Phase evolution of boron nitride and carbide during chemical vapor deposition

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Chemical Vapor Deposition

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Background photo: Cropped photo of the night sky and northern lights in Kiruna, Sweden. Photo taken by Gabriele Tripiti during our trip in December 2020.

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Description: Over and under the title are five plan view scanning electron micrographs of crystalline materials investigated in this work. Additional scattered salt and sugar crystals seen on the cover are a vector image purchased from LarTrehubova/Shutterstock.com.

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If you got the will to do it,
but lack the skills to do it good,
Ask for help.

-Kings of Convenience
Abstract

Thin films of Boron Nitride (BN) and Boron Carbide (BC) possess properties that make them attractive for various applications. Epitaxially grown BN exhibits potential for optoelectronic devices, as piezoelectric materials, and graphene technology. Epitaxial BC is a semiconductor that could allow bandgap tuning and has potential applications in thermoelectric and optoelectronic devices. Both BN and BC material systems, generally deposited using chemical vapour deposition (CVD), are limited by the lack of control in depositing epitaxial films. In my thesis work, I have studied the evolution of various crystal phases of BN and BC and the factors that affect them during their CVD processes.

I deposited and compared the growth of BN on Al₂O₃(0001), (11̅20), (11̅02) and (10̅10) substrates and used two organoboranes as boron precursors. Only Al₂O₃(11̅20) and Al₂O₃(0001) rendered crystalline films while the BN growth on the remaining substrates was X-ray amorphous. Furthermore, the less investigated Al₂O₃(11̅20) had better crystalline quality versus the commonly used Al₂O₃(0001). To further understand this, I studied crystalline BN thin films on an atomic scale and with a time evolution approach, uncovering the influence of carbon on hexagonal BN (h-BN). I showed that h-BN nucleates on both substrates but then either polytype transforms to rhombohedral-BN (r-BN) in stages, turns to less ordered turbostratic-BN or is terminated. An increase in local carbon content is the cause of these changes in epitaxial BN films during CVD. From the time evolution, we studied the effect of Al₂O₃ modification on h-BN nucleation during CVD. The interaction between boron and carbon during BN growth motivated studies also on the B:C materials.

B:C was deposited using CVD at different temperatures on 4H-SiC(0001) (Si-face) and 4H-SiC(0001)[11̅1̅0] (C-face) substrates. Epitaxial rhombohedral-B₄C (r-B₄C) grew at 1300 °C on the C-face while the films deposited on the Si-face were polycrystalline. Comparing the initial nucleation layers on both 4H-SiC substrates on an atomic scale we showed that no interface phenomena are affecting epitaxial r-B₄C growth conditions. We suggest that the difference in surface energy on the two substrate surfaces is the most plausible reason for the differences in epitaxial r-B₄C growth conditions.

In this thesis work, I identify the challenges and propose alternative routes to synthesise epitaxial BN and B:C materials using CVD. This fundamental materials science work enhances the understanding of growing these material systems epitaxially and in doing so furthers their development.
Populärvetenskaplig Sammanfattning


skikten. Framför allt har väldigt kraftfulla mikroskop varit viktiga instrument. Genom att ersätta vanligt synligt ljus med en elektronstråle blir mikroskopet så kraftfullt att man kan se de enskilda atomerna i materialet. När jag studerat skikt som vuxit fram med olika processparametrar har jag hittat små variationer på atomnivå som kan förklara varför olika faser av materialet växer fram.


När jag studerade BₓC kunde jag belägga skikt av B₄C på ytor av kiselkarbid (SiC). Vi upptäckte att en SiC-yta som avslutats med kolatomer var bättre att växa B₄C på än en SiC-yta som avslutats med kiselatomer. För att förstå vad som gav denna skillnad tog jag hjälp av elektronmikroskopet. Vi kunde visa att skillnaden i B₄C-kristalltillväxten på de två kiselkarbidsnitten beror på skillnaden i tillgängligheten av kolatomer mellan de två ytorerna. Mera kolatomer verkar görs det enklare att börja bilda B₄C-kristallen på ytan. Men även här verkar för mycket kolatomer på ytan förstöra tillväxten av B₄C.

Sammanfattningsvis har mitt avhandlingsarbete bidragit med mer detaljerad kunskap kring hur kristallfaserna av BN och BₓC styrs av olika parametrar i CVD-processen. Detta bidrar med ett par pusselbitar till att kunna skapa tunna skikt av materialen på ett mera kontrollerat sätt för att, till slut, kunna använda dem för nya tillämpningar.
Preface

This thesis is the result of my PhD studies, conducted between December 2019 and May 2024 at the Thin Film Division of the Department of Physics, Chemistry and Biology (IFM) at Linköping University.

This work was supported by the Swedish Research Council contract 2017-04164.

During the course of research underlying this thesis, I was enrolled in Agora Materiae, a multidisciplinary doctoral program at Linköping University, Sweden. Agora Materiae is supported by the International Interdisciplinary Laboratory for Advanced Functional Materials (AFM).

During my studies I was a student council representative at the Department level (IFM); DoStuC and at a university-level association (section); LiUPhD.
Acknowledgement

I confidently write this thesis work thanks to the talented individuals who have taught and supported me in my educational journey as a PhD candidate. I never had to search far for guidance and support whenever I needed it and I got it even when I didn’t expect it. I truly appreciate my colleagues, friends, and family who were always there for me. You have my heartfelt gratitude.

I want to sincerely thank my supervisor Hans Högb erg for all his guidance throughout my studies. For all the discussions and showing me the different ways to approach a research question or a discussion point. Your valuable input has given my work another dimension. I appreciate how you are always positive about my results, even when I was doubtful. I am grateful for all the help you have given me and the light-hearted recommendations you gave for my trips.

I am grateful to my co-supervisor Henrik Pedersen for the guidance with my research and in other parts of my learnings as a PhD candidate. Working with you inspires me to be more efficient and decisive in my approach to problems. You have always made a safe environment for me to share my concerns in both research and outside of it. Thank you for all the fruitful discussions and for training me on how to navigate the various obstacles I faced during my PhD candidacy.

I am grateful to both of my supervisors. I think we made a great team.

I want to thank Laurent Souqui for training me to use Maggan. For helping in the repairs and maintaining this reliable but admittedly troublesome reactor at the beginning of this project. For training me in different characterisation techniques and for all the contributions to our manuscripts. I have learned a lot from you and enjoyed the time spent outside of work. I am grateful for my fellow Boron boy, Arun Haridas Choolakkal. For your support in solving the reactor issues together and for being my officemate with whom I could openly discuss science and more.

I am grateful for all the training and help I received with different characterisation techniques. I’m thankful to Justinas Palisaitis for the training in TEM sample preparation, for performing the TEM measurements and for showing me how to do the data analysis. Sebastian Ekeroth for training me in different research skills during my Master thesis work including SEM, XRD and PVD. Arnaud Le Febvrier and Fredrik Eriksson for helping me with my questions related to XRD. Mauricio Sortica at the Tandem Laboratory in Uppsala for all the help with the ERDA measurements.
I want to thank all my co-authors for their contributions, in particular, Per Persson for the valuable discussions and input to the manuscripts and Ivan Gueorguiev Ivanov for his help with Raman.

I thank the present and past members of the Pedersen Group. Our discussions and feedback given during the meetings have helped push my work forward. I thank my friends in the unit, Johan and Claudia for their constant support. I thank my friends in Agora Materiae for the research seminars and the fun times on the study trips. Caroline Brommesson for your support through the mentor program and for inviting me to organise a study visit myself, I learned a lot from it. I am grateful to the members of DoStuC for the interesting work projects and activities, it was a pleasure working together. I thank the members of the Thin Film Division for their input and feedback during the division meetings. Through these different groups, I met many interesting people and made some friends as well. I have thoroughly enjoyed our time together, especially when we connected beyond our work. I thank Samiran, Jui-Che, Pernilla, Anton, Marcus, Guzlada, Pamburayi, Pentti, Jing-Jia, Rodrigo, Davide, Victor, Nikos and many others for the fun times after work, conferences and study visits.

I made some great friends outside the university during this project, their support and ability make me excited for what comes after work is something that I truly appreciate. I thank in particular Gianluca, Gabriele, Izabella, Joakim, Sid, Kristoffer, Johan, the British gang and Lars for tolerating my goofy tendencies. I am grateful to my middle-school friends, Bikram and Harjot, we are apart in distance but it felt like you were with me throughout my PhD studies. I thank my friends and cousins back home and the international friends I met in Sweden. I appreciate your welcoming nature no matter how long distance or time separated us or how bad my long-distance communication can be at times.

I am grateful for my biggest and longest support systems, my Mother, Sonia and my Father, Ajay. I would not be here without you two. Thank you for constantly reminding me that I will always be your kid in your eyes. It humbles and tells me that some things (for better or for worse) will never change.

I want to thank Sofia, the person who gives my life structure and inspires me to do better. She is one of the strongest people I know. Finally, my favourite four-legged creature, Otis is one of the cuddliest and weakest non-people that I know.

-Sachin Sharma, writing this in my office. It’s 7:30 pm in the middle of April, it’s pouring, and I’m dreading the bike ride home. My love-hate relationship with the Swedish weather continues.
List of included articles and contributions

Paper I

Chemical vapor deposition of sp²-boron nitride films on Al₂O₃ (0001), (1120), (1̅1̅02) and (10̅1̅0) substrates

Sachin Sharma, Laurent Souqui, Henrik Pedersen, Hans Högberg

J. Vac. Sci. Technol. A 40, 033404 (2022)

DOI: https://doi.org/10.1116/6.0001672

I planned and performed all the depositions. I conducted sample characterisations and analysed various XRD, SEM, FTIR, and ERDA measurement results. I did the data analysis for all the characterisation results presented in the article. I participated in the discussions with the co-authors. I drafted the manuscript and finalised it by incorporating the comments from the co-authors.

Paper II

The influence of carbon on polytype and growth stability of epitaxial hexagonal boron nitride films

Sachin Sharma, Justinas Palisaitis, Ivan G. Ivanov, Per O.Å. Persson, Henrik Pedersen, and Hans Högberg

Adv. Mater. Interfaces 2024, 2400091

DOI: https://doi.org/10.1002/admi.202400091

I planned and performed all the depositions. I conducted sample preparation for the TEM samples and was involved with the characterisation process of the TEM-based results. I discussed the parameters for Raman analysis. I did the data analysis for all the characterisation results presented in the article. I participated in the discussions with the co-authors. I drafted the manuscript and finalised it by incorporating the comments from the co-authors.
Paper III

The interface between sapphire and chemical vapor deposition grown hexagonal boron nitride

Sachin Sharma, Justinas Palisaitis, Per O.Å. Persson, Henrik Pedersen, and Hans Högberg

In Manuscript

I planned and performed all the depositions. I conducted sample preparation for the TEM samples and was involved with the characterisation process of the TEM-based results. I did the data analysis for all the characterisation results presented in the article. I participated in the discussions with the co-authors. I drafted the manuscript and finalised it by incorporating the comments from the co-authors.

Paper IV

Texture evolution in rhombohedral boron carbide films grown on 4H-SiC(0001) and 4H-SiC(0001) substrates by chemical vapor deposition

Laurent Souqui; Sachin Sharma; Hans Högberg; Henrik Pedersen

Dalton Trans., 2022, 51, 15974-15982

DOI: https://doi.org/10.1039/D2DT02107B

I assisted in the depositions of the samples. I performed cross-section SEM measurements and analysed the data. I analysed the ToF-ERDA data and applied the results in the right context. I conducted rocking curve XRD measurements and analysed the results. I contributed with comments on the article draft and was involved in scientific discussions with the co-authors.
Paper V

On the origin of epitaxial rhombohedral-B₄C growth by CVD on 4H-SiC

Sachin Sharma, Laurent Souqui, Justinas Palisaitis, Duc Quang Hoang, Ivan G. Ivanov, Per O.Å. Persson, Hans Högberg and Henrik Pedersen

Submitted for publication

I planned the study. I conducted sample preparation for the TEM samples and was involved with the characterisation process of the TEM-based results. I suggested parameters for Raman analysis. I did the data analysis for all the characterisation results presented in the article. I participated in the discussions with the co-authors. I drafted the manuscript and finalised it by incorporating the comments from the co-authors.

Articles not included in the thesis

Paper A

Rhombohedral and turbostratic boron nitride: X-ray diffraction and photoluminescence signatures

Matthieu Moret, Adrien Rousseau, Pierre Valvin, Sachin Sharma, Laurent Souqui, Henrik Pedersen, Hans Högberg, Guillaume Cassabois, Jianhan Li, J. H. Edgar, Bernard Gil

Appl. Phys. Lett. 119, 262102 (2021)

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I planned and performed all the depositions. I performed all the XRD-based characterisations and analysed the results. I wrote the text regarding the deposition technique, boron nitride introduction, and the XRD analysis. I contributed with comments on the article draft and was involved in scientific discussions with the co-authors.
I performed the depositions. I performed the XRD and SEM-based characterisations and analysed the results. I contributed with comments on the article draft and was involved in scientific discussions with the co-authors.
# Table of contents

1. Introduction ............................................................................................................. 1

2. Material systems investigated .................................................................................. 3
   2.1. Boron Nitride ........................................................................................................ 3
       2.1.1. Properties and Applications of sp²-Boron Nitride ........................................... 5
   2.2. Boron Carbide ...................................................................................................... 6
       2.2.1. Properties and Applications of Boron Carbide ................................................ 8

3. Chemical vapour deposition ....................................................................................... 9
   3.1. CVD configurations ............................................................................................... 9
   3.2. Fundamentals of Thermal CVD ............................................................................ 10
   3.3. Horizontal Hot-Wall CVD system used - "Maggan" ............................................. 13

4. CVD of sp²-Boron Nitride and Boron Carbide ......................................................... 17
   4.1. Precursors used in this work ............................................................................... 17
   4.2. Substrates used in this work ............................................................................... 19
       4.2.1. Al₂O₃ substrates used for sp²-Boron Nitride .................................................... 19
       4.2.2. SiC substrates used for Boron Carbide ............................................................ 21

5. Characterisation Techniques .................................................................................... 23
   5.1. X-ray Diffraction Techniques ............................................................................. 23
   5.2. Microscopy techniques ....................................................................................... 28
       5.2.1. Scanning Electron Microscopy ...................................................................... 28
       5.2.2. Transmission Electron Microscopy ................................................................. 31
5.3. Ion beam technique

5.3.1. Time-of-Flight Elastic Recoil Detection Analysis

5.4. Spectroscopy techniques

5.4.1. Fourier Transform Infrared Spectroscopy

5.4.2. Raman Spectroscopy

6. Summary and contribution to the field

7. Future outlook

8. References

Included Papers
1. Introduction

Historians used material systems like the Stone, Bronze, and Iron Ages to define different periods because important aspects of any civilisation have been heavily influenced by the technology and tools available to them. In modern times, material properties have become more diverse to keep up with technological and industrial advancements. This diversity motivates the research on complex material systems that are not mined but instead synthetically designed and synthesised for their specific properties and applications. Today, modern-day electronics are at the forefront of technological advancements. Their needs heavily rely on the advancements in Materials Science, specifically in semiconductor materials.

Boron nitride (BN) is a type of semiconductor compound that belongs to group-13 nitrides or III-nitride group of semiconductor materials. Although it is not as mature as other group-13 nitrides like gallium-, aluminium- or indium-nitride, a lot of promising properties for this compound have already been reported. However, despite its potential, crystalline BN is not yet being used as a stand-alone semiconductor material for industrial-scale applications. This is mainly due to the challenges in synthesising BN thin films that can sustain phase pure continued epitaxial growth. As a consequence of this, crystalline BN research in recent times has focused more on few-layer 2D BN growth and its applications. The first part of this thesis work is motivated by the need to further our fundamental understanding of the factors, both global and local, that influence epitaxial BN growth conditions in chemical vapour deposition (CVD). Working with many characterisation techniques in combination, and by using different deposition parameters, I identify the possible reasons for the formation of different BN phases and suggest deposition routes that could circumvent their formation to grow phase pure epitaxial BN thin films.

The next part of this work is motivated by the observed relationship between boron, carbon, and nitrogen during BN thin film deposition resulting from the precursors used. The boron precursors that have been employed to deposit BN films are the organoboranes, triethylborane $\text{B(C}_2\text{H}_5)_3$ (TEB), trimethylborane $\text{B(CH}_3)_3$ (TMB) and $\text{NH}_3$ as the nitrogen precursor. In the absence of $\text{NH}_3$, I can
investigate the relationship between boron and carbon in another boron-based material system, Boron Carbide (B\textsubscript{4}C). B\textsubscript{4}C, as a ceramic has seen more frequent use in industrial applications, but is another material that, in its crystalline form, is promising for various semiconductor applications. With the recognised stable ratios of B\textsubscript{4}C or B\textsubscript{2}C\textsubscript{5}, epitaxial growth of B\textsubscript{4}C is observed as rhombohedral-B\textsubscript{4}C (r-B\textsubscript{4}C) in this work. An analytical approach, in the same vein as the one used for the BN material system, allows me to further the fundamental understanding of the epitaxial growth conditions for r-B\textsubscript{4}C in CVD. I also note some similarities in the role of carbon for both the epitaxial rhombohedral-BN and epitaxial rhombohedral-B\textsubscript{4}C material growth in CVD.

A consequence of this work is the realisation of appropriate characterisation routes to accurately identify the different BN and B\textsubscript{4}C phases present for the respective films grown, for analysis both on a global film scale and on an atomic scale. Improved phase identification and material characterisation would lead to a better understanding of the grown films which in turn enables further optimisation of the deposition process for these materials.
2. Material systems investigated

2.1 Boron Nitride

Stoichiometric boron nitride (BN) is a compound material made of equal parts of boron and nitrogen atoms that are alternatively linked. Boron is a group-13 metalloid which is found abundantly in nature while nitrogen is a group-15 non-metal that is commonly found in its inert diatomic form N₂. While BN is primarily a synthetic material, in the last decade, it has been found naturally in the earth’s mantle in its cubic BN (c-BN) form. Synthetic BN exists in various structural forms, these forms can be further divided based on its orbital bonding: hexagonal-BN (h-BN) and rhombohedral-BN (r-BN) are sp²-hybridised while cubic-BN and wurtzite-BN (w-BN) are sp³-hybridised crystal phases. There has always been a huge interest in synthesising phase pure sp³-hybridised BN forms, but their research is limited by the difficulties associated with material synthesis. The relative thermodynamic stability of the four polytypes h-BN, r-BN, c-BN, and w-BN has been calculated and illustrated in Figure 1.

Figure 1: Calculated p-T phase diagrams at a composition of BN, illustrating (a) the relative thermodynamic stability between r-BN and h-BN and (b) the thermodynamic stability of boron nitride, including the four polytypes, r-BN, h-BN, c-BN, and w-BN. The inset in (b) highlights for clarity the stabilities of r-BN and c-BN in the low-temperature and low-pressure region. Reprinted with permission from J. Vac. Sci. Technol. A 37, 040603 (2019). ©Copyright 2019, American Vacuum Society.
The calculation in Figure 1(a) finds r-BN to be more stable than h-BN at typical CVD conditions i.e., below atmospheric pressure 0.1 GPa and temperatures below 1900 K. In Figure 1(b) the author’s calculations found that neither h-BN nor w-BN is thermodynamically favoured at the investigated temperatures and pressures. These results give some insight into the challenges associated with synthesising certain BN phases.

![Figure 2: Crystal structures of sp²-boron nitride; hexagonal boron nitride is illustrated on the left and rhombohedral boron nitride is illustrated on the right.](image)

Out of the well-ordered sp²-hybridised forms of BN, h-BN has attracted the most interest in this research field while r-BN has received relatively limited attention. One of the reasons for this difference is due to the difficulties associated with material and phase characterisation⁷,⁸ which can be attributed to the similarities in the h-BN and r-BN structures. Both h-BN and r-BN consist of the same 2D honeycomb-shaped basal planes consisting of alternating B and N atoms, but these planes are instead stacked differently with respect to the layer below, albeit with similar spacing between the basal planes, as illustrated in Figure 2. As shown, h-BN has an AAA... stacking sequence of the basal
planes where the basal plane above the underlying plane is rotated 180° with respect to each other (the rotated plane is denoted by A’). While r-BN has an ABCA… where the identical planes are instead shifted with respect to the underlying previous plane by 0.145 nm.

The less-ordered forms of sp²-hybridised BN include amorphous BN (a-BN) and turbostratic-BN (t-BN). a-BN lacks any well-defined crystal structure and may include a mixture of sp²- and sp³-hybridised bonds. While t-BN consists of the same BN basal planes as h-BN and r-BN but instead lacks long-range order, so the 2D basal planes are bent, rotated, or translated with respect to each other.

2.1.1 Properties and Applications of sp²-Boron Nitride

BN in its sp²-hybridised form has an attractive property envelope that makes it promising for a wide range of applications. It is mechanically robust⁹,¹⁰, given its higher interlayer integrity it is even more promising than graphene for mechanical reinforcement applications¹¹. BN is also chemically inert¹², its biocompatibility has enabled recent studies for its applications in biotechnology¹³–¹⁶. Thermally, BN is stable¹⁷ and conductive¹⁸–²¹ which further improves its versatility. The less-ordered a-BN is a promising ultra-low dielectric material that can, given its mechanical properties, also act as a diffusion barrier.²²–²⁴ In the past t-BN was studied to form ordered phases of BN²⁵–²⁷, recently some characterisation tools have been used to identify more t-BN properties²⁸,²⁹. In general, given its material properties, t-BN can replace graphite in applications like lubricants and polymer fillers but additionally as insulators, for thermal and protective coatings etc. BN is also isoelectronic to carbon and is analogous to graphite, including similar lattice constants, making ordered phases like h-BN a suitable material to progress graphene technology. There are many reports of graphene-h-BN heterostructures and heteroepitaxial growth.¹⁷,²⁰–²⁴ One dissimilarity that h-BN has compared with graphene is its structural symmetry. Graphene has identical atoms in its structure, while h-BN does not. In the absence of a centre of symmetry, the broken inversion symmetry of h-BN monolayers allows for piezoelectric properties, this has led to recent studies on h-BN for this application.³⁵–³⁹ Although r-BN shares this structural property and potential for piezoelectricity in addition to the above-mentioned properties, the literature on properties and applications of r-BN is relatively limited. Beyond the material properties already mentioned, h-BN and r-BN’s wide bandgap (r-BN’s being
slightly smaller than h-BN), high electron mobility and low refractive index motivate investigations on sp²-BN for the various optoelectronic properties that can be used for device applications.40–49

2.2 Boron Carbide

Boron carbide (BC) is a compound material formed from boron and carbon atoms. Carbon is a group-14 non-metal that is found in all organic compounds while pure carbon in bulk generally exists as diamonds or graphite. The B–B and B–C bonds in BₓC materials, specifically the elemental ratios in the compound structure, control the crystal structure and its material properties. As evidenced by the phase diagrams, in Figure 3 (a), carbon has a wide solubility range in stable BₓC.50 From the different phases, the BₓC phase is considered the stoichiometrically stable phase, its solid solutions with boron and carbon are depicted in Figure 3 (b). BₓC is in equilibrium with free carbon51, this has made estimations of free and combined carbon hard to characterise in the past52.

Figure 3: Phase diagram of boron carbide after (a) depicting BₓC₂ as the stoichiometrically stable phase and presuming the presence of several low-temperature phases, and (b) depicting the more widely accepted BₓC as the stoichiometrically stable phase, with solid solutions with B and C on each respective side. Reprinted with permission from J. Am. Ceram. Soc., 94 [11] 3605–3628 (2011).50 ©Copyright 2011, The American Ceramic Society.
In this work, we focus on the B₄C phase. The rhombohedral and hexagonal unit cells of BC are illustrated in Figure 4. The boron atoms in B₄C form caged structures which leads to the characteristic network of boron icosahedra seen in boron carbide. Rhombohedral boron carbide (r-B₄C) is a widely accepted crystalline phase of boron carbide as shown by its unit cell in Figure 4. While diffraction measurements provide information on the crystal structure, the atomistic placements and positioning of boron and carbon atoms in the B₄C structure are still discussed. This is due to the similarities in $^{11}$B and $^{12}$C isotopes.

*Figure 4: Boron carbide lattice showing a correlation between the rhombohedral (red) and the hexagonal (blue) unit cells. Inequivalent lattice sites are marked by arrows. Reprinted with permission from J. Am. Ceram. Soc., 94 [11] 3605–3628 (2011).*
2.2.1 Properties and Applications of Boron Carbide

Boron carbide is a hard ceramic material which has unique mechanical properties like high hardness, ballistic resistance, low density, wear resistance etc., which is why it is typically employed as an abrasive material, as industrial components or as plate armour material. Its mechanical stability, chemical inertness and high boron content also make B$_4$C a promising material for neutron converter layers in solid-state neutron detection where $^{10}$B converts neutrons to detectable particles. B$_4$C has also been used to further graphene properties and applications. B$_4$C’s high melting point of around 3500 °C further improves its versatility for applications. The wide range of composition and material stability makes B$_4$C attractive for optoelectronic applications and radiation-resistant heterostructures. The thermal stability and availability of B$_4$C gives it good thermoelectric performance at high temperatures, this is why it is considered an important candidate for high-temperature thermoelectric conversion applications.
3. Chemical Vapor Deposition

Chemical Vapor Deposition (CVD) is a technique used for depositing solid material by creating chemical reactions between vapour or gaseous sources of various reactant materials. The deposition process takes place inside machines called CVD reactors. The reactant materials used are volatile molecules called precursors, which consist of compounds containing the atoms required to form the solid deposition. The gas that does not react with the precursors is used for dilution and/or as a transporting medium to carry the precursors into the reactor cells from the precursor containers is called the carrier gas. Before the deposition, a substrate, a surface on which solid deposition is intended to occur, is placed in the reactor. Two types of reactions take place between the precursors to form the deposited material on the substrate: gas phase reactions in the gas phase and surface reactions that take place on the substrate or the growing material on the substrate.

3.1 CVD configurations

Different mechanisms enhance or activate the reactions in CVD techniques, and this differentiates each form of CVD and they are named appropriately based on the activation mechanism that is used. Thermal CVD, Plasma-Enhanced CVD, and Photo CVD are the most common techniques used. Thermal CVD is the most utilised form, and it has further subcategories in reactor design based on how heat is applied to the reactants.

In a cold wall CVD setup, only the substrate and its holder are heated, while the walls remain relatively cold. This setup prevents any premature parasitic reactions between the precursors before reaching the substrate surface. However, the localised heat source in this design creates temperature gradients above and on the substrate surface, leading to uneven film growth.
On the other hand, the hot wall reactor design involves heating all sides of the reactor walls, leading to uniform heat distribution in the growth region of the reactor cell. The drawback of this approach is that it unintentionally deposits material on the reactor walls, and has higher energy requirements. However, it typically allows for higher growth uniformity over the substrates. The hot wall CVD reactor can have two configurations, depending on the gas (carrier gas + precursor) flow direction, namely, horizontal, and vertical reactor setups. In the vertical configuration, the gas flow direction is perpendicular to the substrate surface, while in the horizontal configuration, the gas flow is parallel to the substrate surface. In this work, we use a horizontal hot-wall CVD configuration.

3.2 Fundamentals of Thermal CVD

As the name suggests, temperature is the most important parameter of the hot-wall CVD configuration that is used in this work. There are three main mechanisms involved in CVD, these are transportation of the growing species to the surface, adsorption of these species, and gas and surface reactions. Temperature influences which factor limits the growth rate of any material. These factors form three growth regimes wherein the different temperature ranges lead to the different growth regimes:

a) Kinetics limited (low temperature) - The growth rate in the low-temperature regime increases exponentially with temperature because it is limited by the reaction kinetics. In this regime, the rates of several thermally activated processes, like the gas phase reactions, diffusion of adatoms at the surface and nucleation, are greatly affected by small temperature variations. Consequently, the growth rate becomes very sensitive to small changes in temperature leading to unstable and non-reproducible material growth.

b) Mass transport limited (intermediate temperatures) - In the medium to high-temperature regime, as the system has enough energy for chemical reactions, the growth rate is determined solely by the mass transport to the substrate surface (also affected by the boundary layer discussed later), rather than the temperature.
c) Thermodynamics limited (high temperature) - In the high-temperature growth regime, the growth rate is significantly reduced due to thermodynamic limitations. This is because there is now an increased desorption rate from the substrate surface. Additionally, parasitic reactions in the gas phase reduce reactant availability and material decomposition due to increased vapour pressure of the solid material which also causes a decrease in the growth rate.

The transition of growth regimes with changes in reciprocal growth temperature is shown in Figure 5.

![Figure 5: Transition of growth regimes with change in reciprocal growth temperature.](image)

Once the reactor has reached the necessary conditions for the CVD process, which includes a particular pressure and temperature, the process starts by transporting precursors from their containers into the reactor cell. A mixture of carrier gas and precursor molecules is used for the bulk gas flow to the reactor. Gas phase and surface reactions on the substrate surface occur, and the CVD deposition begins, as shown in Figure 6.
From the chemical interactions depicted in Figure 6, we see how film growth is affected by the transportation of reactant species, reactant species adsorption, surface reactions, and by-product desorption as discussed earlier. When gas flows over a substrate, it creates shear forces, which result in a slower flow of gas just above the substrate, leading to the formation of a boundary layer. The thickness of this boundary layer impacts the growth rate and homogeneity of the thin film. A thicker boundary layer generates a higher growth rate and a more homogeneous film. The thickness of the boundary layer can be adjusted by controlling the gas flow velocity and pressure, as the reactants need to diffuse through the boundary layer to reach the growing surface. When the pressure is low, the precursors can easily reach the surface and react. However, when the pressure is high, it becomes more difficult for the precursors to penetrate the boundary layer, which slows down the growth rate making mass transport limited. This is how pressure also influences the growth regimes mentioned before. As the pressure increases, the gas phase reactions become more significant, but as the pressure decreases, the occurrence of gas phase reactions reduces. The thickness of the boundary layer decreases with a decrease in pressure, and surface reactions become more significant meaning that the substrate temperature and rate of adsorption/desorption become more important.
3.3 Horizontal Hot-Wall CVD system used - “Maggan”

This thesis work utilised a hot-wall CVD reactor named "Maggan". Figure 7 depicts the reaction cell of one of the horizontal Hot-wall CVD reactor cells in Maggan. The susceptor is the part of the reactor cell where the substrates are placed for heating. I employed a graphite susceptor coated with Tantalum Carbide (TaC) as it can withstand high temperatures and has a longer life cycle before corroding or breaking down under our CVD conditions. RF coils around the quartz cell are used to heat the region where the susceptor containing the substrate is placed. The graphite insulation is used to secure the susceptor in place and safeguard the quartz tube from high temperatures. A quartz gas liner is used to deliver the boron precursor, which helps prevent parasitic reactions from occurring between the precursors before reaching the substrate.

![Figure 7: Schematic diagram for the reaction cell of the horizontal Hot-wall CVD reactor ‘Maggan’. CAD drawing is reused with permission from Mikhail Chubarov.](image)

The Maggan reactor operates differently from most modern reactors. In most modern reactors, the functions are computer-controlled and mostly automated once a CVD recipe with process conditions
is fed to the computer. However, the valves in Maggan need to be operated manually using flip switches. Its manual operation includes most functions such as gas valve opening/closing, process pressure control using reactor cells, and flow rates through switches and dials.

This means that the operator needs to be aware of possible local pressure build-ups in gas lines and the appropriate order in which reactor cells and lines need to be pumped. During the beginning stages of this thesis project, the reactor underwent maintenance and repairs, which included the removal of a turbomolecular pump due to oil leaks. As a result, the reactor base pressure has been limited to as low as approximately 2 mbar throughout this work. We generally use 1cm x 1cm substrate pieces that are placed in this susceptor. The ideal position for substrate placement is the middle of the susceptor, as this is the position at which the pyrometer that measures the substrate temperature is calibrated. I regularly calibrate the pyrometer, which we use to measure the substrate temperature, using a Si melt test.
Figure 8 depicts the Maggan reactor's active pipelines and instrumentation information. Here we can observe the gas supply system along with the essential subsystems that are connected to the primary reactor cell. Maggan underwent multiple modifications to adapt to CVD of various material systems such as silicon carbide and gallium nitride in the past. The last major upgrade of Maggan was over a decade ago, which allowed the use of metal-organic precursors to deposit thin films of Boron nitride and Boron Carbide.
Figure 9: A standard CVD process, as conducted in Maggan, described in 5 stages.

The general stages of a CVD process in Maggan are illustrated in Figure 9. After the appropriated flows are selected using dials, the process starts with temperature ramping up to a base stabilisation temperature only in the presence of the carrier gas (1). Then the temperature is generally stabilized, for example for 5 mins during BN growth (2). The temperature is then ramped up to the growth temperature, and NH3 may be introduced for nitridation of the Al2O3 substrate in a BN CVD process (3). Once the growth temperature is reached and if a buffer needs to be grown then the precursors are adjusted for this growth now and maintained for the buffer growth time (4). After this step (or the step before this if the buffer layer is not grown), the optimised precursor flows are introduced from the quartz gas liner, and material growth begins and is continued for the growth time (5). After the growth time has ended, the precursor flows are stopped, and the heating is removed so the temperature can naturally drop in a low carrier gas ambient. The substrates are allowed to cool over time, and then they can now be removed after appropriate flushing of the reactor cell to get rid of any gas remnants.
4. CVD of Boron Nitride and Boron Carbide

4.1 Precursors Used in this work

For BN growth, NH₃ is generally used as the nitrogen precursor in thermal CVD. Alternatives like nitrogen halides are dangerous as they are explosive while nitrogen oxides are strong oxidizers. NH₃ is a clean and easy-to-handle precursor that cracks more easily than nitrogen gas (N₂) in a thermal CVD process.

There are a variety of options regarding boron precursors that can be used for BN growth, each with its benefits and drawbacks. From the alternative boron precursors used in recent literature, diborane (B₂H₆)⁷⁹–⁸³ is the most used boron hydride while BCl₃⁸⁴–⁸⁸ is a common boron halide. Boron hydrides benefit from having hydrogen as a by-product but are often considered dangerous if not handled properly due to their explosive and poisonous nature. Boron halides are safer, being non-explosive on their own, but would result in halogen incorporation in BN films due to a strong affinity to boron. There are also single-source precursors which contain both nitrogen and boron, from these borazine (B₃N₃H₆) is the most investigated⁸⁹–⁹³ for h-BN monolayer or epitaxial BN growth. The use of organoboranes TEB and TMB for BN growth is discussed below.

For B₄C, both TEB and TMB can be employed as a single source precursor as organoboranes already have boron and carbon species. Boron carbide has already been deposited in the past using the thermal CVD reactor used in this work.⁹⁴,⁹⁵
Figure 10: Precursors used for Boron Nitride and Boron Carbide film CVD used in this work are shown with their ball and stick as well as bond-line notations. The boron precursors are triethylborane $\text{B(C}_2\text{H}_5\text{)}_3$ (TEB), trimethylborane $\text{B(CH}_3\text{)}_3$ (TMB) and $\text{NH}_3$ is the nitrogen precursor that is used. The TEB and the $\text{NH}_3$ ball and stick models are edited versions of the original vectors by the author Benjah-bmm27 available in the public domain. The TMB ball and stick model is an edited version of the original vector published online by the author PishT.9

<table>
<thead>
<tr>
<th>Precursor</th>
<th>TEB</th>
<th>TMB</th>
<th>$\text{NH}_3$</th>
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<tr>
<td>Ball &amp; stick and bond-line notation</td>
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<td><img src="image" alt="TMB" /></td>
<td><img src="image" alt="NH3" /></td>
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The boron precursors used in this work for thermal CVD of both BN and B$_4$C are TEB and TMB. $\text{NH}_3$ is used as the nitrogen precursor for BN growth. The ball-and-stick and bond-line structures of these three precursors are shown in Figure 10. The decomposition reaction of $\text{NH}_3$ is straightforward compared to the different chemical pathways of TEB and TMB. TMB is reported to undergo $\alpha$-H elimination reactions to release $\text{CH}_4$ and $\text{BH}_3$ when it reacts with $\text{H}_2$ (the preferred carrier gas during deposition) with negative Gibbs free energy in up to three consecutive reactions in the gas phase.97 TEB is reported to instead dominated by $\beta$-eliminations of $\text{C}_2\text{H}_4$ that result in the release of $\text{BH}_3$.94 In Paper II, we discuss the influence of carbon on epitaxial h-BN and r-BN films, here we reference the different chemical pathways for the organoboranes discussed and how they influence the carbon species that are brought to the sample surface during CVD.
4.2 Substrates used in this work

4.2.1 Al₂O₃ substrates used for sp²-Boron Nitride

Sapphire or α-Al₂O₃ substrates are often employed in CVD of epitaxial BN. Its rhombohedral crystal structure in (0001) Al₂O₃, as depicted in Figure 11, is suitable for r-BN and h-BN. The high melting point of around 2050 °C is higher than the temperatures that are used for thermal CVD of crystalline BN. At high temperatures, in the presence of nitrogen, it undergoes surface nitridation forming AlN, the lattice mismatch between AlN and h-BN was calculated to be 3.43%. Literature on the thickest CVD-grown epitaxial BN films, excluding t-BN phases, have been generally observed when growing...
on Al₂O₃ substrates. The properties and past literature on Al₂O₃ motivated the use of these substrates in this work.

In Paper I, we explore the possibility of using the different cuts of Al₂O₃ as shown in Figure 12 to grow epitaxial BN. Following our findings, we investigated epitaxial BN growth conditions in Paper II and Paper III on two cuts: Al₂O₃(1120) and Al₂O₃ (0001) substrates, further described by their ball-and-stick models in Figure 12. In Paper III we investigate the influence of the substrate and BN film interface, on a local atomic scale, on epitaxial h-BN growth.

![Figure 12: Ball-and-stick stacking model representations of Al₂O₃ crystal structures. (a) shows the Al₂O₃ crystal along the [0001] (b) shows the top view for the two Al₂O₃(1120) and Al₂O₃ (0001) substrates. Crystallographic data for the α-Al₂O₃ crystal is taken from SpringerMaterials (online database).](image)
4.2.2 SiC substrates used for Boron Carbide

Silicon carbide (SiC) substrates are known for their high thermal conductivity, mechanical strength, and wide bandgap. It also has a high melting point of 2730 °C. The lattice mismatch of 6H-SiC was calculated with h-BN was even lower at 2.44%. However, the SiC depositions only led to r-BN nucleation directly, not h-BN. We used 4H-SiC as substrates to deposit the B,C films in this work. The ball-and-stick stacking model for two sides of the 4H-SiC, 4H-SiC (000\text{\textbar}1) commonly referred to as the C-face and 4H-SiC (0001) commonly referred to as the Si-face are shown in Figure 13. We expect SiC to be ideal for r-B,C epitaxy given its suitability with other boron-rich solids. In Paper IV we find differences in growth of r-B,C on the Si-face and C-face on a global scale. These films are also grown under different CVD conditions. In Paper V we analyse the interface on a local scale to determine the cause for these differences in epitaxial film growth conditions on the two substrates.

Figure 13: Ball-and-stick stacking model representations of 4H-SiC crystal structures. (a) shows the SiC crystal along the [0001] (b) shows the top view for the SiC(0001) and the SiC(000\text{\textbar}1) substrates. Crystallographic data for the SiC crystal is taken from SpringerMaterials (online database).
5. Characterisation Techniques

I start each characterisation section by describing my contribution to each technique. This contribution entails the preparation of samples required prior to analysis, operating the equipment to obtain raw data and information using each characterisation technique, interpreting and applying the analysis in a suitable scientific context, and presenting the results.

The primary characterisation techniques used in this work include advanced thin film X-ray diffraction (XRD) analysis, Transmission electron microscopy (TEM) based techniques, Time-of-Flight Elastic Recoil Detection (ERDA) analysis and scanning electron microscopy (SEM). Spectroscopy techniques like Fourier Transform Infrared Spectroscopy (FTIR) and Raman spectroscopy are used to support and strengthen our primary results.

5.1 X-ray Diffraction Techniques

I have performed all the XRD analyses independently, worked with the equipment myself, chosen the parameters for the analyses, interpreted the results and applied the acquired data in the right scientific context as shown in this work.

XRD techniques offer a non-destructive route to examine the structural information of the investigated material. The structural information gathered including the material phase present, crystal quality, lattice information, preferred orientation, film thickness, crystallite size, etc. depends on the type of X-ray configuration used. XRD techniques are based on the interaction of X-rays from the X-ray source in the measurement tool with the electrons in the sample material that is being investigated. Every X-ray technique consists of an X-ray source, a sample holder, and a detector. Constructive interference in crystalline materials, from X-ray diffracted adjacent parallel planes as recorded by the detector is then used to quantify and characterise the crystal structure.
The condition for constructive interference is determined by Bragg’s law:

\[ n\lambda = 2d \sin \theta \]

Here \( n, \lambda, d, \) and \( \theta \) denote the order of diffraction, the incident X-ray beam’s wavelength, the distance or d-spacing between two adjacent planes of a given miller index(hkl), and the incident beam’s angle respectively.

Figure 14: Schematic configuration of XRD \( \theta/2\theta \) scan with an illustration of X-ray diffraction from atomic planes in a crystalline sample.

A common primary XRD investigation configuration, used to identify the contained phases and film crystallinity, is a \( \theta/2\theta \) scan. The \( \theta/2\theta \) XRD configuration is illustrated in Figure 14. In the \( \theta/2\theta \) configuration, only the crystal planes that are parallel to the sample surface are detected. When Bragg’s law is fulfilled, it results in intensity maxima, which are plotted as peaks in the measurement data. Using a material XRD database for reference, the sample and its phases can be identified by its characteristic \( 2\theta \) peak position from the pattern obtained through this measurement.
Figure 15 depicts a θ/2θ scan where two sample data are stacked and plotted together for comparison. The samples were grown with different deposition parameters so differences in the measurement are expected. In the measurement, we observe intensity peaks from the Al₂O₃ substrate, the AlN buffer and the BN film growing on the two samples. The peak shifts, peak intensities, and differences in full-width half maximum of the peaks between the two samples are used to compare the crystal information for the thin films grown in these samples. Paper I and Paper IV show how θ/2θ scans are used to investigate and gather structural information on the BN and B₄C films grown respectively.
More advanced XRD analysis, for example, epitaxial or textured thin films, require additional XRD techniques to supplement and further resolve the crystal information of those samples. For this, a diffractometer needs to be capable of sample movement in different directions and rotation along different axes. Omega (ω) is the angle between the incoming beam and its projection onto the sample surface plane. Phi (ϕ) is the rotation around the surface normal. Chi (χ) is the angle between the surface normal and the X-ray scattering vector. The angles with respect to the sample surface are illustrated in Figure 16.
Figure 17: X-ray φ-scan (Phi-scan) of epitaxial AlN film growing on Al₂O₃ (0001). AlN {101̅} measured at χ = 61.5°, and Al₂O₃ {112̅3} measured at χ = 61.2°. The intensity is on a linear scale.

Azimuthal scans like Pole figure and phi(φ) scan measurements allow measurement of diffracted planes that are not parallel to the sample surface. These are performed to analyse the distribution of crystallographic orientations or textures within a sample. φ-scans in XRD are used to study the distribution of crystallographic orientations around a specific axis of rotation in a sample. In φ-scans, the sample is rotated around a selected axis, and X-ray diffraction patterns are recorded at different rotation angles. By analysing the intensity of diffraction peaks as a function of rotation angle, phi scans provide information about the distribution of crystallographic orientations around the selected axis (χ). A φ-scan is shown in Figure 17 for AlN growing on Al₂O₃. Multiple φ-scans at different χ ranging from 0°- 90°, plotted in 2D, is then referred to as a pole figure. Pole figures provide information about the overall distribution of orientations within the sample. In Paper I we use φ-scan measurements and in Paper IV we use pole figure measurements.

A rocking curve measurement, which is also called the ω-scan is used to investigate how well the crystallites of a certain orientation in a crystalline sample are aligned with respect to each other. To perform this type of measurement, the angle between the incoming and detected beam, which is the 2θ, is fixed, while the angle between the incoming beam and sample surface normal that is the ω, is
changed. In Figure 18 an example of the $\omega$-scan measurement is taken for a BN sample. The full-width half maximum of the peak can be used to get information on the crystalline quality of the BN film grown. This measurement technique is used in Paper I and Paper IV for the BN and B$_4$C films respectively.

![Graph showing rocking curve measurement](image)

**Figure 18:** Example of a rocking curve measurement, referred to also as $\omega$-scan, taken for a crystalline BN sample. The dotted line corresponds to the $\omega$-angle, which is half of the 2$\theta$ angle for the r-BN (000$\ell$) peak at 26.5°. The intensity is on a linear scale.

5.2 Microscopy techniques

5.2.1 Scanning Electron Microscopy

I have performed all the SEM analyses independently, worked with the sample preparation and the equipment myself, chosen the parameters for the analyses, interpreted the results and applied the acquired data in the right scientific context as shown in this work.

SEM is a technique used to investigate the surface morphology and chemical composition of a sample. It involves scanning the surface of the sample with an electron beam, which produces various signals containing sample information. These signals include secondary electrons, backscattered electrons,
and characteristic X-rays. By analysing these signals, bright and dark regions can be observed on the SEM micrographs, indicating differences in the chemical composition of the sample. Image contrast is related to the differences in film composition as well as film morphology. Figure 19 illustrates the different signals and the interaction volume between the incident electron beam and the sample surface.

![Incident Electron Beam](image_url)

**Figure 19:** An illustration depicting the teardrop-shaped interaction volume and the signals produced by the interaction of the electron beam with the sample in SEM.

The SEM setup is visualised in Figure 20. The in-lens detector used for the in-lens detector mode may also be located within the column of the microscope, depending on the instrument design. The SEM setup consists of a vacuum chamber where the sample and the SEM equipment are contained, and it operates under high vacuum conditions. SEM imaging has been employed in this work to study film growth and surface morphology. Additionally, cross-sectional SEM has been used to estimate the thickness of the films.
Preliminary film composition was investigated using Energy-Dispersive X-ray spectroscopy (EDS), an integrated tool in SEM. EDS analyses the film composition by using an electron beam interaction that results in characteristic X-ray emission. Figure 21 shows a top-view (plan-view) SEM micrograph, where well-ordered BN features are observed to be surrounded by a seemingly less-ordered BN film.
5.2.2 Transmission Electron Microscopy

For TEM-based analysis techniques, I have worked closely with an expert in the technique. I did all the sample preparation myself using the Focused Ion Beam (FIB) instrument. I was present with the TEM expert during the data acquisition and suggested the parameters for the data collection. I analysed the raw data independently, interpreted the results and applied the acquired data in the right scientific context as shown in this work.

Figure 22: Simplified electron beam path for transmission electron microscopy analysis. The illumination system consists of the electron gun, the accelerator and a combination of condensing lenses which can either be used to produce a spread beam for conventional TEM mode or a focused probe for scanning transmission electron microscope (STEM) mode. The imaging system consists of the objective lens, projection lenses and various detectors.
TEM is an analytical tool that uses a high-energy electron beam to visualise the structure of materials. TEM offers high-resolution imaging and compositional information from the analysed material. This high-resolution imaging enables material information at an atomic scale, this is in contrast to techniques like XRD, which only analyses the sample on a bulk scale. The basic setup for TEM consists of an electron gun that supplies the incident beam, electromagnetic lenses and aperture for beam control and detection. This setup enables the selection of various imaging modes that allow the imaging and spectroscopy of materials. It can operate in broad illumination and focused beam (scanning) modes. The transmission process enables higher resolution data in TEM compared to SEM analysis. A simplified electron beam path for TEM analysis is illustrated in Figure 22.

The process of creating a thin TEM sample involves thinning down samples to ultra-thin thicknesses, specifically for this particular characterisation technique. To achieve this, we use a TEM cross-sectional sample preparation technique called focus ion beam (FIB) lift-out. FIB employs a focused beam of ions to selectively remove material from a sample surface. The ion beam is focused on a very small spot size, typically in the range of nanometers, allowing for precise material removal. To protect the region of interest from damage, we locally deposit a protective layer of platinum. We then use the focused ion beam to thin down the region of interest to the desired size and create a trench around the selected area. The trench exposes the underlying material, allowing for further thinning. Once we reach the desired thickness, we lift out the remaining region of interest, referred to as the TEM lamella, from the sample and transfer it to a TEM grid. Afterwards, we thin down the TEM lamella again until it reaches the required electron transparency. However, the time spent in sample preparation using this technique is often dictated by the possible failure at any of these stages of FIB. Regardless, FIB offers a high-resolution, efficient, selective, and small-volume material route towards TEM sample preparation when compared to other traditional methods.

High-resolution imaging in TEM (HRTEM) is an effective method for extensive material characterisation, especially for crystalline materials. It can be used to determine the phase, segregation, transition or stacking structure of a material. It can also help in crystallographic analysis, including lattice spacing, phase identification, orientation, grain boundaries, and local morphology. Additionally, it is possible to identify interlayers and learn about the growth surface, its uniformity or interface roughness. In Figure 23, you can see an HRTEM image of a B,C thin film grown on 4H-
SiC(0001) substrates. As shown in the image, the film grows epitaxially and directly on the substrate surface.

Figure 23: Cross-section HRTEM micrograph of B,C film grown on 4H-SiC(0001) substrates are taken along the (1120) zone axis of the substrate. EELS maps and EDX maps for a similar film region are also shown for the same sample. This is an example of the technique described in this section so is taken from a similar but not the same region as shown in the micrograph.

In addition to imaging, the TEM can also be used to analyse the composition of a sample. In electron energy loss spectroscopy (EELS), we can measure the energy lost as the electron beam passes through the sample. This technique is used to determine the specific elements as the energy loss is characteristic of the elements present in the sample. The resulting spectrum provides information about the sample's chemical and electronic properties, such as its elemental composition, chemical bonding, and electronic structure. Since the EELS data has a high resolution, we can also gather elemental data from each line of pixels on the micrograph obtained in STEM-EELS, plotting these results in what is called a stacked EELS edge spectrum. Stacked EELS enables the characterisation of individual layers within the sample, providing the same information insights on a more local scale. Energy-Dispersive X-ray Spectroscopy (EDX) is another TEM-based technique that can be used to analyse the elemental composition of materials. EDX is an analytical technique that can detect characteristic X-rays emitted from a sample when it is bombarded with electrons. When excited, each element in the sample emits X-rays with specific energies, allowing for the identification of elements present in the sample. The elemental maps obtained from both EELS and EDX for B,C film grown on 4H-SiC(0001) substrate
are shown for example in Figure 23. TEM techniques have been used extensively in Paper II, Paper III, and Paper V to investigate the morphology, crystal plane stacking, phase determination and compositional analysis of the films deposited.

5.3 Ion beam technique

5.3.1 Time-of-Flight Elastic Recoil Detection Analysis

For the ToF-ERDA analysis, I have worked closely with an expert in the technique. I prepared the samples, described them, and the investigation needed, and then sent them forward to our collaborators from The Tandem Laboratory at Uppsala University, Sweden. I analysed the raw data independently, interpreted the results and applied the acquired data in the right scientific context as shown in this work.

Figure 24: (Left) Scatterplot from a ToF-ERDA measurement of a BN film. Five samples were measured for the ERDA composition plot shown on the right. Each composition measurement is taken from a different sample, for example, the scatterplot shown in the left part has raw data to form the composition calculated for ‘sample 1’ in the plot shown to the right.
ToF-ERDA uses ion beams of high energy to probe the sample material, with this analysis we get quantitative information on the elemental composition and depth profiles of the sample. The principle is based on elastic scattering of ions, by measuring the outgoing energy and time-of-flight of the recoiled sample atoms we can get information on the sample composition. This is a good technique to measure light elements including hydrogen. We can also use this technique for density or thickness measurements if either of the two is known. The obtained raw data was analysed using the Potku software. Figure 24 shows the energy vs. ToF scatterplot, on the left, formed from the raw data. The individual elements and their isotopes are determined in the Potku software, and this is used to form the plot shown in Figure 24 on the right. We used this technique to determine film composition as discussed for the BN films in Paper I and Paper III and for B:C films in Paper IV and Paper V.

5.4 Spectroscopy techniques

5.4.1 Fourier Transform Infrared Spectroscopy

I have performed all the FTIR analyses independently, worked with the equipment myself, chosen the parameters for the analyses, interpreted the results and applied the acquired data in the right scientific context as shown in this work.

FTIR is a fast, non-destructive analytical tool that uses the interaction between the sample material and infrared radiation (IR) to get information on the bonds in molecules in the investigated sample. On exposure to the IR, the sample's molecules absorb specific wavelengths of light which is characteristic of the bonds present in molecules of the sample material. The resulting radiation that leaves the sample, called the absorption spectrum (or transflectance spectrum), gives chemical information on the sample. In practice, FTIR spectroscopy can operate in transmission mode or reflection mode depending on the sample and substrate used. For thin films, the IR spectrum can consist of both the reflection from the film surface as well as the transmission of the IR through the film, reflected from the substrate. This combination, the sum of the reflected and transmitted spectrums, is called the transflectance spectrum, which has its advantages.

Figure 25: (Left) Illustration of an FTIR measurement of a thin film on a partially reflective substrate. (Right) FTIR measurement of a BN thin film sample that is grown on an AlN buffer on an Al₂O₃ substrate.

The beam path and measurement setup for this technique is illustrated in the left portion of Figure 25 while an example FTIR spectrum taken for a BN film growing on an Al₂O₃ substrate is shown in the right portion of Figure 25.

5.4.2 Raman Spectroscopy

For the Raman analysis, I have worked closely with an expert in the technique. I prepared the samples, described them, and the investigation needs, and then sent them forward to our collaborators at the same university. I analysed the raw data independently, interpreted the results and applied the acquired data in the right scientific context as shown in this work.

Raman spectroscopy is based on inelastic scattering of photons. The Raman spectra in crystals are subject to some selection rules which are well investigated, therefore, the spectrum gives valuable information on the phase, chemical composition, chemical bonds etc. of the material investigated, including for amorphous materials. If the scattered photon has lower energy, thus a longer wavelength, it results in what is called Stokes Raman scattering. If the molecules in the sample are in an excited state, the scattered photon will gain energy and scatter at a shorter wavelength, this is called anti-Stokes...
Raman scattering. The Raman spectra are usually represented as a graph of the scattered light intensity versus the so-called Raman shift, where zero shift corresponds to the energy position of the laser line and positive Raman shifts (most often in energy units of cm\(^{-1}\)) describe the Stokes part of the spectrum. The elastic scattering of light of the same energy and hence same wavelength is called Rayleigh scattering. Figure 26 (top) shows the three forms of light interaction in the example of a molecule.

![Figure 26](image)

**Figure 26**: (Top) The three types of scattering that occur when a sample is illuminated in Raman scattering. (Bottom) Example Raman spectra taken from Al\(_2\)O\(_3\) (11\(\overline{2}\)0) and Al\(_2\)O\(_3\) (0001) substrates a bulk BN reference sample. The sp\(^2\)-BN Raman peak at 1370 cm\(^{-1}\) is observed for the h-BN sample.

Figure 26 (bottom) shows the Raman spectra measurement for three samples: bare Al\(_2\)O\(_3\) (0001), bare Al\(_2\)O\(_3\) (11\(\overline{2}\)0) and bulk hexagonal BN. The two sapphire cuts, Al\(_2\)O\(_3\) (0001) and Al\(_2\)O\(_3\) (11\(\overline{2}\)0), show the same phonon modes manifested as peaks in the spectrum, but with different intensity ratios owing
to the selection rules. The bulk h-BN reference sample shows the characteristic peaks depicting BN chemical bonds present in the material. Raman spectroscopy is used in Paper II and Paper V to investigate the state and presence of carbon in the BN and r-B4C samples.
6. Summary and contribution to the field

The first motivation of this work is the improvement of our fundamental understanding of growing thick epitaxial boron nitride thin films in CVD. The work with organoboranes; TMB and TEB as boron precursors in BN deposition enabled their use as a single source precursor to epitaxially grow and understand another material system, boron carbide in CVD. The full contribution of this work is thus split into three learning outcomes:

1) Epitaxial BN thin films in CVD (Papers I, II and III)
2) Epitaxial B₄C thin films in CVD (Papers IV and V)
3) Commonalities between r-BN and r-B₄C (Papers II and V)

1) Epitaxial BN thin films in CVD (Papers I, II and III)

In Paper I, we deposited and compared BN films on different cuts of sapphire which included Al₂O₃(1120), Al₂O₃(11̄02), Al₂O₃(101̄0) and commonly used Al₂O₃(0001). As described in Section 4.3, the properties of Al₂O₃ substrates make it an attractive substrate for depositing BN thin films. This aspect motivated this study to investigate other orientations of Al₂O₃ using our previously optimised CVD parameters and using both TMB and TEB to cover both organoboranes. BN films were deposited on all substrates investigated, as confirmed using FTIR spectroscopy, but XRD results confirmed that epitaxial BN films only deposited on Al₂O₃(1120) and Al₂O₃(0001) while the films were X-ray amorphous on the remaining two substrates. The epitaxial BN film growth is evidently dependent on the growth orientation of the AlN buffer that grew on each substrate, which was the same for Al₂O₃(1120) and Al₂O₃(0001) albeit with better crystal quality on Al₂O₃(1120) and with
slightly better r-BN film crystallinity. This study showed that Al₂O₃(1120) is also a suitable substrate
to grow epitaxial BN alongside the generally used Al₂O₃(0001). This is why we continue working
with Al₂O₃(1120) and Al₂O₃(0001) in the following studies on epitaxial BN. While we gained
global information on the deposited films.

In Paper II and Paper III, we looked at the films on a local scale using SEM and TEM-based analytical
characterisation techniques. In Paper II, we focus on the influence of carbon on epitaxial film growth.
Considering the boron precursors description in section 4.1, we recognise that organoboranes should
release considerable carbon atoms. For this investigation, we also used both TMB and TEB to deposit
BN films on Al₂O₃(1120) and Al₂O₃(0001) substrates. Through our investigations, we discovered
two distinct types of BN growth morphologies in our samples. The first is the minority case, where h-
BN grows in truncated pyramidal-shaped structures, reaching up to only 4 nm before transitioning to
r-BN and growing up to 70 nm in total. The second is the majority case, where the surrounding film
grows epitaxially as h-BN, but is not limited to 4 nm, and grows up to 10 nm without any uniform
polytype transition to r-BN. In the first case, there was no carbon incorporation in the pyramidal BN
structures, and the polytype transition was due to local stress relaxation from the underlying AlN
buffer surface, as described in a previous report⁹⁹. For the second case, we observed carbon
incorporation in EELS, and the h-BN growth terminated either with a layer of carbon (TEB-grown
films) or transitioned in small patches to r-BN in the presence of carbon, and then to less ordered t-
BN (TMB-grown films). The literature discussed in the study reported that r-BN always nucleates
instead of h-BN when growing on a carbon-containing surfaces. We suggested that the two different
morphologies exist due to the differences in their early epitaxial BN growth conditions which are
influenced by two different growth mechanisms. Firstly, the carbon-induced transition in the majority
film shown in our results and secondly, stress relaxation from the underlying surface for the scattered
structures growing in the absence of carbon. The common denominator is that all BN growth
terminates due to carbon poisoning. We also suspect that there may be a difference in the surface
diffusion of carbon on the two BN polytypes or the two film morphologies, but these implications
were too speculative to include in the publication. The remaining outstanding question was why the
pyramidal regions were present only locally on the film surface and what influenced their formation.

In Paper III we investigate this aspect, the difference must be at the interface of the BN film and the
AlN buffer grown below most of the film and the scattered pyramidal structures. As of writing this
work, these results are still being discussed between the co-authors. We see, using HRTEM, a trend where at the edge of every pyramidal BN structure there are nano-sized pit-shaped substrate modified regions for both the Al₂O₃(1120) and Al₂O₃(0001) substrates. We have observed an additional AlON interlayer, analysed using EDX,ToF-ERDA and EELS, between the AlN and the epitaxial BN film. This layer seems to be amorphous and should form due to the diffusion of oxygen from the Al₂O₃ to the AlN. We argue that the diffusion of oxygen is higher from the nano-sized substrate-modified regions. The apparent thicker AlON layer under the pyramid compared to the rest of the film supports this argument. We believe that the stress relaxation from higher lattice mismatch to the varying AlON underlying surface could induce the earlier polytype transition from h-BN to r-BN in the pyramidal regions described in Paper II and Paper III.

II) Epitaxial B₄C thin films in CVD (Papers IV and V)

In Paper IV, we investigated the growth of B₄C films using TEB at different temperatures ranging from 1100–1500 °C, and on two substrates 4H-SiC (0001) and 4H-SiC (0001). These substrates are described in detail in Section 4.2.2. We found that it is possible to grow epitaxial r-B₄C (phase composition learned using ToF-ERDA) at 1300 °C growth temperature on 4H-SiC (0001) in our CVD process. XRD and SEM revealed that higher deposition temperature results in co-deposition of graphite, and lower deposition temperature results in polycrystalline boron carbide on the same substrate. Whereas for the same set of CVD experiments, the B,C films were all polycrystalline on 4H-SiC (0001). Specifically polycrystalline r-B₄C (ToF-ERDA) for the experiment at 1300 °C on 4H-SiC (0001). This was far from the expected results as we expect the commonly used epi-ready 4H-SiC (0001) to support epitaxial growth and not the less utilised 4H-SiC (0001). We speculate, in the discussion section, on the various factors that can influence this difference in epitaxial growth conditions on the two substrates. Since the primary investigation for crystallinity used in this study is advanced XRD techniques which look at the film on a global scale, experimentally proving any speculation, specifically related to film nucleation and the film/substrate interface, was beyond the scope of the results in this study. In Paper V, we investigate the films grown at 1300 °C on 4H-SiC (0001) and 4H-SiC (0001) locally using TEM-based characterisation techniques. We observed differences in the film morphology of polycrystalline and epitaxial films using SEM and TEM. The
polycrystalline films grew dense and uniformly, while the epitaxial films showed distinct voids and grew as individual columns after a critical thickness. We investigated the r-B4C film/substrate interface on both substrates and found no apparent surface roughness/etching differences or additional carbon-based interlayer formation on either substrate. Moreover, Raman spectroscopy on the films revealed that carbon accumulation on the epitaxially growing film surface could contribute to the apparent differences in film thicknesses on the two substrates. We questioned if the higher carbon availability for the epitaxial r-B,C film for the 4H-SiC (000\overline{1}) surface compared to the 4H-SiC (0001) surface, due to a different interaction with the precursor, was the reason for epitaxial growth. However, this consideration was too speculative and lacked further evidence beyond the EELS analysis alone. We suggest that thermodynamics, specifically the differences in surface energy on the two substrates is the most plausible reason for the epitaxial and polycrystalline growth observed on the 4H-SiC (000\overline{1}) and 4H-SiC (0001) substrates respectively.

3) Commonalities between r-BN and r-B\textsubscript{4}C (Papers II and V)

Using organoboranes, specifically TEB, for epitaxial growth of r-BN and r-B\textsubscript{4}C in CVD, we have observed some similarities in the role of carbon during film growth. The thickest epitaxial films for both materials show a morphology that leads to growth structures which are taller and have isolated growing surfaces compared to the surrounding film. For r-BN, we see truncated pyramidal structures, while for r-B\textsubscript{4}C, we observe individual columns that also appear to be in the shape of pyramids in cross-sectional microscopy. In both cases, the epitaxial growth rate is much lower than expected, and we have found an apparent carbon accumulation on the surfaces of these structures. The carbon exists in the form of free carbon, as indicated by Raman and HRTEM results. Both r-B\textsubscript{4}C and r-BN grew epitaxially in the [0001] direction, and both structures are expected to terminate with boron atoms. However, while carbon, in controlled quantities, is necessary for epitaxial r-B\textsubscript{4}C growth, it is not suitable for epitaxial BN growth in CVD.
7. Future outlook

To advance epitaxial sp²-BN for its various semiconductor applications, we need a better understanding of the properties and uses of all the polytypes. However, it has been a challenge to answer specific questions about the differences in properties between h-BN and r-BN due to limited literature on r-BN. Therefore, I recommend further research and analysis into r-BN as a viable, more stable sp²-BN polytype to grow thick epitaxial films. This will require collaborations with different research groups that have expertise in material property investigations geared towards applications. We have collaborated in the past (Paper A) and continue to communicate with other research groups towards this goal.

To increase the visibility of r-BN research, we call for careful material characterisation of epitaxial sp²-BN films. As described in the review article by Chubarov et al., and corroborated by the results in this work, unless one uses a combination of high-resolution electron microscopy tools with careful sample preparation to get local information and with advanced thin film x-ray diffraction techniques to get global film information, it is not possible to suggest that the grown epitaxial BN films are phase pure (for example h-BN studies found in the literature are often limited in their characterisation). With good characterisation practices, more r-BN growth can be identified and thus investigated for its specific properties that would differ from the more investigated polytype, h-BN.

Another technique that can enable us to get more epitaxial sp²-BN film information is reciprocal space mapping (RSM). RSM is a powerful XRD technique used to study the crystallographic properties of epitaxial thin films. It provides valuable information about the structural quality, strain, lattice mismatch, and crystal orientation of the films. We can learn more about the lattice mismatch, strain/relaxation and related mechanisms, the defects and dislocations and the epitaxial growth quality. This technique would enable further optimisation of the growth processes and tuning film properties to match application requirements. However, XRD techniques are limited by the poor X-ray scattering of light elements (for example, B, C, N) and RSM intensity in particular is further hampered by the need for asymmetric reflections.
Based on the results from this work, the use of carbon-containing precursors such as organoboranes is not suitable for thick epitaxial h-BN and r-BN growth. In Section 4.1, alternative precursors are discussed. However, compared to 2D or amorphous BN growth, there is relatively less research on thick epitaxial sp²-BN film growth with other precursors. Regarding substrates, our results on Al₂O₃, as well as the literature, suggest that CVD processes under 1250 °C may be suitable for growing epitaxial sp²-BN, as higher temperatures can lead to local substrate modification in hydrogen ambient in CVD. At higher temperatures, our results in Paper III indicate that Al₂O₃(1120) is more stable than Al₂O₃(0001) in CVD, which has also been reported before⁹⁴. If phase pure epitaxial r-BN growth is desired, 3H-, 4H-, and 6H-SiC are more suitable as they nucleate directly without any h-BN incorporation. While out of these 6H-SiC has been preferred for this deposition in the past⁹⁹,¹⁰⁵, the r-BN only grows as individual pyramidal structures rather than a continuous film, which can be a significant drawback depending on the application. In Paper II, we also bring up the implications of r-BN growth on carbon-containing surfaces for graphene technology and graphene heterostructures with sp²-BN. This is another aspect that needs to be investigated further.

Based on the literature, it is evident that the growth of epitaxial r-B₄C is far less studied as compared to epitaxial BN. Although our investigation of epitaxial growth for r-BₓC films has shown promising results, more research is needed to fully understand the film properties and optimise the growth process. In Paper V, we observed that carbon accumulation hindered material growth, but the film still grew to a thickness of >300 nm. However, the presence of local voids and the growth morphology consisting of individual columns becomes a concern as the film grows thicker. Unlike r-BN growth on SiC, the r-BₓC film initially seems to nucleate uniformly at lower film thickness up until a critical thickness. The film growth process parameters investigated in Paper IV have provided a broad understanding of the optimal growth conditions, but further optimisations in connection with proper characterisation techniques, including additions like RSM would advance this process further. Our work on this material has been repeatable but for reproducibility and to advance epitaxial r-BₓC research, there is a need for more research from other groups on this material system. Advancements would motivate further material growth and property investigations for the intended semiconductor applications discussed in Section 2.2.1. Finally, r-BₓC or more broadly, r-BₓC research also benefits from the growing interest in other boron-rich solids for semiconductor applications.¹¹¹–¹¹³
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Papers

The papers associated with this thesis have been removed for copyright reasons. For more details about these see:

https://doi.org/10.3384/9789180755221
Phase evolution of boron nitride and carbide during chemical vapor deposition

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