem remains elusive, this thesis provides a working solution that is usable in device fabrication.

7.2 On h-BN Thin Films as Encapsulating Layer for InSe Transistors

As the thesis focused on applications of synthesized h-BN thin films with controllable microstructures, h-BN thin films were deposited onto devices to study its effect on device performances as an encapsulating layer. The alignment of h-BN tuned via the reactive gas flow rate ratio was first studied. It was found that through the control of gas flow rate ratio of nitrogen gas, the alignment of the h-BN thin films is controllable. There exists an interval from 20% to 30%

in which sputtering in this mixed nitrogen environment can result in aligned h-BN thin films. The resultant thermal conductivity of the orientated h-BN thin film was measured to be 300% more than that of the polycrystalline h-BN thin film.

The thermal conductivities of both the aligned and the polycrystalline h-BN drop by around 40% at higher temperatures (measured from room temperature to 300 °C), this highlights the superior stability of the h-BN thin films deposited. Post-encapsulation, the InSe transistor becomes semiconducting. The encapsulation remains good even after two months and the device remains functional. This highlights that the h-BN thin films function well as an encapsulating layer.

7.3 On h-BN Thin Films as a Novel Memory Resistive Device

A second method of sculpturing the microstructure of h-BN thin films was experimented with. Control of the alignment of h-BN was shown to be attainable via the control of average power supplied to the target. The higher average power supplied to the target during sputtering tends to result in a polycrystalline microstructure. The bandgap of the dense polycrystalline h-BN is lower (5.33 eV) than that of the porous aligned h-BN (5.77 eV). The thermal conductivity of the orientated h-BN film is about 354% more than that of the polycrystalline h-BN thin film. The thermal conductivities of both h-BN thin films, both polycrystalline and aligned, are relatively stable, they are within a 25% margin from room temperature up to 300 °C. The memory device was shown to be working. The proposed mechanism for such an action is the migration of oxygen vacancies, resulting in a conductive filament between the electrodes. However, the endurance of the memory device is still low as compared to industrial standards. Furthermore, the porosity of the h-BN film may have degraded the capacity of the thin film to perform its memory effect.

7.4 On Isotopically Enriched h-BN Thin Films as Heat-Dissipative Layer on High-Powered Transistors

Using dual magnetron HIPIMS sputtering, isotopically enriched and controlled h-BN thin films can be deposited, as it was shown experimentally. The Raman and FTIR spectra of these isotopically modified h-BN thin films have phonons with energies that are dependent on the films' isotopic compositions. Comparing to the isotopically varied samples (i.e. isotopically-unenhanced h-BN films), the thermal conductivity of h-B¹⁰N and h-B¹¹N were improved more than twice. The

origins of such an improvement in thermal conductivity are well understood, isotopic scattering of phonons is reduced in its extent in an isotopically pure thin film.

The percentage enhancement of thermal conductivity at 300 °C for all the samples is around 8.5%. Although, one should expect a decrease in thermal conductivity at higher temperatures due to Umklapp scattering, in this case, the enhancement in the alignment of h-BN at high temperatures may bring about a stronger effect resulting in an increment in the thermal conductivity of the thin films, outweighing the effects of Umklapp scattering. The dielectric constant of the h-BN films deposited ranges from 4 – 7, in the same order of magnitude as it is in the literature. Post-deposition on GaN substrate, sheet resistivity increases, Hall mobility decreases, and for all the samples, the sheet concentration decreases, with the exception of h-B¹⁰N, whose value increased slightly. These results are well explained by the deposition process and evidenced through the strong ion implantation. h-B¹⁰N was deposited on a GaN-AlGa_xN HEMTs. The results show that h-B¹⁰N passivated GaN-AlGa_xN HEMT is feasible.

In this work, control of microstructure is neglected as compared to depositing isotopically controlled/enriched h-BN thin films. The control of isotope composition was given a higher priority due to the novelty of using dual magnetron sputtering to deposit isotopically controlled h-BN samples. This adds to the material engineer's toolkit. Now, such an engineer is able to make use of sputtering, with all its associated advantages, to deposit isotopically enriched h-BN.

7.5 Future Work

7.5.1 On the Deposition using a Pure Boron Source

Alignment of h-BN thin film using a pure boron source was achieved. However, the thin film is porous as seen from the TEM images. The porosity of the thin films is still not well understood. Furthermore, at room temperature, the films deposited interact strongly with moisture in the atmospheric once exposed. This severely degrades the quality of the film, converting residual boron species within the sample into boric acid, rendering the film to be unsuitable for device application. Future work can be done on investigating how to create a dense aligned h-BN thin film from a pure boron source at room temperature that does not degrade upon exposure to the atmosphere.

Also, more work needs to be done to understand the mechanism of how the gas flow ratio affects the alignment of the h-BN thin films deposited. For instance, to investigate the veracity of the proposed mechanism, possible evidence gleaned from atomic measurements of stoichiometry may lend credence to this mechanism. Alternatively, mass spectrometry techniques may investigate how ion bombardment of different species (nitrogen vis-à-vis argon) may result in stress differential, influencing the degree of alignment of deposited films.

7.5.2 On Encapsulating Layer on InSe Transistors

The mobility of the encapsulated InSe transistors at room temperature is around $6.3 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ about 10 times lower than MoS₂ transistors. As HIPIMS uses highly energized ions to deposit h-BN, the ion implantation process may have caused damage to the structure of InSe near the channel surface. A method that allows for aligned h-BN to be deposited with little damage done to the device and continues to maintain the aligned nature of the h-BN deposited needs to be sought after.

Unfortunately, this thesis does not explore the industrial applications of these devices and how h-BN can be deposited at a scale using HIPIMS that is suited for industrial needs. Further work and effort can be used to tackle the wide-scale applications of h-BN films at the industrial level on perfecting the technique to deposit h-BN thin films on electronic devices, such as HEMTs.

7.5.3 On Isotope Engineering of h-BN Thin Films

Dual magnetron sputtering with B¹⁰ and B¹¹ targets does give rise to isotopically modified h-BN thin films. However, the microstructure of such thin films is unknown, and the influence of different deposition parameters is yet unknown. It is possible that new sculpturing of h-BN thin films with isotopic variations can be done through the control of deposition parameters of each of the magnetrons. However, parameter studies of dual-magnetron sputtering may be challenging due to the doubling of deposition parameters. Statistical techniques may need to be used to explore a substantial portion of the parameter space to infer the outcome of possible experiments and from it, derive a possible optimal set of values for the deposition parameters and to verify it via actual experiment. Coupled with the issues faced by sputtering with pure boron sources, a solution in the direction of discovering a mechanism to isotopically-enrich lanthanum hexaboride can be

considered. Sputtering of boron-10/11 enriched lanthanum hexaboride would create a dense, aligned and isotopically-pure h-BN thin film at room temperature. However, the cost of such enrichment may be prohibitive and for applications that are sensitive to lanthanum concentration, this method may not be suitable.

7.5.4 On h-BN as Passivating Layer on AlGaN/GaN HEMTs

It seems that the ion implantation of boron or nitrogen ions penetrates deeply into the layered structure of HEMTs, interrupted the working of the 2-dimensional electron gas (2DEG), causing a drop in the mobility of the electrons. Similarly, a solution that preserves the structure of HEMT or any underlying transistor while obtaining an aligned h-BN as passivation layer should be sought. A trade-off here is easily seen. A highly energized deposition will bring about an aligned h-BN film deposited on the underlying substrate while damages the substrate due to high ion impact. Mobility of the underlying substrate may be regained via annealing but how annealing influence the alignment of the film remains unclear. Future work may explore how post-deposition annealing or other processes may alter the microstructure of the as-deposited h-BN thin film. Other deposition techniques utilize low-energetic ion bombardment, possibly via the control of deposition parameters or via other PVD methods and/or using a different boron-containing target as a deposition source.

7.6 Final Concluding Remarks

This thesis aims to bring the advantages of h-BN through the micro-sculpturing of its microstructure to advance the performances of opto-electronic devices. It does so primarily by making use of h-BN superior thermal properties and stability at elevated temperatures. It also took advantage of the dual-sputtering HIPIMS technique to control the films isotopic composition. The thesis gives a first impression of how the h-BN thin films can be applied to various electronic devices and some results on its viability have been obtained and presented. More exploration into this exciting application space awaits future researchers to devote their time and energies. Primary emphasis should be on synthesizing usable thin films to be applied than to perfect the deposition conditions as the latter would yield little rewards.