Chemical vapour deposition of sp^2 -hybridised B-C-N materials from organoborons

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Linköping 2019

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Cover:

Front side:

Up left: top view scanning electron micrograph (SEM) of sp^2 -BN grains and 3C-SiC grains on Si(111).

Up right: top view SEM of r-BN grains on ZrB_2 , surrounded by a-BN.

Bottom left: top view SEM of the surface of a 1.5 μm thick r-BN film deposited from TMB covered with a-BN.

Bottom right: top view SEM of rhombohedral boron carbide grains on silicon carbide.

Back side:

Up: cross section SEM of DRAM structures of aspect ratio 60:1 (low magnification) and a- B_xC film deep in the trenches (high magnification).

Bottom, from left to right: top view SEM of sp^2 - BC_xN_y nanowalls deposited from plasma CVD, with increasing degree of disorder and complexity.

During the course of research underlying this thesis, Laurent Souqui was enrolled in Agora Materiae, a multidisciplinary doctoral program at Linköping University, Sweden.

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Printed in Sweden by LiU-Tryck, Linköping, 2019

ISSN 0345-7524

ISBN 978-91-7929-944-6

Abstract

Thin films of sp^2 -BN are promising materials for graphene and deep-UV optoelectronics. They are typically deposited by thermally activated chemical vapour deposition (CVD) from triethylboron (TEB) and ammonia (NH_3) at 1500 °C, albeit in a narrow process window. The aim of this thesis is to establish a better understanding for and to develop CVD of sp^2 -BN, B_xC and BC_xN_y further. This has been done by fundamental studies of the gas phase and surface chemistries of the organoboron precursor trimethylboron (TMB), studying new substrate materials and by studying plasma CVD.

From previous experience with TEB, TMB has been investigated as an alternative precursor. From a study on the gas phase chemistry of TMB in argon and hydrogen ambient, B_xC films can be deposited from 600 °C at 5000 Pa and the B/C ratio reaches 3 at susceptor temperatures of 1000 °C. Supporting calculations show that TMB dissociates mainly by α -elimination of CH_4 in both ambient, although H_2 -assisted elimination also occurs in hydrogen ambient. Furthermore, we have demonstrated deposition of B_xC films in features with high aspect ratios (up to 2000:1) at 700°C and 5000 Pa, which are much higher temperature and pressure conditions compared to most surface-controlled CVD processes. This was enabled from competitive adsorption of radicals from TMB and H_2 on the growing surface. Deposition of sp^2 -BN from TMB and NH_3 was performed between 1200 °C – 1485 °C. The use of TMB instead of TEB allowed for the deposition of epitaxial rhombohedral-BN (r-BN) on nitridated sapphire from 1300 °C and in a wider process window (3000 to 9000 Pa, NH_3 /TEB from 321 to 1286) and three times higher deposition rate, but at a cost of a higher carbon contamination. The epitaxial relationships are $r - BN(0001) \parallel w - AlN(0001) \parallel \alpha - Al_2O_3(0001)$ out-of-plane and in-plane $r - BN(1120) \parallel w - AlN(1120) \parallel \alpha - Al_2O_3(1000)$ and $r - BN(1120) \parallel w - AlN(1120) \parallel \alpha - Al_2O_3(\bar{1}000)$, as determined by ϕ -scan measurements.

For growth on silicon, we studied the feasibility of depositing sp^2 -BN at 1300 °C, 7000 Pa, and NH_3 /TEB = 321. Pre-treatments from TEB and NH_3 were applied in order to stabilise the silicon surface. It resulted in the growth of amorphous boron nitride (a-BN), regardless of the pre-treatment. We brought into light a memory effect involving boron carbide and silane (SiH_4) that permitted the growth of orientated crystalline or turbostratic BN grains on the silicon surface, as determined by X-ray

diffraction and scanning electron microscopy images. In contrast to the temperature sensitive Si substrate, epitaxial zirconium diboride (ZrB_2) templates were studied as a conductive alternative high- substrate to the sapphire (insulator) and silicon carbide (wide bandgap semiconductor). ϕ -scan measurements showed that r-BN grows with the epitaxial relationship: $r - BN(0001) \parallel ZrB_xN_{x-1}(111) \parallel ZrB_2(0001) \parallel SiC(0001)$ and $r - BN(11\bar{2}0) \parallel ZrB_xN_{x-1}(220) \parallel ZrB_2(11\bar{2}0) \parallel SiC(11\bar{2}0)$. The coverage of the surface by epitaxial r-BN grains is found to increase with upon silane exposure prior to growth.

In addition, microwave-plasma-activated CVD was studied as an alternative deposition technique. sp^2 - BC_xN_y films were deposited from TEB and an $Ar-N_2$ plasma in an approach similar to a 2^3 - factorial design. We observed the effects of the absorbed microwave power, the total gas flow and the N/Ar ratio on the growth rate, composition and morphology. Two deposition regimes were found whether nitrogen or argon is the main gas. The films showed high boron and nitrogen (up to 46 and 41 at. %, respectively) contents and the composition was found not to vary significantly with the deposition parameters. The morphology of the film evolves from granular films to nanosheets. The use of plasma enabled using optical emission spectroscopy to get insight into the deposition chemistry. The relative permittivity κ of the sp^2 - BC_xN_y films could be varied between 3 and 35. A strong correlation was found between carbon content and increase of κ .

Populär Sammanfattning

Bornitrid (BN), är en förening mellan lika delar av grundämnena bor och kväve. Då bor och kväve står på varsin sida om kol i det periodiska systemet är det inte oväntat att BN på många sätt liknar kol med avseende på egenskaper. På samma sätt som kol kan bilda både diamant och grafit, kan BN också bilda olika kristallstrukturer med väldigt olika egenskaper. Skillnaden i egenskaperna mellan diamant och grafit uppkommer när kol-kol-bindningarna skapar olika vinklar mellan sig. När atomer skapar bindningar med $109,5^\circ$ vinkel, som i diamant, kallas det att atomerna är sp^3 -hybriderade. I grafit är istället atomerna sp^2 -hybridiserade och vinklarna är mellan bindningarna 120° . Detta skapar en struktur av skikt som bara är en atom tjocka och där skikten i kristallen hålls ihop med svagare bindningar oftast sammanfattande som van der Waals bindningar. sp^3 -hybridiserad BN bildar, precis som kol hårda, kubiska kristaller, så kallad kubisk bornitrid. sp^2 -hybridiserad BN bildar antingen hexagonala eller romboiska kristaller.

En viktig skillnad mellan grafit och sp^2 -BN är att grafit leder elektrisk ström medan sp^2 -BN är en halvledare. Den elektriska ledningsförmågan hos sp^2 -BN kan justeras genom att tillsätta en kontrollerad, liten mängd andra atomer än bor och kväve i sp^2 -BN-kristallen. Detta kallas för att dopa kristallen. Om man gör en kristall av en halvledare och i olika sikt av kristallen justerar den elektriska ledningsförmågan så får man en struktur som utgör grunden för all modern elektronik. sp^2 -BN är alltså väldigt intressant för att göra elektronik av. Egenskaperna hos sp^2 -BN gör att materialet är väldigt bra för att till exempel ljusdioder som kan sända ut ultraviolett (UV) ljus. Sådana ljusdioder skulle kunna användas för att rena vatten eftersom UV-ljuset kan döda bakterier.

Bor kan också bilda kemiska föreningar med kol, så kallade borkarbider. Borkarbider har typiskt väldigt komplicerade kristallstrukturer och oftast innehåller de mycket mera bor än kol, de benämns ofta B_xC . Borkarbider är också halvledare vilket gör dem intressanta för elektronik, men borkarbider är även väldigt hårda och används därför i skottsäkra västar. Bor kan även bilda föreningar med både kol och kväve, då kallas de borkaronitrider (B-C-N) och får egenskaper som är en blandning av bornitrider och borkarbider. En spännande egenskap hos grundämnet bor är att isotopen ^{10}B , med fem protoner och fem neutroner i atomkärnan, är ovanligt bra på att reagera med neutroner i en kärnreaktion. Neutroner är, som namnet antyder, elektriskt neutrala och därför väldigt svåra att detektera. Neutroner måste därför reagera med något som kan skapa en laddad partikel som

går att detektera. Bornitrider, borkarbider och borkaronitrider kan därför användas för att konstruera neutrondetektorer.

Om man ska göra elektronik eller neutrondetektorer av BN, B_xC eller B-C-N behöver man skapa ett tunt skikt, eller film, av materialet. En av de vanligaste teknikerna för beläggning eller tillväxt av tunna filmer kallas CVD, efter engelskans chemical vapour deposition, ungefär kemisk ångdeponering på svenska. I CVD används gasformiga ämnen (reaktanter) vars molekyler innehåller de atomer som behövs för att bygga upp filmen. Dessa reaktanter får kemiskt reagera med varandra och med den yta där filmen växer till som ett fast material från ångfasen (kondensation) behövs energi, varför CVD typiskt utförs vid höga temperaturer. Om man vill sänka temperaturen kan man tillföra elektrisk energi från urladdningar i ett plasma. Denna avhandling syftar till att öka förståelsen för och utveckla CVD av sp²-BN, B_xC och B-C-N. Som gasformig borreaktant har antingen trietylbor (TEB – B(C₂H₅)₃) eller trimetylbor (TMB – B(CH₃)₃) använts. Eftersom de även innehåller kol har de även fungerat som kolkälla. För kväve i skikten har ammoniak eller kvävgasplasma studerats.

I avhandlingens första del har TMB-molekylens egenskaper i CVD studerats. Med en blandning av CVD-experiment, där B_xC belagts, och här har beräkningar utförts för att kartlägga sönderdelningen av TMB och de molekylfragment som bildas ur den processen då vätgas eller argon är närvarande. TMB-molekylens ytkemi har också studerats varvid en intressant effekt upptäcktes. Vid låga temperaturer kan väteatomer hindra TMB-molekylens sönderfallsprodukter från att binda till ytan. Detta gör att de kan diffundera längre in i trånga porer och växa B_xC-film längre ned i komplexa strukturer. TMB-molekylen användes sedan i CVD av romboidisk-BN där den gav en stabilare CVD-process jämfört med TEB.

I avhandlingens andra del studeras CVD av sp²-BN på olika material. Ett väldigt vanligt material att använda som bas i elektronikstrukturer är kisel. Eftersom kisel smälter vid 1400 °C måste CVD av sp²-BN på kisel göras vid lägre temperaturer än vanligt. CVD av sp²-BN på kiselytor kräver också att kiselytan modifieras lite för att sp²-BN-kristallen ska passa så bra som möjligt på den. Denna modifiering kan göras genom att exponera kiselytan för någon av de gasformiga reaktanterna innan man börjar belägga sp²-BN. Flera modifikationer av kiselytan som provades resulterade i sp²-BN filmer utan kristallordning, så kallade amorfa filmer. Men genom att förbelägga reaktorns väggar med ett tunt lager borkarbid och att etsa det i efterskott kunde kristallin sp²-BN deponeras på kisel. Ett annat material som har studerats är zirkoniumdiborid, ZrB₂. Detta är ett elektriskt ledande material som tål den höga temperaturen som krävs för att deponera sp²-BN med CVD – typiskt 1500 °C. Romboidisk-BN kunde deponeras på ZrB₂ och r-BN kristallerna ordnade sig efter ZrB₂ kristallerna, i så kallad

epitaxiell ordning. ZrB_2 kristallen styr alltså hur r-BN kristallen ordnar sig. Det visas även att ett mellanlager av $\text{ZrB}_x\text{N}_{1-x}$ bildas mellan ZrB_2 och r-BN.

I sista delen av avhandlingen studeras hur B-C-N filmer kan deponeras vid låga temperaturer, cirka 300 °C, genom att ersätta de höga temperaturerna med plasmaurladdningar. En plasma CVD-process med ett plasma bestående av argon och kvävgas, kvävgasen fungerar som kväverektant, och TEB som bor- och kolreaktant, studerades på ett systematiskt sätt. Mängden kol i filmerna kunde till viss mån styras genom att variera plasmaeffekten, gasflöden och förhållandet mellan kväve och argon. Filmerna som växtes påvisade en låg densitet och visade sig vara väldigt bra elektriska isolatorer då om kolinnehållet var lågt.

Résumé

Le bore et l'azote, étant situés de part et d'autre du carbone dans la classification périodique des éléments, le BN et le carbone sont donc isoélectroniques. Le carbone peut cristalliser sous forme de graphite ou de diamant. Dans le cas du graphite, chaque atome de carbone est lié à trois autres par de fortes liaisons covalentes, ce qui résulte en un feuillet de carbone avec une structure en nid d'abeille. On dit que les atomes de carbone sont en hybridation sp^2 . Chaque feuillet est lié l'un à l'autre par des forces électrostatiques faibles, les liaisons de Van der Waals. Dans le cas du diamant, chaque atome de carbone est lié à quatre autres par des liaisons covalentes. Dans ce cas, l'hybridation du carbone est dite sp^3 . De la même façon, le BN peut former des cristaux similaires au graphite, que l'on nommera BN à hybridation sp^2 (sp^2 -BN), ou similaires au diamant que l'on nommera BN à hybridation sp^3 (sp^3 -BN). La synthèse du sp^2 -BN est le fil rouge de cette thèse.

Tout comme le graphite, le sp^2 -BN peut former un cristal hexagonal (h-BN) où l'empilement des feuillets se répète de façon ABAB..A ou un cristal rhomboédrique (r-BN) où les feuillets s'empilent suivant la séquence ABCABC..A. Il peut arriver que les feuillets s'empilent de façon désordonnée. Auquel cas, la symétrie du cristal est perdue et le matériau est dit turbostratique (t-BN). Il est aussi possible que les atomes ne forment pas de feuillets, mais soient connectés les uns aux autres de manière aléatoire. Dans ce cas, le matériau est amorphe (a-BN). La principale différence entre le BN et le graphite est que le BN est un isolant électrique alors que le graphite est un conducteur. Plus précisément, le BN est un semi-conducteur à large bande. En tant que semi-conducteur, les propriétés du BN peuvent être réglées par l'addition contrôlée d'impuretés choisies (dopage). Le terme large bande fait référence à la bande interdite du matériau ; une large bande interdite implique que le transfert d'électron de la bande de valence vers la bande de conduction du matériau demande plus d'énergie. Inversement, la désexcitation radiative d'un électron de la bande conduction vers la bande de valence produit de la lumière dont la longueur d'onde sera plus courte. Ainsi, le BN devient intéressant pour les applications en électronique de puissance ou à hautes températures ; et pour les composants optoélectroniques qui fonctionnent dans l'ultraviolet (par exemple pour la désinfection de surfaces ou l'assainissement de l'eau). Enfin, du fait de leurs

structures cristallines semblables, le BN est un substrat de choix pour le graphène, qui n'est autre qu'un, ou, tout au plus, quelques feuillets de graphite.

L'association du bore et du carbone produit des carbures de bore (B_xC). Les carbures de bore ont une grande variété de compositions. Les carbures riches en carbone sont similaires au graphite, tandis que ceux riches en bore sont superdurs (leur dureté est supérieure à 40 GPa) et ont une structure particulière d'icosaèdres liés entre eux par des chaînes triatomiques. Les carbonitrures de bore, qui sont des composés ternaires de bore, de carbone et d'azote, ont des propriétés qui se situent entre celles du carbone pur et du BN. Les composés borés ont généralement d'excellentes propriétés mécaniques. De plus, l'isotope ^{10}B du bore possède une grande section efficace des neutrons et la possibilité d'enrichissement de ces composés avec l'isotope ^{10}B du bore les rend très attractifs pour la fabrication de détecteurs de neutrons.

De nos jours, la plupart des composants électroniques sont fabriqués par le dépôt de couches minces sur un substrat. La technique de dépôt utilisée dans cette thèse est la technique de dépôt chimique en phase vapeur (abrégée CVD, de l'anglais *Chemical Vapour Deposition*). Cette technique est l'une des plus utilisée dans le domaine de l'industrie électronique. Les couches minces sont synthétisées par la réaction de molécules – les précurseurs – qui contiennent les éléments constitutifs du dépôt souhaité ; dans notre cas le bore, le carbone et l'azote. Les réactions peuvent être activées par un apport de chaleur (CVD thermique) ou par l'intermédiaire d'une décharge plasma (CVD activée/assistée par plasma ou PACVD, de l'anglais *Plasma Activated/Assisted CVD*). Les précurseurs du bore et du carbone utilisés pendant cette thèse étaient les organoboranes triéthylborane (TEB, $B(C_2H_5)_3$) et triéthylborane (TMB, $B(CH_3)_3$) tandis que les précurseurs d'azote étaient l'ammoniaque (NH_3) en CVD thermique et le diazote (N_2) en CVD assistée par plasma.

La première partie de cette thèse est centrée sur l'étude de la chimie autour de la molécule TMB. L'étude de la décomposition du TMB sous atmosphère d'argon et d'hydrogène entre 700 et 1200 °C indique que ce précurseur est une source de bore viable et dont la cinétique de réaction est plus lente que TEB. En outre, on a observé un effet d'inhibition du processus de croissance des couches minces par l'hydrogène. Cet effet a été mis à profit afin de déposer des couches minces dans des structures à grand

rapport de forme. L'étude de la chimie du TMB nous a conduit(s) à déposer r-BN de façon épitaxielle sur des substrats de saphir nitrurés. Comparé au procédé équivalent basé(s) sur le TEB, le procédé basé sur le TMB est plus robuste, plus rapide et permet de déposer des couches minces de r-BN à plus basse température mais avec plus de carbone.

La seconde partie consiste en l'étude de la formation du sp^2 -BN sur différents substrats : le silicium (Si) et le diborure de zirconium (ZrB_2). Le silicium est le matériau le plus utilisé dans l'industrie micro et nanoélectronique. Par conséquent, la possibilité de déposer un matériau sur un substrat en Si ouvre la voie pour son intégration dans les technologies actuelles. Le choix d'utiliser le Si comme substrat impose des contraintes technologiques importantes pour la CVD thermique du BN. Cela est dû, d'une part, à une discordance de maille très grande entre les réseaux cristallins des deux matériaux et, d'autre part, du fait du bas point de fusion du Si ($1414\text{ }^\circ\text{C}$) qui force le procédé à opérer en deçà de $1300\text{ }^\circ\text{C}$. Par conséquent, les films ainsi déposés sont souvent amorphes. Nous avons choisi de modifier la surface du Si avant de déposer le BN, en la faisant réagir avec le carbone ou l'azote. Cependant, cela n'a engendré aucune cristallisation du BN. Néanmoins, nous avons mis en évidence un effet mémoire impliquant la présence et l'érosion du carbure de bore rhomboédrique sur les surfaces du réacteur. Par l'intermédiaire de cet effet mémoire, nous sommes parvenus à déposer des couches minces de t-BN sur le silicium. Le second substrat, ZrB_2 , a un point de fusion à $3245\text{ }^\circ\text{C}$, ce qui permet de déposer le BN à $1500\text{ }^\circ\text{C}$. La croissance du r-BN sur le ZrB_2 est épitaxielle et un prétraitement au silane (SiH_4) réduit la formation concurrente d'une phase amorphe. La stabilité du ZrB_2 est aussi mise à rude épreuve, comme le montrent la formation d'une couche intermédiaire entre le BN et le ZrB_2 , la présence de creux et d'autres défauts.

La dernière partie de cette thèse concerne la synthèse de carbonitride(s) de bore. Ces couches minces ont été déposées par CVD activée par plasma micro-onde, ce qui permet de déposer des films à basse température (autour de $300\text{ }^\circ\text{C}$). Les réactifs employés dans ce procédé ont été l'argon, le N_2 et le TEB. Ce dernier joue le rôle de source unique de bore et de carbone, tandis que l'activation du N_2 par le plasma permet de l'utiliser comme source d'azote. Les effets la puissance absorbée par le plasma, le flot total de gaz introduit et le ratio entre le diazote et l'argon sur la composition et la morphologie des couches minces, ont été étudiés de façon systématique. Selon les paramètres utilisés, leur morphologie pouvait varier

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entre couches minces lisses et couches minces constituées de nano-murs et leur permittivité électrique variait entre 3 et 35.

Preface

This thesis concludes four and a half years of research at the Thin Film Physics division of the department of Physics, Chemistry and Biology at Linköping University.

This thesis is focused on the synthesis of sp^2 -hybridised BN by CVD and explores the synthesis of boron carbides and carbonitrides. In order to put this work in context, it presents the different materials in the B – C – N system, gives an overview of the different synthetic approaches and describes various characterisation techniques that can be used to characterise such materials; with their strengths and weaknesses. The results of the research that was done during my Ph.D. studies are gathered in Chapter 8 (“Contribution to the fields”) and explained more in detail in the papers.

The work was supported by the Swedish Foundation for Strategic Research (SSF) and contract IS14-0027, the Swedish Government Strategic Research Area in Materials Science on Functional Materials at Linköping University (Faculty Grant SFO-Mat-LiU no. 2009-00971) and the CeNano program at Linköping University.

Acknowledgement

First of all, I would like to thank late Prof. Anne Henry that offered me the opportunity to join this interesting project and supervised me during the first part of my Ph.D. studies and Dr. Hans Högborg (HANS) and Prof. Henrik Pedersen (Henke) that took over the supervision. Thank you for everything!

I thank Dr. Mikhail Chubarov for training me as a grower and helping me out from afar when Maggan was up to no good, as well as Dr. Mewlude Imam for teaching me PACVD. Finally, I thank Dr. Kostas Sarakinos and Dr. Per Eklund that convinced me to apply to this position, in spite of my apprehension about Chemistry.

I thank Sven Andersson, Thomas Lingfält, Dr. Ildiko Farkas, Roger Karl Hans Carmesten, Jörgen Bengtson, Harri Savimäki, Dr. Thomas Ederth, Dr. Fredrik Eriksson, Dr. Chun-Xia Du, Dr. Urban Forsberg, Hasan Dzuho, Dr. Per Sandström, Jonas Rosberg and Dr. Roger Nilsson for the help with the equipment; Dr. Naureen Gahfoor, Dr. Melike Yilzidhan, Dr. Grzegorz Greczinsky, Dr. Susann Schmidt, Dr. Cecilia Goyenola, Dr. Polla Rouf, Babak Bakhit, Dr. Carina Höglund, Dr. Sohail, Bela Nagy, Dr. Einar Sveinbjörnsson and Dr. Fredrik Eriksson for the help with measurements; Anette Frid, Åsa Forsell, Louise Gustafsson and Therese Dannetun for the administrative work; Martin Pettersson for printing; Prof. Jordi Altimiras and Prof. Per-Olof Holtz, Dr. Fredrik Karlsson and Dr. Caroline Brommesson and Karina Malmström for the good management of Agora Materiae.

I want to thank all the members and former members of the Thin Film Division. In particular in HANS's unit: Claudia "Big Sister" Schnitter who has been watching [after] me since we were master students (many years of cakes!), Johan Nyman, – who, I heard, is directing a horror movie involving not only chain saws and falling trees, but also electric arcs, melting and explosive gases – and Sachin Sharma who will continue the BN project and who I must thank for fixing a few typos in the present thesis.

I also give special thanks to the members of the Pedersen group: Hama "Hamatite" Nadhom, Polla "ALDman" Rouf, Jin-Jah "JJ" Huang, Nathan O'Brian, Karl Rönnby, Petro Deminskyi, Rouzbeh Samii and Christian Militzer; as well as Prof. Sean Barry and Sydney "Butters" Buttera, for all the CVD/ALD and all the fun!

I would like to acknowledge all my friends and colleagues from Agora, IFM and LiU (or close enough). I may not be able to cite all of you - I am afraid, I would need to write an extra thesis Chapter for this – but here are a few: Víctor GP (Totem master, co-founder of the Wednesday Muffin Quest

and accomplice in the *flygande grisar* conspiracy), Davide G (pioneer of the last shot theory), Катя for her remote support, ALF, Alexandra Ş, Mathias F, Clio, Tim, Indre, Alexandra K, Lida from the other side, Melike and Onur, Ingemar, Judit, Kevin, Marius, Anna-Guilia, Hassan, David, Andrejs, Mr. Lai, Sebastian, Tetsu, Katherine, Michelle, Rafa, Tina, Hongling, Lianlian, Mister Max, Samiran, Nikos, Alexis, Muhammad, Florent, Mathieu, Camille and Guillaume, Ali and Alex, Julien and Aylin, Stanislav, Mikhail V, Marek, Valdas, Dr. Armakavicius, Petit Matse, Victor E, Robert B, Robert P, the omnipresent Martin E, Erik (Yu-Hsiang), Pei Hsuan, M. Bulle, Thomas Ö, Rasmus, Tedjaswi, Chara, Nina T, Nina S, Nuala, Zamaan and more.

Talking about chemistry, my fellow musicians also deserve a big thanks, as clearly would not have made it through the years without you. First to The Freeloaders: Aaron Marshall (frontman, altsax), Kiriakos Domanos (piano, keyboard), Jonas Ralmé (everything, including bass), Olof Rundquist (trumpet) and Irene Lorenzo Ramírez (altsax) and ex-Freeloaders Deni Chan (guitar), Esther Desmet (trumpet) and Christopher Tholander (trumpet). Special thanks to Lenam Malmberg (vocals, guitar mixing) who invited me in her crazy project(s). Thanks finally to the jammers, in particular Aleksandar Maksimović (accordion), Ömer Kus (guitar and bass), and Vineeth Chandrasekharan Pandalai (drums), Bo Lu (guitar, vocals), Mathieu Linares (percussions, vocals), Big Sister (keyboard) and Víctor (guitar and *coffee metal*).

From France, I also need to acknowledge the Bianchi family and Elina for their eternal support, as well as a group of engineers that had to bear with me, rather than support me: Soann, Inès, Hari, Frère Guillaume, Marion, Nico, Melina, Jean-Rob, Anne-Maelys, Fanny, JB, et le pied de coc...

Finally, I cannot neglect the support from my family, in particular: Manmie épi Papi, ki toujou ka raplé mwen fok mwen tjiénbé rèd, Maman and Papa who regularly made sure that my hair and beard did not grow too much and Andy, who seem to prefer to dig up stuff from the past rather than create the future and is still probably convinced that the average temperature in Linköping is 30° C.

Laurent Souqui

Written at Linköping, the 4th November 2019, with nice weather, 3 °C outside, a lot warmer inside, high on sugar and caffeine.

List of articles and contribution to articles

Paper I:

Gas Phase Chemistry of Trimethylboron in Thermal Chemical Vapor Deposition

Mewlude Imam, **Laurent Souqui**, Jan Herritsch, Andreas Stegmüller, Carina Höglund, Susann Schmidt, Richard Hall-Wilton, Hans Högberg, Jens Birch, Ralf Tonner, and Henrik Pedersen, *J. Phys. Chem. C* **121**, 26465–26471, (2017)

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Paper II:

Surface-Inhibiting Effect in Chemical Vapor Deposition of Boron–Carbon Thin Films from Trimethylboron

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Paper III:

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Paper IV:

Chemical vapor deposition of sp^2 -boron nitride on Si(111) substrates from triethylboron and ammonia: effect of surface treatments

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Paper V:

Rhombohedral boron nitride epitaxy on ZrB_2

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Paper VI:

Plasma CVD of B-C-N thin films using triethylboron in argon-nitrogen plasma

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Chapter 1: Introduction

This thesis is driven by the achievement of high-quality sp^2 -hybridised boron nitride films for applications such as electronics, optoelectronics, graphene-based electronics and neutron detection. Proof of concept of such devices can be found in the literature¹⁻⁵, but while most of the research of the last decade focused essentially on 2D-BN layers, the production of thick and large-area epitaxial sp^2 -BN films is still a challenge. This thesis pursues and extends the works on epitaxial sp^2 -BN deposited by chemical vapour deposition from organoborons and ammonia (MOCVD).

In order to get some insight into the organoborons chemistry involved in boron nitride CVD, the decomposition of the boron precursor trimethyl-boron (TMB, $B(CH_3)_3$) was studied. This inevitably led to the study of boron carbides and their deposition chemistry. This constitutes the first line of research of this thesis.

The second line of research focuses on the development of new routes for BN epitaxy by trying alternative precursors and substrates. It attempts to understand and solve some of the issues that have been reported in MOCVD, *e.g.* competitive growth of amorphous phases, the role played by silicon in the deposition process.

The third line of research, albeit using a similar deposition chemistry, deviates from the firsts two, as the focus is on amorphous films. Microwave plasma activated CVD is used to produce amorphous boron carbonitride smooth films and nanowalls with promising dielectric properties.

The various boron compounds in the B-C-N system related to this thesis are presented, as well as their properties and (potential) applications. The different deposition methods and relevant characterisation techniques employed are also presented and the different synthesis approaches to boron carbides, nitrides and carbonitrides are reviewed and compared to this work.

Chapter 2: Boron carbides, nitrides and carbonitrides

Boron (B), carbon (C) and nitrogen (N) are the three lightest elements of the p-bloc of the periodic table (Figure 2.1), hence respectively the fifth, sixth and seventh lightest elements in the universe.

					He
B	C	N	O	F	Ne
Al	Si	P	S	Cl	Ar
Ga	Ge	As	Se	Br	Kr
In	Sn	Sb	Te	I	Xe
Tl	Pb	Bi	Po	At	Rn
Nh	Fl	Mc	Lv	Ts	Og

Fig. 2.1: p-block of the periodic table of the elements. B, C and N are in bold.

Boron is a group 13 (former group III) metalloid of symbol B, 40th most abundant element in the Earth crust, yet the production exceeds that of silicon. Unlike the other elements of the group 13 that are metals, boron exclusively forms covalent bonds with itself resulting in peculiar icosahedral or honeycomb structures. These icosahedral structures are found in most boron-rich compounds such as many metal borides or boron carbides. The boron honeycombs are mostly found in metal diborides with the formula MB₂ (where M is a metal), in which the metal atoms are intercalated between boron sheets; or in the 2D material borophene. The

main applications of boron are in the manufacturing of ceramics, glass and fibreglass, as well as in agriculture. As most boron compounds show high hardness, boron is used in the hardening process known as boriding. Boron is also commonly used as glass-forming material. Finally, the isotope ^{10}B is a non-radioactive neutron absorber and represents 20 % of natural boron, which makes it a promising material for neutron devices.⁶

Carbon (C) is a non-metal of group 14 (former group IV). It is relatively abundant (15th element in the Earth crust). Pure carbon is usually found as graphite or diamond. Carbon is also found in many inorganic compounds (*e.g.* carbides, cyanides and carbon oxides) and is found in all organic compounds. Carbon is a versatile element due to its ability to hybridise its atomic orbitals 2s and 2p_x, 2p_y and 2p_z into sp, sp² or sp³, which offers variety of structures and properties.

Nitrogen (N) is a non-metal of group 15 (former group V, known as the pnictogen group). It is usually found as dinitrogen (N₂, nitrogen gas) which is the main constituent of Earth's atmosphere (78 %). It is also found in inorganic compounds (*e.g.* nitrides) and in organic compound as functional group (*e.g.* amine, imine).

In spite of their different compositions and structures, boron carbides, nitrides and carbonitrides share many similarities: they are light ceramics, with outstanding mechanical properties, high melting points, high crystallisation temperatures, and high chemical stability.

2.1 Boron carbides

Boron carbides are compounds of boron and carbon. The most technologically important boron carbide phases can be sorted in three different groups: boron-substituted graphites, amorphous boron-carbon mixtures and rhombohedral boron carbide. Less common crystalline phases such as tetragonal B₂₅C^{7,8} and B₅₁C⁷ or orthorhombic B₈C⁷ or B₈C₁₈⁸ have also been reported. There have also been theoretical works on superhard B₄C₃ cubic phases^{9,10}, but no synthesis has been reported yet.

2.1.1 Boron-substituted graphite

Boron-substituted graphites are boron carbides with high carbon content. Therefore, they adopt a structure similar to graphite. The boron content can be as high as 50 at. %¹¹. The substitution of carbon by boron in the

honeycombs disturbs the stacking of the layers. As a consequence, boron substituted graphite is often reported to be turbostratic^{11–16} (Figure 2.2), *i.e.* long range order remains out-of-plane but does not exist in plane¹⁷. As a result, the density of boron-substituted graphite is lower than the density of graphite.¹² The presence of boron enhances the electrical conductivity^{12,15} and opens a bandgap in the electronic structure of graphite¹⁸. The presence of B in the honeycomb also modify significantly the way graphite interacts with atomic hydrogen. According to DFT calculations, the strength of a C-H bond on the graphite surface is around 67.5 kJ/mol¹⁹ but increases up to 267 kJ/mol if a neighbouring carbon is substituted by a boron atom.²⁰ The adsorption energy increases even further (337 kJ/mol) if hydrogen interacts with two neighbouring B atoms to form a hydrogen bridge.²⁰ Additionally, the barrier for H-adsorption of 17 kJ/mol¹⁹ vanishes.²⁰ Hydrogen is also found to diffuse more easily on and through the graphite planes in case of boron-substituted graphite and to recombine at a faster rate.^{20,21} This supports the inhibited deposition of a-B_xC films in hydrogen ambient (see section 2.1.2 and **Paper II**). We also attempted to use boron-substituted graphite as a buffer for sp²-BN growth (see Chapter 8: Contribution to the field).

Fig. 2.2: Representation of turbostratic BC showing the lack of long-range order in-plane and four possible distributions of the B atom in the graphite lattice. Reproduced from ref¹¹.

2.1.2 Amorphous boron carbide

Amorphous boron carbide (a-B_xC) consists in boron and carbon covalent network without long-range order. They can have a high boron content^{22–28} (sometimes above 80 at.%) and may contain a significant fraction of hydrogen (a-B_xC:H)^{22–24,26,27,29–31}. While hydrogen free a-B_xC is of interest

for neutron detectors³², a-B_xC:H films present a low electrical permittivity while being structurally strong³³. As most boron-containing carbon material, a-B_xC is believed to interact with hydrogen in a similar fashion as boron-substituted graphites and is predicted to be promising material for hydrogen storage.³⁴

The CVD of amorphous boron carbide was investigated in **Paper I** and **Paper II**. In particular, we report in **Paper II** a conformal CVD process for a-B_xC thin film based on hydrogen adsorption.

2.1.3 Rhombohedral boron carbide

Rhombohedral boron carbide (r-B_xC) is a crystalline boron-rich form of boron carbide. Although boron carbide is often associated with the stoichiometry B₄C, it constitutes a solid solution which composition varies from B₄C to B_{10.5}C corresponding to carbon content of 20 to 8.7 at.%. Its structure consists in eight icosahedra located at the vertex of the rhombohedral unit cell and linked together along the long diagonal by a chain of three atoms (Figure 2.3).³⁵ The chain is parallel to the c-axis of the crystal. The composition of the icosahedra varies between B₁₂ and B₁₁C while the chain can be BBC or CBC.³⁶ Albeit the most accepted structure, there are still some discussion regarding the position of carbon or the structure of the chains. It is worth noting that this structure is the archetype of boron-rich phases such as boron subphosphide (B₁₂P₂), suboxide (B₆O), subarsenide (B₁₂As₂), subnitride (B_{12+x}N₂) and subcarbonitride (B₁₂(CBN)).

Fig. 2.3: Hexagonal unit cell of rhombohedral $B_{13}C_2$. C atoms are in black, B atoms are in pink. The dimensions of the cell are $a = b = 5.6 \text{ \AA}$, $c = 12.1 \text{ \AA}$, $\alpha = \beta = 90^\circ$, and $\gamma = 120^\circ$.^{37,38} The two transparent circles representing atoms from the adjacent cell, the blue solid lines revealing the B_{12} icosahedron, the red dashed lines indicating the bond in the chains, the black dotted lines indicating the bonds between icosahedra are guides for the eyes.

Boron carbide has a melting temperature of 3500°C . Its density increases from 2.47 to 2.52 g/cm^3 with increasing carbon content.³⁹ Boron carbide is one of the most chemically stable compounds. It resists to oxidation in air by forming a passive layer of boron trioxide.^{40,41} The oxidation remains limited up to 1200°C .⁴¹ Boron carbide is not corroded by most acidic and alkaline solutions. It can however be fully oxidised by molten salts (sodium carbonate, Na_2CO_3) and hot oxidising agents (sulfuric acid, H_2SO_4).⁴² Halides such as chlorine and bromine react with boron carbide at 600°C and 800°C , respectively, to form boron halides⁴².

Boron carbide presents, like most covalent solids, high mechanical properties. It is the third hardest known material. The bulk modulus of single-

crystal boron carbide is around 237 GPa.⁴³ Besides its mechanical properties, boron carbide also presents interesting electrical properties. It is an intrinsic p-type semiconductor with a bandgap between 0.48 and 2.1 eV⁴⁴⁻⁴⁶ and presents metallic grey appearance. It has a high thermal conductivity between 4 and 10 W/m/K and a Seebeck coefficient that is over 200 $\mu\text{V/K}$ above 500 °C (300 $\mu\text{V/K}$ at 1000 °C).⁴⁷

Due to its low density, easy synthesis, and high hardness, boron carbide is the chosen material for defence applications such as plate armours for soldiers and tanks; it is also used as industrial abrasive. Finally, boron carbide is a potential high-temperature thermoelectric material thanks to its electrical conductivity and Seebeck coefficient that increase with temperature, while its thermal conductivity remains constant⁴⁷.

Finally, we found that rhombohedral boron carbide can be etched by dihydrogen (H_2) and mixtures of silane and H_2 , and plays a role in the chemical vapour deposition of boron nitride (see **Paper IV**).

2.2 Boron nitrides

Boron nitrides are compounds of boron and nitrogen. As most boron compounds, boron nitrides can be divided into two groups: stoichiometric BN (or boron mononitride), which is isoelectronic and structurally similar to carbon, and rhombohedral boron subnitride, which presents similarities with rhombohedral boron carbide. Other reported controversial subnitrides such as tetragonal B_{50}N_2 ⁴⁸ will not be discussed in this section.

2.2.1 Boron mononitrides

Boron mononitride (BN) or simply boron nitride is a binary compound of boron and nitrogen with a stoichiometry 1:1. It is isoelectronic to carbon and adopts similar structures; namely hexagonal (h-BN), rhombohedral (r-BN), cubic (c-BN) and wurtzite (w-BN). In h-BN and r-BN, B and N are sp^2 -hybridised and form 2D honeycomb sheets bonded together by Van der Waals forces. In c-BN and w-BN, B and N are sp^3 -hybridised and form a covalent network.

The phases of BN share many similarities with their corresponding allotropes of carbon. The melting point of BN is 2973 °C. The strong B – N bond confers to BN outstanding mechanical properties: the Young modulus of single sp^2 -BN sheet is around 850 GPa⁴⁹ and the bulk modulus of c-BN is 400 GPa^{50,51}. This value is also predicted for the bulk modulus of w-BN⁵¹. It contributes to the superhardness (*i.e.* Vickers hardness above 40 GPa) of c-

BN⁵² and w-BN⁵³. Pure crystalline BN differs from carbon as it is always a dielectric (or, at most, a wide bandgap semiconductor), regardless of the crystal structure. This is due to the ionicity of the B – N bond induced by the higher electronegativity of the nitrogen atom with respect to boron atom.⁵⁴ It also has a higher chemical stability than carbon and is preferred to graphite and diamond for the melting and machining of ferrous alloys.

The thermodynamics of BN phases is rather complex. The phase diagram of BN with respect to temperature and pressure is still discussed. Unlike carbon, for which diamond is metastable with respect to graphite, the cubic allotrope is considered as being the stable phase of BN at standard conditions.^{55–57} The only occurrence of BN in nature is reported as c-BN inclusion in the mineral Qingsongite.⁵⁸ Another strong difference is found regarding the stability of the rhombohedral polytype. While rhombohedral graphite essentially appears as a stacking fault in natural graphite⁵⁹, rhombohedral boron nitride as often be synthesised as a majority phase^{60–68} (see **Paper III and V**) and is predicted to be the most stable one at chemical vapour deposition conditions.⁶⁹

As for carbon, boron nitride synthesised far from equilibrium can be stable as an amorphous material, a-BN. This material can be either purely constituted of sp²-hybridised bonds or be a mixture of sp²- and sp³-hybridised bonds (respectively referred to as a₂-BN and a₁-BN in Reference⁷⁰). The former is usually an under-dense soft material while the second is similar to so-called diamond-like carbon (DLC).

2.2.2 Structure of sp²-hybridised boron nitride

sp²-hybridised boron nitride (sp²-BN) refers to boron nitride compound in which boron and nitrogen are essentially sp²-hybridised. This term regroups a-BN, t-BN, r-BN and h-BN whose differences are summarised in Table 2.1

Table 2.1: differences in structural properties of sp^2 -BN

sp^2 -BN		Long range order	Stacking sequence
h-BN	“White graphite”	All directions of space	AB
r-BN			ABC
t-BN		Between planes	Undefined
a-BN		None	Undefined

Because of their similarities with graphite, h-BN, r-BN and t-BN are often referred to as “white graphite”. In h-BN, the honeycombs sheets are stacked so that B atoms (respectively N atoms) of a layer are above the N atoms (respectively B atoms) of the layer below. This can be intuitively explained as a way to optimise the electrostatic interactions between B cations and N anions and was shown to be the most energetically favourable stacking (Figure 2.4(a)).⁷¹ Consequently, the eclipsed AB stacking of h-BN differs from the so-called Bernal stacking of graphite, where the carbon atoms in each layer are above the centre of the rings of the layer below.

Fig. 2.4: Unit cells of (a) h-BN ($a = 2.504 \text{ \AA}$, $c = 6.667 \text{ \AA}$) and (b) r-BN ($a = 2.504 \text{ \AA}$, $c = 10.000 \text{ \AA}$), both orientated with the $[11\bar{2}0]$ direction facing the reader. The nitrogen atoms are in blue and boron atoms are in orange. The black dashed lines indicating the alignment of each atoms with respect to the one below are guides for the eyes.

In r-BN, each layer is staggered so that either all the cations are above anions, or all anions are above cations. This stacking was shown to be

metastable in bilayer BN with only slightly higher energy (0.4 meV/atom) than the eclipsed AB stacking.⁷¹ The ABC stacking sequence of r-BN (Figure 2.4(b)) is comparable to the one of rhombohedral graphite.

The turbostratic forms of boron nitride (t-BN) including most pyrolytic BN (p-BN) or highly orientated pyrolytic BN (HOPBN), consist in BN honeycomb sheets that are parallel or almost parallel to each other, but that are rotated, translated and/or bent with respect to each other (as shown for t-BN on Figure 2.2).^{17,72} This results in a larger distance between the honeycomb sheets to accommodate for electrostatic repulsion.

2.2.3 Properties of sp^2 -hybridised boron nitride

The properties of h-BN, r-BN and t-BN are anisotropic due to the difference in bonding in-plane (covalent) and out-of-plane (Van der Waals) and their respective crystal structures. h-BN is a wide bandgap semiconductor with an indirect bandgap⁷³ around 5.9 eV^{73–75} and with a low refractive index (2.13 parallel to the c-axis, 1.65 perpendicular to the c-axis).^{74,76} Magnesium is found to be a *p*-type dopant of crystalline sp^2 -BN (polytype non reported).⁷⁷ According to calculations, doping of h-BN with silicon is difficult⁷⁸ and experimental attempts indicate that Si is a deep donor in crystalline sp^2 -BN. The thermal conductivity at 300 K of h-BN is about 400 W/m/K in plane and 5 W/m/K out-of-plane, and these values are expected to be even higher for monoisotopic h-BN.⁷⁹ The in-plane thermal conductivity of h-BN is comparable to that of copper (401 W/m/K) and silver (429 W/m/K).⁸⁰

The literature on the properties of r-BN is scarce. r-BN is predicted to be a wide bandgap semiconductor with an indirect gap equal to or slightly smaller than the one of h-BN.⁸¹ This is supported by the work of Xu *et al.* who measured a CL emission at 5.76 eV.⁶² The absence of symmetry centre in the rhombohedral crystal induces polarisation in the crystal, consequently pyroelectric properties⁸² and, potentially, piezoelectric properties. The reported values for thermal conductivity were 180 W/m/K and 2.8 W/m/K, respectively in-plane and out-of-plane at 293 K.⁸² Si interstitial doping was calculated to be more feasible in the case of r-BN.⁷⁸

In spite of the variable quality of t-BN samples, most early characterisation of sp^2 -BN was performed on t-BN due to the lack of big enough h- or r-BN crystals, sometimes without any distinctions. Baronian and Zunger *et al.* found that the bandgap of t-BN is similar to the one of h-BN, with an absorption edge around 5.8 eV^{83,84} while lower bandgap values were estimated by Noreika and Francombe (4.9–5.2 eV⁸⁵) and Zupan and Kolar (4.3

eV⁸⁶) . The in-plane thermal conductivity of HOPBN were found to be around 240 W/m/K at 300 K in reference ⁸⁷ and around 300 W/m/K at 300 K in reference⁸⁸. The disparities in the values may be due to the quality of the sample⁸⁹ and to differences in the measurement techniques. The out-of-plane thermal conductivity was found to decrease from 2.5 to 1.7 W/m/K between 100 K to 800 K.⁸⁷ t-BN was also used to investigate the possibilities of doping. *p*-type doping was achieved using zinc⁹⁰ and beryllium⁹¹ ; *n*-type was achieved using sulphur⁹² and silicon⁹³. Still, the enhancement of the conductivity by doping must be assessed carefully, given the presence of grain boundaries in the studied materials.

Amorphous boron nitride differs from r-, h- and t-BN by being intrinsically isotropic. a-BN thin films are often reported to be hydrogenated^{94–100} and have tuneable stoichiometry^{96,101–104}. The band gap of a-BN can be as high as 5.7 to 5.9 eV^{96,102}, but lower values such as 3.8 eV⁹⁴ or 5.04 eV⁹⁹ were also reported. The dielectric constant of a thin a-BN film was estimated to be 3.7 and the dielectric strength estimated as high as 6×10^6 V/cm⁹⁴; ultrathin a-BN show dielectric strength up to 9.8×10^6 V/cm.¹⁰⁵ The refractive index of a-BN is in the range of 1.6 to 3.4.^{94,96,97,99,101,106} The main issue with a-BN is the chemical stability. a-BN films with high content of N – H bonds or halogen impurities are highly hygroscopic^{94–97} while they become inert otherwise^{94–96}. The hydrogen content can be reduced by addition of hydrogen in the gas phase⁹⁹ or annealing¹⁰⁷. a-BN also has high thermal stability: annealing of a-BN up to 700 °C does not induce crystallisation nor oxidation and reduces the stress in the films (dehydrogenation).^{95,97,107}

While the data on h-BN are usually consistent, there is a broad dispersion on the data measured on t-BN and a-BN and an evident knowledge gap on r-BN properties. Nevertheless, all forms of sp²-BN are of technological importance. h-BN, r-BN and a-BN are of interest essentially for applications in electronics and optoelectronics. These applications usually require films with low densities of defects and incoherent grain boundaries. h- and r-BN are promising material for deep UV optoelectronic devices thanks to their wide band gap and low refractive index. They could also be used for power electronics thanks to their high thermal conductivity and high dielectric strength (up to 12×10^6 V/cm)¹⁰⁸. Finally, h- and r-BN can be used as insulating substrates for graphene. Similarly, a-BN is of interest in electronics for Si doping¹⁰⁹ and as a pinhole-free dielectric layer^{96,105}. It was found that a-BN could act as a varistor.⁹⁴ t-BN can essentially be used in any application where the graphitic structure is needed but the crystalline perfection of h- or r-BN is not required. It is used for a wide range of application such as crucible, solid lubricant (*e.g.* in cosmetics), additive for lubricants and mechanical reinforcement, oxidation protective layers, release layer for

electronic devices as in¹¹⁰. As for boron carbides, BN-based neutron detectors can also be realised regardless of the crystallinity.^{3,4,111}

2.2.4 Boron subnitride

Rhombohedral boron subnitride was first synthesised by the high-pressure high-temperature method (HPHT) by compressing a mixture of boron and boron nitride powder at 7.5 GPa and 1700 °C.¹¹² Although it is agreed that boron subnitride has a structure similar to rhombohedral boron carbide, there are still debates regarding the stoichiometry of the compound. The stoichiometry B_6N was first proposed¹¹² but was the stoichiometry $B_{13}N_2$ was found to be more in agreement with X-ray diffraction data^{113–115}. However, none of these structures, represented in Figure 2.5(b) and (c), respected the electron counting rules: B_6N lacks two electrons and $B_{13}N_2$ has an extra one.¹¹⁶ An electron precise boron subnitride of stoichiometry of $B_{38}N_6$, which corresponds to a solution of B_6N and $B_{13}N_2$ in proportions 1:2, was then proposed.¹¹⁶

Fig. 2.5: Chains of (a) $B_{13}C_2$ and B_4C , (b) B_6N and (c) $B_{13}N_2$. N atoms are in blue, B atoms are in orange.

The electrical and mechanical properties of boron subnitride have mostly been calculated.¹¹⁷ B_6N and $B_{13}N_2$ are predicted to show metallic

conduction be while $B_{38}N_6$ should be a semiconductor. Boron subnitride should be a superhard, brittle material with a bulk modulus predicted to be around 230 GPa.

An early synthesis of an amorphous hydrogenated boron subnitride by CVD (B_6NH_x) was reported.¹¹⁸ Attempts to synthesise boron subnitride using MOCVD were not successful (see Chapter 8: Contribution to the fields).

2.3 Boron carbonitrides

Boron carbonitrides (BC_xN_y) are ternary compounds of boron, carbon and nitrogen. BC_xN_y are of interest for many applications as their properties are sought to be either similar to or between those of carbon and boron nitride. BC_xN_y can be separated into two categories: the soft phases that are essentially sp^2 -hybridised and the superhard phases that comprises sp^3 -hybridised covalent networks or boron icosahedra.

2.3.1 sp^2 -hybridised BC_xN_y

sp^2 -hybridised BC_xN_y are soft low-density materials with B, C and N forming sp^2 -hybridised bonds. Their properties are between the ones of sp^2 -BN and graphite, which is the main motivation for their synthesis. The composition of the films usually found in a triangular region roughly delimited by B, BN and C as shown in¹¹⁹. The curve between BN and C can be interpreted as the tendency of nitrogen to form stable volatile compounds (*e.g.* N_2) rather than getting incorporated in the films. Furthermore, the bonding structure of BC_xN_y reveals that B, C and N may either form an homogeneous network of B – C, B – N, C – N, C = N, B – B, C = C or C – C bonds^{120,121} or segregate into carbon and boron nitride domains as in¹²². Finally, sp^2 - BC_xN_y thin films are often hydrogenated and may contain sp^3 -hybridised inclusions.^{123,124} sp^2 - BC_xN_y thin films are usually amorphous^{119,123,125–137} or with a turbostratic graphitic structure^{13,138–145}. Crystalline phases can be obtained at high temperatures and high pressures.¹⁴⁶ In spite of the wide range of stable compositions and structures that are available, they are strongly dependent on the deposition method and chemistry (see Chapter 7).

As their properties are sought to be between those of graphite and sp^2 -BN, sp^2 - BC_xN_y thin films are usually semiconductors with properties that can be tuned with the composition. The band gap ranges between 0.02 and 5.5 eV (from thermal¹¹⁹ and optical method²⁴, respectively), electrical

resistivity 1.28 and $2.0 \times 10^7 \Omega \cdot \text{cm}$ ^{139,141} at room temperature and reported values of the dielectric constant are between 1.9 and 8.9 (capacitance measurements)^{147,148}. The optical properties are also composition-dependent, as seen by the reported values for the refractive index, ranging from 1.3 to 2.5 at 632.8 nm ^{148,149}. The transmission of light through these films can be up to 93% in the range $400\text{--}2500 \text{ nm}$ and is decreasing with increasing C content.^{130,150} $\text{sp}^2\text{-BC}_x\text{N}_y$ have also investigated as hard materials^{133,134,136,144,150} (around $\sim 15 \text{ GPa}$ up to 30 GPa), as solid lubricants^{119,131,133} and as oxidation barriers for the integration high- κ oxides (*e.g.* HfO_2)¹³².

2.3.2 Superhard boron carbonitrides

The other motivation for exploring the B – C – N system was to synthesise materials with the outstanding mechanical properties of diamond, in particular superhardness, combined to the chemical and thermal stability of c-BN. Cubic phases of various compositions were synthesised by HP-TP methods above 20 GPa and 1800°C .^{151–154} c- BC_2N and c- BC_4N proved to be superhard materials with hardness between those of c-BN and diamond.^{153,154} Such crystalline phases can only be synthesised above 18 GPa to avoid phase separation¹⁵³, which cannot be afforded with a low pressure method like CVD. One of the approaches has been to use vapour deposition techniques (*e.g.* PACVD, RF-sputtering, ion beam assisted deposition) that utilises ion bombardment to deposit amorphous BCN films with high content of sp^3 -hybridised bonds, similar to diamond-like carbon. PACVD diamond-like BC_xN_y films have a wide range of compositions and show microhardness values between 20 and 40 GPa .^{137,144,149,155,156} Decrease of hardness in diamond-like BC_xN_y films correlates with increasing carbon^{134,144,149} and hydrogen¹⁵⁵ contents.

Rhombohedral boron subcarbonitride has been recently calculated to be a stable compound with a crystal structure similar to rhombohedral boron carbide, but with N – B – C chains connecting the boron icosahedra (Figure 2.6).¹¹⁶ No synthesis of this compound has been reported. Synthesis by chemical vapour deposition is challenging (See Chapter 8).

Fig. 2.6: Triatomic chain in rhombohedral $B_{12}(CBN)$. C atoms are in black, N atoms are in blue and B atoms are in orange.

2.4 sp^2 -hybridised nanostructures in the B-C-N system

The study of nanostructures based on sp^2 -hybridised materials in the B-C-N system constitutes a vast research field that combines properties of materials with the physical properties that emerge at the nano-scale. Common sp^2 -hybridised nanostructures are nanotubes, nanosheets (e.g. graphene), nanoribbons (patterned nanosheets or opened nanotube), nanowalls (vertically orientated nanosheets) and fullerene (e.g. C_{60}).¹⁵⁷ Most of these nanostructures were first carbon-based and were rapidly extended to other materials, in particular BN and BC_xN_y .

2.4.1 Nanowalls

Nanowalls (NW) are, by definition, sp^2 -hybridised nanosheets that are vertically orientated with respect to the substrate surface. As mentioned earlier, first reports of nanowalls are related to the study of carbon nanostructures.^{158,159} BN ^{160–165} and BC_xN_y ¹⁶⁶ nanowalls were reported later on. The two preferred synthesis methods for NW are microwave plasma CVD (MW-PACVD) and thermal CVD.

The mechanism of formation of nanosheets but can be summarised in 3 steps:

1. Stabilisation of the sp^2 -hybridised material with respect to the sp^3 -hybridised counterpart (e.g. diamond) ^{160,167,168}
2. Orientation towards the normal to the substrate ^{167–169}
3. Suppression of other growth directions ^{168,170}

The first step can be done by the mean of H^{167} or C_2^{168} in case of carbon NW. Etching along the c-axis by fluorine has also been proposed for stabilising BN NW ¹⁶⁰. The orientation of the NW is thought to be due to lateral field effects¹⁶⁷ or crowding effects (*i.e.* the initial clusters grow flat until they meet and then curl upward to grow vertically)^{161,165,168,169}. The suppression of other growth directions can be explained by shadowing of smaller sheets¹⁷¹ and by support from adjacent sheets ¹⁷⁰.

Nanowalls have high surface-to-volume ratio and are therefore of interest for storage and catalytic applications. BN NW have interesting non-wetting properties (superhydrophobicity)^{160,161} and as most nanostructures, BN and BCN NW are interesting for electronic¹⁶³ and optoelectronic^{160,163–166} applications.

BC_xN_y NW deposited by MWPACVD with interesting dielectric properties are presented in **Paper VI**.

Chapter 3: Chemical vapour deposition

Chemical vapour deposition (CVD) gathers deposition techniques that consists in the formation of a solid from the vapour phase by the use of chemical reactions between volatile compounds such as gases and vapours. These compounds, called precursors, contain the elements constituting the solid to be synthesised.

The precursors are often diluted in a carrier gas and carried to the deposition zone by convection. There are two types of reactions that are relevant in chemical vapour deposition: gas phase reactions and surface reactions. Gas phase reactions occurs when precursors molecules dissociate or collide with other species, leading to the formation of new species in the gas phase. In the vicinity of the substrate, the gas speed drops and the reactive species from the gas phase must diffuse through a boundary layer in order to reach the surface.

These species may or may not adsorb to the surface. This can be represented by a sticking coefficient. If they manage to adsorb to the surface they can stick, diffuse, get incorporated in the growing film (or structure) or react with other species on the surface, leading to the formation of a cluster. A particular case occurs when the crystalline orientation of deposited films is dictated by the crystal structure of the substrate surface. This is called epitaxial growth and is used to deposit films that are similar to single crystals. Epitaxy is particularly used in the semiconductor industry.

Chemical vapour deposition processes exist in various forms and are attributed acronyms reflecting the activation mechanisms, the chemistry in play or specificities of a particular process. The chemical reactions can be activated using heat¹⁷² (thermal CVD, hot-wire CVD), light (Photoactivated CVD) or plasmas (Plasma-enhanced/-assisted CVD) of different kinds (*e.g.* DC, inductive, microwave, ECR). Some processes use a particular precursor chemistry such as halide (HCVD), hydride CVD or metalorganic CVD (MOCVD).^{173,174} CVD processes can also be classified depending on their operating pressure: atmospheric pressure (APCVD), low pressure (LPCVD), high vacuum (HVCVD) or high pressure (HPCVD)¹⁷⁵. Finally, pulsed processes such as pulsed pressure chemical vapour deposition (PPCVD)¹⁷⁶, flow-rate modulation epitaxy (FME)¹⁷⁷ or atomic layer deposition (ALD)¹⁷⁸ are also of technological importance. The differences between these processes influence the importance of gas phase or surface reactions, the transport processes, the need of carrier gas, the choices of substrates, the properties of the coating (structure, morphology, composition) and the complexity of the CVD tool. Most of these variants are discussed in^{179,180}.

3.1 Thermally activated chemical vapour deposition

3.1.1 Principle of thermally activated chemical vapour deposition

Thermal CVD or thermally activated CVD uses heat to activate the chemical reactions that take place in the deposition process. It is the most conventional way to perform chemical vapour deposition and, unless stated otherwise, CVD implicitly refers to this technique. CVD is usually applied below atmospheric pressure, down to ~ 1000 Pa, below which one enters the LPCVD regime.¹⁷⁹ As reactions take place in the vicinity of the hot surfaces, one may choose to heat only the substrate(s) (cold wall reactor) or to place the substrate(s) in a furnace (hot wall reactor). In a cold wall reactor, the deposition occurs essentially at the substrate and growing film surfaces and allows to minimise reactant depletion, but strong temperature gradients can lead to non-uniform deposition.¹⁷⁹ In a hot wall reactor, the temperature profile is almost uniform, but deposition occurs on the substrates and on the susceptor walls. This can cause maintenance issues and also means that the precursor efficiency is lower since more precursor is consumed than necessary.¹⁷⁹ CVD reactors exist in diverse geometries, but one can distinguish two main designs: the horizontal flow reactors and vertical flow reactors. In the horizontal CVD reactors, the incoming flow is parallel to the substrate surface while it is perpendicular for vertical reactors. In any case, CVD reactors are usually designed so that the flow is laminar.

3.1.2 Processes behind thermally activated chemical vapour deposition

The most important parameter in CVD is the deposition temperature. As mentioned in the previous section, there are three main mechanism that are involved in chemical vapour deposition: transport of the growing species to the surface, adsorption of these species and surface reactions. The surface reaction rates increase exponentially with temperature T , while mass transport increases proportionally to $T^{\frac{3}{2}}$. As a result, mass transport is much faster than surface reactions at low temperatures. This is defined

as the kinetically limited regime. At higher temperatures, surface kinetics become significantly faster than mass transport. This is defined as the transport-limited regime. However, if one increases the temperature even higher, it leads to an increase of the desorption rate. The effective deposition rate then decreases exponentially with respect to the temperature, it is called the thermodynamically limited regime. These regimes are represented in Figure 3.1 and discussed in^{179,180}.

Fig. 3.1: Arrhenius plot representing the three ideal deposition regimes. Note that the bottom x-axis represents the reciprocal temperature $1/T$ *i.e.* the highest temperatures are on the left (small $1/T$ values) and the lowest ones on the right (high $1/T$ values).

The second most important parameter is the partial pressure of each precursor, *i.e.* the concentration of each precursor. Assuming a non-reacting ideal gas mixture, the partial pressure of precursor “*i*” p_i can be estimated by Dalton’s law:

$$p_i = \frac{V_i}{V_{tot}} p_{tot} \quad (1)$$

where V_i is the volume of the precursor “*i*”, V_{tot} the total volume of the gas mixture and P_{tot} the total pressure. In the kinetically limited regime, the deposition rate R at a given temperature is proportional to the partial pressure of the precursors. Considering one precursor, first order Langmuir adsorption and an excess of adsorption sites, it can be written as:

$$R \propto k_{ads}k_r p_i \quad (2)$$

where k_{ads} and k_r are the adsorption and reaction rate constants, respectively. One can consider more complex adsorption behaviours, reactions involving more precursors or orders of reaction different from 1, if it is found to be more adapted to a given system. As the surface reactions are limiting the deposition process, the deposition rate is also dependent on the number of free sites on the surface. As result, there is a maximal partial pressure of precursor beyond which the deposition rate saturates.

In the case of transport limited regime, the deposition rate is limited by the diffusion of the precursor species through the boundary layer, hence by the diffusion coefficient D and the thickness of the boundary layer d :

$$R \propto \frac{D}{d} p_i \quad (3)$$

The thickness of the boundary layer is dependent on the gas speed which in turns increases proportionally to the total flow and to the inverse of the total pressure. The diffusion coefficient of a species in the gas containing species 1 and 2 can be described with Chapman-Enskog theory¹⁸¹:

$$D \text{ (cm}^2/\text{s)} = \frac{7.436 \times 10^{-3} T^{\frac{3}{2}} \sqrt{\left(\frac{1}{M_1} + \frac{1}{M_2}\right)}}{p(\sigma_1 + \sigma_2)^2 \Omega} \quad (4)$$

where T is the temperature, M_1 , M_2 are the molar masses of respectively species 1 and 2, p is the total pressure, σ_1 , σ_2 are the collision diameters of respectively species 1 and 2, and Ω is a temperature-dependent integral and can be taken as ~ 1 . As a consequence, CVD performed at higher total pressures (close to atmospheric pressure) affords to reach the transport limited regime at lower temperatures, while LPCVD) tends to extend the kinetically limited regime to higher temperatures.

3.1.3 Horizontal hot-wall CVD reactor

The thermal CVD reactor used in this thesis was a hot-wall CVD reactor (See schematics on Figure 3.2 and Photo on Figure 3.3). The upstream part of the CVD tool consists in a system of gas lines and purifiers. Although they were already quite pure, dihydrogen (H_2) and ammonia (NH_3) were further purified using a palladium membrane purifier and a getter purifier, respectively. The flows of the gases were set by Mass Flow Controllers (MFCs).

In case of liquid sources such as triethylboron, the vapour was extracted by bubbling the carrier gas through the liquid. The bubbler

temperature being fixed, the extracted precursor flow F_{prec} was related to the carrier flow $F_{carrier}$ by the relation:

$$F_{prec} = \frac{P_{prec}}{(P_{bub} - P_{prec})} F_{carrier} \quad (5)$$

where P_{bub} is the pressure in the bubbler and P_{prec} the vapour pressure of the liquid precursor. The pressure in the bubbler was regulated by the mean of an electronic pressure controller (EPC). The flows of the precursors could be separated before reaching the hot zone to avoid parasitic reactions (*e.g.* adduct-formation, ligand exchange) by the mean of a quartz liner.

Fig. 3.2: Simplified schematics of the Hot-wall CVD reactor.

The CVD reactor is where the chemical reactions, hence the deposition, takes place. In this thesis, the reactor consisted in a fused-silica tube, in which lied an elliptical graphite susceptors coated with silicon-carbide (SiC) and tantalum-carbide (TaC), surrounded with graphite insulation. The SiC coated susceptors were used for boron carbide deposition (from 600 °C to 1200 °C), while the TaC coated ones were used for boron nitride deposition (from 1000 to 1600 °C), due to the corrosiveness of NH_3 at these deposition temperatures.

The downstream part takes care of the by-products, *i.e.* the reaction products that should not partake in the deposition process and, in some cases, of the unreacted precursor molecules. As some of these species can

be harmful to the operator, the CVD tool or the environment, they must be neutralised. This can be done by the use of scrubbers or, in our case, an extra furnace.

Fig. 3.3: Cells of the horizontal hot-wall CVD reactor “Maggan”, showing fuse-silica tubes and RF coils around the hot zone (glowing).

3.2 Microwave plasma-activated chemical vapour deposition

3.2.1 Plasma assisted chemical vapour deposition

Plasma CVD is commonly referred to as PACVD or PECVD (for plasma assisted/activated or plasma enhanced CVD, respectively). PACVD is a chemical vapour deposition method that involves the ignition of a plasma to allow or help the deposition. A PACVD plasma usually contains neutrals and ions in atomic or molecular form, as well as electrons. The reactions in such a plasma mostly occur by collisions of these species with electrons, ions, highly reactive radicals, excited molecules and photons. This allows to use thermally stable gases such as N_2 or CO as reactant. Moreover, charged particles in PACVD, particularly ions, play a significant role in film deposition. Because electrons are lighter and usually cooler in non-thermal plasmas, they tend to diffuse-out of the plasma through the walls. As a consequence, a negative surface potential forms at the vicinity of the surface : the plasma sheath. The plasma sheath will accelerate electrons towards the plasma and ions towards the surface. Ion bombardment results in secondary electron emission, surface activation, film densification and re-sputtering. Although the deposition temperature plays a similar role as in thermal CVD, PACVD can be operated at much lower temperatures as long as the discharge is maintained. PACVD is commonly used to deposit films on temperature-sensitive substrates or to deposit metastable materials (*e.g.*

diamond). Finally, the light emanating from the plasma allows the use of non-intrusive techniques such as Optical Emission Spectroscopy (OES) to obtain chemical and physical information on the deposition process.

3.2.2 Microwave discharges

In microwave plasma CVD (MWPACVD), the plasma is generated and maintained by the mean of a high frequency electromagnetic radiation, usually 2.45 GHz (wavelength 12.24 cm). At such a high frequency, the amplitude of oscillation of both ions and electrons are small and the discharge is mainly maintained from collisions between electrons and neutrals.¹⁸² Microwave discharges operate from low (few Pa) to atmospheric pressure. Microwave plasmas employed in CVD usually have high electron densities ($\sim 10^9 - 10^{12} \text{ cm}^{-3}$), low ion energies and electron temperatures of a few eV.^{94,183} Higher production of metastable species makes microwave plasmas more performant for reaction gas activation (*e.g.* nitrogen) than lower frequency plasmas.^{183,184} Ion bombardment is often considered to be mild in microwave discharges, because the ion temperature is low and because the ions only see the average of the field of the microwave. For these reasons, MWPACVD is often performed with substrate bias in order to increase the energy of the ions. However, one needs to keep in mind that the flux of ions impinging the surface tends to be higher in microwave discharges than in lower frequency ones.¹⁸⁵ It was shown that a combination of high plasma powers and low pressures (to increase ion mean free path) enhances ion bombardment in unbiased trimethylboron-argon and triethylboron-argon microwave discharges.^{29,31}

3.2.3 Plasma CVD reactor

Most PACVD tools has a more complex design and is comparatively more costly than their thermal counterparts. There are many kinds of plasma used in CVD (*e.g.* direct current, pulsed, radiofrequency, microwave) and numerous technological solutions have been developed for each of them. This section describes the MWPACVD reactor used in the context of this thesis, with emphasis on the microwave generation as the other constituents are similar to thermal CVD tools.

Fig. 3.4: MWPACVD system "Kermit" running.

The MWPACVD reactor used in this thesis was a bell jar type reactor (see photo in Figure 3.4 and schematics in Figure 3.5). The microwave was generated from a magnetron head (2.45 GHz, up to 2500 W) and transmitted through a rectangular waveguide equipped with three-way circulator. The matching unit consisted in three metallic stubs separated by 5.5 cm that could be extended or retracted manually. An antenna located at the end of the waveguide and coaxial to the chamber directs the wave towards the chamber.

The bell jar constituting the plasma chamber was made of fused silica, which has high transmittance from middle ultraviolet (200 nm) to far infrared. It was surrounded by a metallic grid (so-called closed structure)¹⁸² and cooled by both air and water. The graphite substrate holder was not heated and not biased.

Fig. 3.5: Schematics of the MWPACVD system "Kermit".

3.3 Current challenges in chemical vapour deposition

CVD is nowadays a well-established thin film deposition technique, owing to the scalability of the processes, the absence of line of sight and the quality of the layers. There are three main challenges that CVD has to face today. The first one is ethical in essence and aims to drive CVD towards safer, cleaner and more environment-friendly processes. A lot of work must be done on the precursor-side, but the trend is there: the substitution of diborane by triethylboron for BN CVD, development of precursors for InN CVD that reduce NH₃ waste¹⁸⁶ are two examples.

The two others are essentially technological and are inherent to CVD itself: selective deposition and conformality. The selectivity of a CVD process is, given two surfaces A and B, its ability to deposit a material on surface A while surface B remains uncovered. A selective process would allow to skip most of the necessary intermediate patterning steps required by today's micro- and nanoelectronics industry.

Conformality is the ability to deposit a given material inside a high aspect ratio (AR) feature, *i.e.* a feature that is deep and thin. Such features are nowadays very common with the development of nanostructures (*e.g.* nanotube forests, nanoparticles) and nanoelectronics (digital access memory (DRAM), vertical interconnect accesses (VIAs)). The main issue

with CVD is that deposition is fast at the opening of the feature, depleting the reactants before they reach the end of the feature and resulting in clogging. The technological solutions to this question are Fluidised Bed CVD for nanoparticles (where the particles are floating in the deposition chamber) and Atomic Layer Deposition (ALD) for most nanostructures. The principle behind ALD is to suppress gas phase reaction by the combination of self-limited growth and precursor-purge cycles. While ALD became a research field of its own, its main drawback remains the deposition rate, which is in the order of a few Å/cycle on a flat surface and decreases proportionally to the square of the aspect ratio of a feature to be coated.¹⁸⁷

3.3.1 Conformal CVD processes

The main issue with high AR features comes from the decrease of the reactant partial pressure due to depletion and the time needed to diffuse along the feature. As a result, the growth rate decreases along the feature, therefore resulting in a low step coverage. The approaches to improve conformality in CVD are quite diverse and ingenious. Some, for instance, utilise the specificity of a technique such as ion bombardment in PECVD to afford conformal growth by an etch/growth mechanism¹⁸⁸ or by enhanced mobility of the growth species¹⁸⁹.

In more general cases, the ideal conditions for conformal CVD growth can be summarised as using LPCVD at low temperatures and high partial precursor pressures.¹⁹⁰ Low temperatures limit the consumption of precursor and low total pressures reduce the probability of gas phase reaction and ensure the transport of the precursor to the bottom of the feature. As mentioned earlier (Section 3.1.2), the growth rate in the kinetically-limited regime is known to saturate for high precursor vapour pressure. Hence, the decrease of the precursor partial pressure along the feature is not significantly affecting the deposition rate; as opposed to the case of low precursor partial pressure.¹⁹⁰ This approach has been used extensively to deposit conformally a variety of thin film (*e.g.* copper, titanium diboride, magnesium oxide).^{191–197} On the contrary, another approach is to perform CVD at high pressures (HP-CVD), so that the mean free path of the molecules is in the nanometre range or below.¹⁷⁵ In this case, the precursors are transported in the high AR features in the same way as observed for macroscale features. Chemical Fluid Deposition¹⁹⁸ takes the advantages of both previous methods by using a supercritical ambient (*e.g.* CO₂ at 20 MPa and 175-

200 °C) which can accommodate three order of magnitude higher precursor concentrations.¹⁹⁸

Another approach consists in utilising the deposition chemistry to reduce the reaction probability: self-termination, surface poisoning, and inhibition are three different ways to deposit conformal films by CVD. As its name implies, self-termination describes a growth process where the density of dangling bonds decreases to the point that no incoming species can bond to the surface, terminating the growth. Surface catalyst poisoning describes a similar behaviour, with the difference that the deposition process is terminated by the addition of another species that bonds strongly to the surface without creating a new dangling bond. This was for instance observed during the deposition of iron films from iron pentacarbonyl $\text{Fe}(\text{CO})_5$ where the ligand, CO, is found to poison the surface and terminate the growth.¹⁹⁹ Interestingly, the growth could be restored by the addition of NH_3 .¹⁹⁹ Inhibition is similar to poisoning, the main difference being that it is a reversible process. Inhibition can be done by increasing the concentration of the precursor ligands²⁰⁰ or by addition of a foreign inhibitor molecule, as in^{201,202} and in **Paper II**.²⁰³ The first case differs from the second because increasing the ligand concentration enables not only to increase competitive adsorption, it can also move the reaction equilibrium backward (recombinative desorption). Besides ligands and inhibitor molecules, the reaction by-products can also induce inhibition, as predicted in Reference²⁰³. Finally, the CVD of stoichiometric compounds using several precursors can be inhibited if one of them is in excess.²⁰³ This has been used to deposit superconformal MgO coatings showing a higher deposition rate at the bottom of the high AR feature than at the top, using $\text{Mg}(\text{DMADB})_2$ and H_2O .^{204,205}

Chapter 4: Characterisation techniques

4.1 X-ray Scattering techniques

4.1.1 X-Ray Diffraction

X-ray diffraction (XRD) is a light scattering technique that allows to investigate the crystal structure of material.

XRD is based on the interaction of X-rays with electrons. X-rays are electromagnetic waves with a wavelength between 0.01 and 100 Å. In laboratory diffractometers, X-rays are usually produced using a copper anode (Cu, 1.54 Å) but other anodes can be found (*e.g.* Cr, Fe, Co, Ni, Mo or Ag)^{206,207}. When an electron interacts with a primary planar X-ray wave, it oscillates and generates a spherical wave of the same energy (elastic scattering). In the case of material without long-range order, most spherical waves emitted by each electron in the material would interfere destructively. In the case of crystalline materials, where atoms are ordered in parallel planes with an interplanar distance of the order of magnitude of the wavelength of the X-rays, there are conditions where the waves interfere constructively resulting in a high intensity secondary planar wave. These conditions can be determined by Bragg's law:

$$2d_{hkl} \sin(\theta_B) = \lambda \quad (6)$$

where d_{hkl} is the interplanar distance between the (hkl) planes, θ_B is the Bragg angle and λ the X-ray wavelength. Bragg's law shows that for a given wavelength, a given plane spacing d will correspond to a given diffracted angle θ .

A more accurate description can be done using the reciprocal space and the scattering vector. The reciprocal lattice is built on the real lattice so that each (hkl) plane in the real lattice corresponds to a reciprocal vector with a norm $2\pi/d_{hkl}$ and a direction that is normal to the planes. The scattering vector $\mathbf{Q}$ is defined as the difference between the wavevectors of the incident and diffracted beams and:

$$|\mathbf{Q}| = \frac{4\pi}{\lambda} \sin(\theta) \quad (7)$$

The Bragg's law is verified when the scattering vector is equal to a reciprocal vector:

$$|Q| \equiv \frac{4\pi}{\lambda} \sin(\theta) = \frac{2\pi}{d_{hkl}} \Rightarrow 2 \sin(\theta) d_{hkl} = \lambda$$

As such, the scattering vector is one of the most important quantities in X-ray diffraction, as it defines both the orientation and the interplanar distance of the family of planes being studied. The direction of the scattering vector can be either fixed or varying depending on the type of measurement. More details about the theory of X-ray scattering and the following techniques are to be found in References ^{206,207}.

Fig. 4.1: $2\theta/\theta$ configuration. The dotted lines indicating the parallel planes are guides for the eye.

The most common type of XRD measurement is the so-called $2\theta/\theta$ (or $\theta/2\theta$). For this measurement the scattering vector is maintained perpendicular to the sample surface by moving simultaneously the X-ray source and the detector as shown on Figure 4.1. As results, only the planes parallel to the sample surface are detected. This measurement is often carried out in a powder diffractometer with fixed height. As its name implies, a powder diffractometer is more suitable for samples with random crystalline orientations such as powders or polycrystalline thin films. Layers with fibre texture and epitaxial layers can also be analysed but extra measurements must be carried out to fully resolve the crystal structures. Some cases, such as films deposited on offcut substrates, require the scattering vector to be slightly tilted with respect to the surface normal. The measurement is then

referred to as $2\theta / \omega$. Amorphous materials may also be characterised and might show broad features - often several degrees broad in a $2\theta / \omega$ scan - and of relatively low intensity.

Most advance XRD techniques for thin film characterisation require a diffractometer equipped with a Eulerian cradle. Such diffractometers offer the possibility to translate the sample laterally (x and y direction) and orthogonally (z direction), and to rotate the sample around the surface normal (ϕ axis) and to rock the sample, *i.e.* tilt the sample normal with respect to z (ψ axis) (See Figure 4.2).

Fig. 4.2: Schematics representing the directions x, y and z and the ψ and ϕ angles with respect to the sample normal (red arrow).

The three most important thin film X-ray diffraction techniques used in this work are: Grazing incidence diffraction (GID, Grazing incidence grazing exit x-ray diffraction), azimuthal scans (ϕ -scans and pole figures) and Grazing incidence XRD (GI-XRD) and they are described in the following paragraphs.

Fig. 4.3: GID configuration. The dotted lines are guides for the eye.

GID is an in-plane diffraction technique. It consists in performing a $2\theta/\omega$ with the sample at a ψ angle between 89 and 90° as shown on Figure 4.3. By doing so, it allows to access the planes that are perpendicular to the sample surface. As a grazing incidence technique, it is a surface sensitive technique with a shallow probing depth and a beam spot spreading beyond the sample surface. The small probing volume induced by the high ψ value tends to limit this technique to epitaxial layers or layers with biaxial textures.

Fig. 4.4: ϕ -scan. The grey dashed line represent the rotation axis (ϕ).

Azimuthal scans allow to record diffraction from planes that are not parallel to the surface, thereby allowing to obtain information on the in-plane distribution of the scattering domains. This can be done by recording a ϕ -scan, where the sample is rotated around the surface normal while ψ , θ and 2θ are fixed (Figure 4.4). It is also possible to record several ϕ -scans for several ψ values. This results in a 2D representation of the distribution of the measured plane spacing and is called a pole figure. An example of pole figure can be found in section 5.3.1 (p51). ϕ -scans and pole figures have their respective advantages and disadvantages: for the same measurement time ϕ -scans allow to record diffractograms with higher resolution than pole figures but are limited to films with biaxial texture and epitaxial films while pole figures can be used to analyse polycrystalline films as well. GID and ϕ -scans can be combined to measure epitaxial thin layers, however extra care must be taken when measuring crystals with 3-fold symmetry

(e.g. cubic, rhombohedral) as the (k00) planes are measured twice (for φ and $\varphi+180^\circ$) resulting in 6 diffraction peaks instead of 3.

GI-XRD is a grazing incidence technique where the incidence angle α is fixed while 2θ is varied. As a consequence, the direction of the scattering vector varies and makes angle of $(2\theta - \alpha)/2$ with surface normal (Figure 4.5). Like GID, GI-XRD is a surface sensitive technique, but it is more suited for polycrystalline samples. α is usually chosen slightly higher than the critical angle of the film to avoid total internal reflection (which occurs in air as solids usually have a refractive index below 1 at X-ray wavelengths).

Fig. 4.5: GI-XRD configuration. The dotted line is a guide for the eye.

Boron, carbon and nitrogen are light elements and are therefore poor X-ray scatterers. Nevertheless, thin film diffraction techniques are amongst the few techniques that allow for the determination of the crystallinity and of polytype of sp^2 -BN. t-BN, h-BN and r-BN can easily be distinguished by a $2\theta/\omega$ in polycrystalline form but the task is more difficult for thin textured films and epitaxial layers. In these later cases, a $2\theta/\omega$ scan can only assess the presence of a textured sp^2 -hybridised material that could be sp^2 -BN but may as well be graphite or BC_xN_y . In case of epitaxial crystals two GID scans, as in **Paper III** and **Paper V**, two φ -scans or two pole figures (one for each polytype, as in^{65,66}) are needed to determine the predominance of h- or r-BN. In case of fibre textures, only pole figures can confirm the polytype (**Paper IV**). Azimuthal scans are also useful to reveal twinning (**Paper III**, **Paper V**, and References^{65,66}). This has been discussed more in detail in the following review.²⁰⁸

4.1.2 X-Ray Reflectometry

X-ray diffraction (XRR) is a light scattering technique that relies on the reflection of X-rays at a surface. In the most general cases, XRR allows to estimate the density and roughness, and in case thin films, their average thickness and interfacial roughness. XRR results must be fitted to a proper model in order to extract accurate values.

XRR consists in a $2\theta/\omega$ scan recorded with a parallel beam at low angles (usually $0.1^\circ < 2\theta < 10^\circ$). A reflectogram can usually be divided into 3 regions: I, II and III.²⁰⁷ Region I often shows an increasing intensity with increasing 2θ and is mostly related to sample shape. Region II forms a plateau of maximal intensity and in region III the intensity falls steeply with increasing 2θ . The critical angle is found between region II, where total internal reflection occurs in the medium of higher refractive index (*i.e.* air in our case), and region III, as beyond the critical angle more of the radiation penetrates through the sample. In case of a thin film and a thin multi-layered sample, the incident beam is partly reflected by the surface and each interface in the sample. All the reflected beams interfere at the detector, forming the characteristic Kiessig fringes of X-ray reflectograms.

The pieces of information that one can obtain by fitting a thin film X-ray diffractogram are the density of each layer, the roughness at the surface and interfaces and thickness of each layer.^{207,209} The critical angle increases with the density of the film. The Kiessig fringes carry two pieces of information: the thickness of each layer and its density. The 2θ difference between two fringes $\Delta_{2\theta}$ is approximately equal to the ratio of the wavelength over the film thickness t_{film} by²⁰⁷:

$$\Delta_{2\theta} \approx \frac{\lambda}{t_{film}} \quad (8)$$

The intensity of the fringes is related to the density contrast between the layers.²⁰⁹ Roughness and interfacial roughness are obtained by fitting the decay of the X-ray beam.^{207,209}

XRR works best with sharp surfaces and interfaces and there is no requirement on the nature of the sample to be analysed (besides being at least a solid or a liquid). Furthermore, the fringe spacing is not dependent on material properties. There are also several drawbacks: the modelling can be challenging for complex systems, films below a few nm or above 100 nm and films with high surface roughness, rough or diffuse interface are

not suitable for the technique. The unavailability of some combinations of film and substrate with high density contrast can also be an issue.

4.2 Microscopy techniques

4.2.1 Scanning Electron Microscopy

Scanning Electron Microscopy (SEM) is a microscopy technique that relies on the interaction of the atoms of a sample surface with an incident electron beam. Such interactions are diverse: emission of secondary electrons, backscattering, emission of electromagnetic radiation which in turn can be used for imaging, spectroscopy or diffraction. In this thesis SEM was mostly used for imaging.

SEM imaging is usually performed by scanning the sample in parallel lines (so-called rastering) with a focused electron beam. The spatial resolution of the microscope is often between 1 and 10 nm depends on energy of incident electrons (1-30 keV) and the size of the probe.

The secondary electrons generated by the interaction of the electron beam with sample surface are attracted by the detector, in which they will be accelerated and converted into photons by the mean of scintillator-photomultiplier system. The two most common type of secondary detectors are the Everhart-Thornley (E-T, so-called “conventional”) secondary electron detectors and the immersion lens (so-called “in-lens”) secondary electron detector. The E-T detectors is placed sideways, out-of-the optical axis of the microscope. The contrast generated by this type of detectors originates from edge effects (See Figure 4.6) and the information in the micrographs is essentially topological.

Fig. 4.6: Schematics representing edge effects in secondary electron imaging. Compared to the flat surface (a), more secondary electrons (represented by blue arrows) escape from the material at edges (b). Inversely, less electrons manage to escape at the bottom of a step (c).

On the contrary, the in-lens detector is located on or inside the last lens of the column and aligned with the optical axis. The measurements require a smaller working distance than with the E-T detector. The contrast generated is partly due to edge effects, but the in-lens detector is also very sensitive to the work function of the material on the surface. The information in in-lens images is not only topological but also depends on the physical properties (*e.g.* electrical conductivity) of the sample. (see **Paper IV**, where a strong contrast between BN and SiC is seen)

The advantages of SEM for studying films in the B-C-N system are the high resolution and the relatively quick sample preparation. SEM offers the possibilities to study complex morphologies with high lateral resolution. It was particularly used to measure thicknesses and average deposition rates (**Paper I, II, III, and VI**), surface coverages (**Paper V**), study film morphologies (**Paper I, IV, and VI**) and deposition processes (**Paper I, IV, and V**). The main issue is the charge build-up, in particular for BN, that leads to deflection of the beam (*e.g.* image distortion) or repulsion of secondary electrons (voltage contrast). Another disadvantage is the limited use of Energy Dispersive X-ray Spectroscopy (SEM-EDXS, SEM-EDX, SEM-EDS) for quantitative compositional analysis as the technique is not suited for light elements, in particular boron.

4.3 Spectroscopy techniques

4.3.1 X-Ray Photoelectron Spectroscopy

X-ray photoelectron spectroscopy is an analytical technique that allows to assess the composition and chemical bonding structure of a surface.

It is based on the photoelectric effect, that is the interaction of light with matter. When a core electron bound to an atom absorbs an X-ray of high enough energy to overcome the ionisation potential of an atom, this electron leaves the core and the excess energy is converted into kinetic energy. The kinetic energy of this so-called photoelectron is the quantity of interest in XPS measurements.

XPS experiment are usually carried out at fixed wavelength. The kinetic energy E_{kin} is related to the binding energy E_B by the relation:

$$E_B = h\nu - E_{kin} \quad (9)$$

where $h\nu$ is the energy of the incident radiation.

Since the binding energy of core electrons is mostly dependant on the nucleus, they allow to easily perform semi-quantitative evaluation of the materials composition. But the most important feature of XPS is the possibility to analyse the materials chemistry. This is due to the fact that it costs less energy to form a cation if there is a high electron density around the original atom. In other words, a photoelectron originating from an atom that is bonded to a more electronegative element (*e.g.* boron to nitrogen) will have a lower kinetic energy (higher binding energy) because such an atom has already its electrons pulled away by the electronegative atom. The opposite is observed if the same atom is bonded to a more electropositive element (*e.g.* boron bonded to zirconium). Hence, the shifts in binding energy from the elemental value in XPS spectra reflects the chemical environment of each atom. Although XPS does not measure chemical bonds, valuable information on the chemical bonding structure can be extracted from chemical shifts.

There are a few limitations regarding XPS. Ultra-high vacuum (UHV) is needed to increase the mean free path of the photoelectrons and allow them to travel through the analyser and reach the detector without being scattered. The mean free path of electron inside the sample still remains short.²¹⁰ One can consider that 95 % of the photoelectrons originate from depths that are around three times the inelastic mean free path *i.e.* in the order of 10 nm. This is why XPS is considered a surface analytical technique. In most cases, surfaces are covered with adventitious carbon and oxygen. This contamination can be removed by sputter-cleaning with an argon gun. If the subsurface of the sample is of interest, a depth profile can be

performed by alternating argon sputtering and analysis, but care must be taken regarding matrix effects (*e.g.* preferential sputtering, intermixing).²¹¹ An issue that can be encountered with insulating samples is differential charging, which leads to shifts in the spectrum and, if too important, prevents the formation of new photoelectrons. Charging must be compensated by the use of an electron flood gun. Finally, hydrogen and helium cannot be directly detected since they do not have core electrons.

Regarding boron carbides and nitrides characterisation, XPS allows to measure boron, carbon, nitrogen and oxygen content without overlaps and high sensitivity (except for boron). In the case of boron carbides, the interesting features are the shifts of B 1s and C 1s depending on structure of the carbide. Reported values for crystalline carbide and B-substituted graphite are gathered in Table 4.1. a-B_xC usually shows a broad peak between 186 and 190 eV for B 1s and often contains hydrogen which makes it difficult to characterise them with XPS.

Table 4.1: reported peak positions for B₄C and sp²-B_xC (commercial B₄C used as standard in ²¹²⁻²¹⁴)

Core	Binding energy (eV)	Attribution	Ref
B 1s	186.5	B-cluster	214–216
	187.1 – 187.8	B bonded to B in B ₄ C	212–214
	188.1 – 188.6	B in sp ² -B _x C	212,214,216
	188.3 - 188.6	B bonded to C in B ₄ C	214,217
C 1s	281.7 – 281.8	sp ³ -C in B ₄ C chain	213,214,218
	282.6	C with at least one B as first neighbour	214
	283.8	C with no B as first neighbour in sp ² -B _x C	214
	282.9-283.7	C in B ₄ C icosahedron	213,217

XPS usually provides less information for BN: B 1s is located around 190.5 and N 1s around 398 eV regardless of the hybridisation.^{219,220} BN samples also tend to suffer from differential charging. Unlike Auger photoelectron spectroscopy, XPS does not allow to differentiate easily the different BN phases.¹⁵⁴ Nevertheless, an extra loss feature, the π -plasmon loss peak, should be observable in case of sp²-hybridisation. This plasmon is seen as a broad low intensity peak located around 199 eV and 407 eV for respectively B and N in sp²-BN¹⁵⁴, and around 291 eV for C in graphite.

4.3.2 Fourier Transform Infrared Spectroscopy

Infrared Spectroscopy relies on the interaction of infrared (IR) light with materials. Metals, for instance, have free electrons that can oscillate much faster than the electric field of IR radiation. As the result they can absorb IR light by oscillating at the same frequency as the incident wave and re-emit a wave of same frequency and a phase change of π . Most materials with metallic conduction are good reflectors in the infrared. This is not the case of insulators which do not have free electrons. The bonding in insulating compounds is often partially covalent and partially ionic, due to the difference of electronegativity of the constituent atoms. The ionic contribution reflects the concentration of the density of negative charges around the most electronegative atoms. As the results, a permanent electrical dipole forms between the atoms. The strength of the inherent electric field generated by the dipole is dependent on the distance between the two atoms. If these atoms oscillate, there will be a given frequency at which the inherent electric field of the dipole will couple with the electric field of the light. If one assumes that atomic bonds follow Hooke's law, the frequency ν is usually given by²²¹:

$$\nu = \frac{1}{2\pi} \sqrt{\frac{k}{\mu}} \quad (10)$$

where k is the force constant representing the stiffness of the bond and μ is the reduce mass defined as:

$$\mu = \frac{m_1 m_2}{m_1 + m_2} \quad (11)$$

where m_1 and m_2 is the mass of each atom forming the bond.

If the frequency of the incident light and the natural frequency of the bond match, and if the symmetry of the crystal allows it, a resonant phenomenon is observed. This resonant phenomenon is called one-phonon absorption or Reststrahlen absorption. The Reststrahlen band is located between the transverse and longitudinal optical modes (TO and LO, respectively) and is characterised by a quasi-total reflection from the crystal. Multi-phonon processes can also occur but are of minor importance in this thesis.

The strength and limitation of IR spectroscopy is that it relies on permanent dipoles. This implies that any compounds with some degree of ionicity can be detected, regardless of its crystallinity. The main differences between amorphous and crystalline phases are seen from the position and

number of bands that can be resolved and their sharpness, as the full width at half maximum (FWHM) of the peak reflects the distribution of oscillators. An IR spectrum can literally be seen as a characteristic signature of a material, and material with a complex structure such as B_4C or $\alpha-Si_3N_4$ can be easily identified. The response from compounds of elements with similar electronegativity such as boron phosphide (BP, the Pauling electronegativity of B and P are 2.04 and 2.19) is weak.²²² Simple elemental compounds have a dull response to IR but defects (*e.g.* vacancies) can give rise to permanent dipoles and respond to IR.²²³ Compounds with metallic conductivity usually simply reflect IR light, so that little spectroscopic information can be obtained.

From a more practical perspective, IR spectroscopy can be performed in transmission or in reflection configuration. Transmittance T is directly related to absorbance A by the relation²²¹:

$$A = -\log(T) \quad (12)$$

Reflectance spectra are often deformed due to dispersion and can be converted into absorbance spectra by the mean of the Kramer-Kronig transform.²²⁴

Fig. 4.7: Schematics representing a FT-IR measurement of a thin film on a partially reflective substrate.

In the case of thin films on a flat surface, a measurement performed in reflection configuration will provide a transmittance spectrum that consists in the sum of the reflectance from the film surface and the transmittance through the film, as shown in Figure 4.7. It must be noted that the light travelling through the film covers twice the distance that it would

cover for the same film thickness and incident angle. In the case of a thin film on a highly reflective surface (*e.g.* a metal), the transreflectance spectra can be approximated as²²⁵:

$$\frac{I}{I_0} = R_{film} + 2T_{film} \quad (13)$$

where I is the measured intensity, I_0 is the incident intensity, R_{film} the reflectance of the film and T_{film} the transmittance through the film. This approximation is not valid anymore when one considers a thick film, as the contribution from the transmittance decreases exponentially with the travelled distance (Beer-Lambert's law). The validity of this approximation is also compromised when the substrate is not a good reflector and the problem becomes more complex when reflection occurs only at specific frequencies (*e.g.* sapphire, as seen in the supporting information of **Paper III**). In this case the absorption peaks from the same material can appear pointing up or down, whether the reflection from the substrate is low or high, respectively. Another feature of thin film IR spectroscopy are thin film or substrate interferences which can be used to estimate thicknesses but can also complicate spectral analysis.^{224,226–231}

Finally, Fourier Transform Infrared Spectroscopy (FT-IR) is a particular method of IR spectroscopy that utilises a Michelson interferometer and Fourier transform to perform and record the spectra. This allows to reduce the measurement times from a few hours to a few minutes (50 scans in about 60 s with 2 cm⁻¹ resolution in our case). It is preferable to perform the measurements using an IR-inactive ambient, most often N₂, so that absorption from water and carbon dioxide (CO₂) is minimised.

Regarding BN characterisation, FT-IR can differentiate the sp²-hybridised phases and sp³-hybridised phases as shown in Table 4.2:

Table 4.2: Resonant frequencies measured on crystalline and turbostratic BN phases. Experimental data and calculations do not agree for w-BN.

Frequency (cm ⁻¹)	BN Phase	Mode	Ref
783	sp ² -BN (h-, r-, and t-BN)	A _{2u} TO, out-of-plane bending	232
824	sp ² -BN (h-, r-, and t-BN)	A _{2u} LO, out-of-plane bending	232
960	w-BN	?	233
1065	c-BN	T ₂ TO	222
1090	w-BN	?	233,234
1120-1150	w-BN	?	233,234
1230-1250	w-BN	A ₁ LO and E ₁ LO ^{235,236}	233,234
1340	c-BN	T ₂ TO	222
1367	sp ² -BN (h-, r-, and t-BN)	E _{1u} TO, in-plane breathing	232
1610	sp ² -BN (h-, r-, and t-BN)	E _{1u} LO, in-plane breathing	232

The TO or LO modes of thin sp²-BN layers can be activated depending on whether the polarisation of light is parallel to the c-axis or not.^{232,237} In case of thick layers, a 2-phonon absorption can be observed in reflectance spectra at around 1550 cm⁻¹.²³² Amorphous sp²-phases show the same absorption bands, but broader.

In case of boron carbide films, sp²-B_xC tends to reflect the light as graphite does, and a-B_xC such as the ones deposited in **Paper I**, usually has featureless spectra. An absorption peak around 1000-1100 cm⁻¹ is typical of B-C bonding. r-B_xC has a peculiar spectrum as shown in **Paper IV** (supporting info) with two strong absorption bands corresponding to chain bending (around 410 cm⁻¹) and stretching (around 1600 cm⁻¹) and many absorption bands related to vibrations within the icosahedra.²³⁸ The relative positions of the bands depend on the composition.^{36,238}

BC_xN_y shows similar spectra as BN, often with broader peaks and potentially additional bands for B-C and C=N bonds at around 1000-1100, 1600-1700 cm⁻¹, respectively.^{120,239}

4.3.3 Optical Emission Spectroscopy

In this thesis, Optical emission spectroscopy (OES) was used to characterise the plasmas generated in PACVD. OES is a non-intrusive technique that relies on the emission of light by excited species. Excited atomic species, including atomic ions, generates light at precise frequencies that corresponds to their electronic levels. Diatomic excited molecular species also emit light, but their spectra consist more in bands rather than peaks. This is explained by the fact that excited molecules can lose energy by vibrations.

OES allows to access only a part of the chemical information in the plasma. Big molecules tend to lose all their excess energy by vibration and relax non-radiatively. In non-collisionless discharges, excited species can also transfer their excess energy to other species in the plasma instead of emitting light. Finally, the spectra of CVD plasmas containing many different colliding atoms become quickly complicated, as the number of potential molecular radicals found in the plasma increases and the signal of each species is likely to overlap with another (so-called interferences).

4.4 Ion beam techniques

4.4.1 Time-of-Flight Elastic Recoil Detection Analysis

Time-of-Flight Elastic Recoil Detection Analysis (ToF-ERDA or ToF-ERD) is an ion beam technique that allows quantitative compositional analysis and estimation of either thickness or density at the condition that the other is known. ERDA relies on the recoil of target atoms by a high energy heavy ion beam. The energies are in the range 10-200 MeV and the ions from C to Au can be used as projectile.^{240,241} ToF-ERDA measures both the energy and the time-of-flight to extract the mass and initial position of the recoiled atoms. As a consequence, all light elements, including hydrogen and helium, can be detected with high mass resolution (^{10}B and ^{11}B give a separate signal) and quantified. In principle, elements that are lighter than the projectile ion will be recoiled, while heavier target atoms or iodine ions themselves can reach the detector under appropriate conditions. In our case, we used a 36 MeV ^{127}I ion beam (**Paper III**). ERDA is not affected by the density of sample. It is therefore possible to combine for instance ERDA and XRR to estimate a thickness or ERDA and SEM to estimate a density. However, the probing depth of ToF-ERDA is limited (depending on the density of the film and incident ion) and the depth resolution can be between

1 and 20 nm depending on experimental conditions²⁴² (e.g. depth, incidence angle).

4.5 Electrical characterisation techniques

4.5.1 C-V measurements

Capacitance-Voltage (C-V) measurements is a type of electrical measurement. It consists in measuring the capacitance *i.e.* the amount of charges that can build up on two electrodes separated by a dielectric.

In our case Al contacts were deposited on the thin film surface and a 100 kHz voltage (20 V peak-to-peak) was applied between the contacts. The application of voltage to a dielectric will deplete isotropically the charge carriers in the contact region. If the contacts are far apart, and their diameter larger than the film thickness (e.g. $L = 5 \text{ mm} \gg d = 500 \text{ }\mu\text{m} \gg t_{\text{film}} = 500 \text{ nm}$), the depletion layers would be localised under the contacts (See Figure 4.8). The system can be modelled as a circuit with two ideal condensers in series, with a dielectric layer of capacitance C_{film} and thickness t_{film} and electrodes of area A_{contact} . From this, one can evaluate the dielectric constant κ (or electrical permittivity) of a film by the mean of the expression:

$$\kappa = 2 \frac{t_{\text{film}} C_{\text{film}}}{A_{\text{contact}} \epsilon_0} \quad (14)$$

where ϵ_0 is the permittivity of vacuum.

The dielectric constant is of interest for the nanoelectronics industry, as the current Si-based dielectrics have reached their limits in terms of permittivity and thinness. There are two types of dielectrics: the ones that have higher permittivity than SiO_2 ($\kappa > 3.9$, high- κ dielectric materials) and the ones that have lower permittivity than SiO_2 ($\kappa < 3.9$, low- κ dielectrics). BN is a low- κ dielectric and the dielectric constant of BC_xN_y film can be modulated between high and low- κ values by changing the film composition (**Paper VI**).

Fig. 4.8: Schematics representing the C-V measurement setup of a dielectric thin film (here $\text{sp}^2\text{-BC}_x\text{N}_y$) on a conductive substrate (here B-doped Si) and the equivalent circuit.

Chapter 5: Thermal chemical vapour deposition of boron carbides

In view of getting better understanding of the chemistry involved in the MOCVD of BN, one needs to understand the deposition chemistry of the precursors. This chapter focuses on the thermal CVD of boron carbides. Although boron carbides have been extensively deposited by other CVD deposition methods such as HWCVD and PECVD, these will not be discussed in this chapter.

5.1 Precursors for boron carbide deposition

Thermal CVD of boron carbide does not show as much variety as PACVD and is typically done using boron halides. Organoborons can also be used single-source precursor for boron carbides as they intrinsically contain both B and C atoms.

5.1.1. Halide CVD

Boron halides are molecules containing boron bonded to halogen atoms *e.g.* fluorine, chlorine, bromine or iodine. They are non-flammable and non-explosive precursors.

Halide CVD of boron carbides usually involves the reaction of a boron halide (*e.g.* BCl_3 , BBr_3) with methane. The commonest gas mixture remains $\text{BCl}_3 + \text{CH}_4$. Halide CVD allows to deposit crystalline boron carbide phases (orthorhombic, tetragonal and rhombohedral phases) above 1100 °C.^{7,42,243,244} Whiskers could be deposited by replacing CH_4 by tetrachloromethane (CCl_4).²⁴⁵ To deposit boron-substituted graphite, more reactive hydrocarbons such as acetylene (C_2H_2)²¹⁴ or benzene (C_6H_6)^{12,14} are used. Halide CVD of boron carbides is associated with the formation of highly poisonous gas (*e.g.* F_2 , HF, Cl_2 , HBr) and corrosive acids (*e.g.* HF, HCl).

5.1.3 Single-source precursors

As organoborons already contain carbon, they can be used as single-source precursors for boron carbides. Trialkylborons such as TEB and TMB, as well as tributylboron (IUPAC: tributylborane, TBB, $B(C_4H_9)_3$) were used to deposit amorphous boron carbide films.^{25,27,28} Triphenylboron (IUPAC: triphenylborane, TPB, $B(C_6H_5)_3$) was used to deposit boron-substituted graphite films.¹⁵ Finally, TMB²⁸ and TEB allow to deposit rhombohedral boron carbide (**Paper I** and **Paper IV**).

There is a marking difference between the decomposition chemistry of TMB and the one of higher trialkylborons. TEB, for example, can let go of its ethyl ligands by a mechanism called β -hydride elimination. This mechanism is described in Figure 5.1. As its name suggests, this mechanism involves one of the hydrogens bonded to a β -carbon of the molecule *i.e.* a carbon in second position from the boron centre. Provided that the energy is high enough, TEB can fold one of the ligands so that the boron centre bonds to one three hydrogens of the β -carbon, weakening the B – C bond. Ultimately, the B – C bond breaks and the ethyl ligand gives away its hydrogen to form a C = C bond and leave as an ethylene molecule (C_2H_4). This process can be repeated for each ligand. This mechanism is the most favourable decomposition path for TEB and accounts for the similar composition of the a- B_xC films deposited in hydrogen and argon.²⁷

Fig. 5.1: Elimination of a ligand of TEB by β -hydride elimination

As TMB does not have any β -carbons, it cannot undergo β -hydride elimination. We found that the most likely decomposition pathway was via α -hydride elimination, as described on Figure 5.2. This mechanism involves one of the hydrogens of an α -carbon and another α -carbon: the hydrogen atom bonds to another methyl group, which then leaves as a methane molecule (CH_4) while the methyl group that has lost its α -hydrogen forms an extra bond to the boron centre and becomes a methylene ligand.

Fig. 5.2: Elimination of a ligand of TMB by α -hydride elimination

The capability to undergo β -hydride elimination or not is reflected by the dissimilarities between TEB and TMB: TEB decomposes from 400 °C yielding films with high B/C ratios, the B/C ratios are similar in both H₂ and Ar ambient and decrease with increasing temperature^{26,27} while, on the contrary, TMB is stable up to 650 °C, depositing films with low B/C ratios that increase with temperature (up to 1000 °C) and with higher B/C ratios in hydrogen than in argon due to H₂-assisted elimination (**Paper I**).

Organoborons have the advantage of having few heteroatoms, most often hydrogen, which prevents the incorporation of impurities. The main drawback of the use of a single-source precursor is that the composition of the deposited film at a given temperature is strongly dependent on the initial composition of the precursor. Additionally, the cracking of the carbonaceous by-products at high temperature will lead to the formation free graphitic carbon, as it was shown with TMB (**Paper I**).

5.3 Substrates for boron carbides CVD

Thermal CVD boron carbides have been deposited on various substrates such as silicon^{27,28,202,245}, α -boron^{243,244}, graphite²⁴⁵, platinum²⁴⁵, titanium²⁴³, copper¹⁴, tantalum¹⁴, molybdenum²⁴³, α -Al₂O₃²⁵, quartz^{14,214}. Single-crystal boron carbides were deposited on tantalum and on BN substrates.⁷ No relationships to the substrates were reported.

5.3.1 Silicon carbide substrates for boron carbide epitaxy

Silicon carbide substrates (4H-SiC, 6H-SiC and 3C-SiC), albeit expensive, are commercially available as wafer up to 8" (4H-SiC). They have

proved to be lattice-matched substrate for epitaxial rhombohedral boron-rich solids such as $B_{12}As_2$ and $B_{12}P_2$ as their in-plane lattice parameter is equivalent to twice the one of SiC. It is somewhat expected that SiC would be an ideal substrate for rhombohedral boron carbide epitaxy. The relative lattice mismatch of a B_4C unit-cell over two unit-cells of SiC is of 9.1 %. However, we found that, if boron carbide grows epitaxially on 6H-SiC, as shown on Figure 5.3 and 5.4, it grows with the following out-of-plane epitaxial relationship:

$$r-B_xC[02\bar{2}1]||6H-SiC[0001]$$

The six-fold symmetry of the substrate result in twinning. Two sets of twins are recorded. The first one at $\psi = 62.7^\circ$ corresponds to $(2\bar{2}01)$ and $(\bar{2}021)$ planes of the crystal with the $[02\bar{2}1]$ direction aligned parallel to the $[0001]$ of the substrate and presents 30 peaks (Figure 5.4, black curve). The second set of twins, at presents 12 peaks has lower intensity and does not present any alignment with the $[0001]$ direction of the substrate (Figure 5.4, blue curve). The poles of the corresponding $(2\bar{2}01)$ and $(\bar{2}021)$ planes should be at $\psi = 83.3^\circ$. Unlike for $B_{12}As_2$ and $B_{12}P_2$ deposition, SiC may not be the ideal substrate for $r-B_xC$ epitaxy.

Fig. 5.3: Pole figure measurements of the $\{02\bar{2}1\}$ family of planes of $r-B_xC$ ($2\theta = 37.7^\circ$) deposited on 6H-SiC at $1500^\circ C$ from TEB in H_2-N_2 ambient. The weak spots at $\psi = 0^\circ$, $\psi = 44.5^\circ$ and $\psi = 62.7^\circ$ belong to $r-B_xC\{02\bar{2}1\}$ and the strong ones are the tails of $6H-SiC\{10\bar{1}3\}$ ($2\theta = 37.963^\circ$, $\psi = 61.5^\circ$).

Fig. 5.4: ϕ -scans measurements of the $\{02\bar{2}1\}$ family of planes of $r\text{-B}_x\text{C}$ ($2\theta = 37.7$) deposited on 6H-SiC at 1500 °C from TEB in $\text{H}_2\text{-N}_2$ ambient, taken at 44.5° (blue) and 62.7° (black). The six sharp high-intensity peaks are the tails of 6H-SiC $\{10\bar{1}3\}$ ($2\theta = 37.963^\circ$, $\psi = 61.5^\circ$). The 30 peaks recorded at $\psi = 62.7^\circ$ (black) belong to twinned crystals with the $[02\bar{2}1]$ perpendicular to the surface and the 12 peaks recorded at $\psi = 44.5^\circ$ (blue) belong to another set of twinned crystals.

Chapter 6: Thermal chemical vapour deposition and epitaxy of sp^2 -hybridised boron nitride

This chapter focuses on the thermal CVD of sp^2 -boron nitrides. The different approaches in term of precursor chemistry and substrates are reviewed in the context of this thesis. Although both sp^2 - and sp^3 -phases of boron nitrides, together with 2D BN and BN nanostructures, have been extensively deposited by other CVD deposition methods such as Hot-Wire CVD and PACVD, they will not be discussed in this chapter.

6.1 Precursors for BN deposition

The most common boron precursors used for BN deposition can be classified in three groups: the hydrides, where boron is bonded to hydrogen; the halides, where boron is bonded to halogens and the organoborons where boron is bonded to organic ligands.

The source of choice for nitrogen is always ammonia, (NH_3) as it is more reactive than nitrogen gas (dinitrogen, N_2), easier to handle than other azanes (*e.g.* hydrazine N_2H_2). Most nitrogen halides are known to be sensitive explosives. Amines have not yet been used in thermal CVD of BN, but rather for BC_xN_y .¹²¹ Furthermore, attempts to use methylamines for gallium nitride deposition indicates that they are not a promising precursor for the thermal CVD of nitrides.²⁴⁶ Nitrogen oxides (*e.g.* NO, N_2O , NO_2) are usually avoided because of they are strong oxidisers.

Instead of choosing a precursor for each element, an alternative way is to use a single-source precursor that contains both B and N atoms and preferably already bonded. Only a few studies utilised single-source precursors in thermal CVD of BN, probably because the high deposition temperatures used for BN deposition quickly resulted in the gas phase decomposition of these molecules.

6.1.1 Hydride CVD

Boron hydrides or boranes are the boron counterpart of hydrocarbons. The smaller borane (BH_3) dimerises via a three centre-bond to form the molecule diborane (B_2H_6). Diborane has been used to deposit BN.^{94,101,109,118,247,248} The films deposited from B_2H_6 are often reported to be amorphous or nanocrystalline below 1000 °C^{94,247} or polycrystalline h-BN

above¹⁰⁹. Unless the deposition is performed in a LPCVD reactor (0.27 Pa in¹¹⁸), the deposition rate is found to drop drastically with the increase of the NH₃ flow^{94,101,247,249} which is a strong drawback considering the high N/B ratios needed in BN CVD. Despite the advantage of containing only hydrogen as a heteroatom, diborane remains an explosive and poisonous precursor.

6.1.2 Halide CVD

As mentioned earlier (see Chapter 5), boron halides are molecules containing boron bonded to halogens.

Boron trifluoride (BF₃) had extensively been studied for c-BN plasma deposition rather than sp²-BN thermal CVD. Pierson²⁵⁰ and Hannache *et al.*²⁵¹ used BF₃ and NH₃ to deposit sp²-BN on BN fibres and into carbon pores, respectively. Hannache *et al.* found that the ideal temperature windows for the deposition of BN was 1100-1200 °C, as the growth rates below 1100 °C were “extremely low” and temperatures above 1200 °C resulted in significant etching of the substrates.²⁵¹ They concluded that their films from BF₃ were poorly crystallised.

Boron trichloride (BCl₃) is one of the most commonly used CVD precursors for boron nitride.^{76,95,251–257} BCl₃ renders amorphous sp²-BN films below 700 °C, t-BN films in the range 700-1600 °C^{252,254,257} and h-BN from 1300^{251–253}. Epitaxial h-BN films deposited from BCl₃ were also reported.²⁵³ Boron tribromide (BBr₃) is mostly used for BN atomic-layer deposition (ALD) rather than CVD, as ALD is usually performed at low deposition temperature and the B – Br bonds are weaker than B – F and B – Cl bonds (435 kJ/mol against 766 kJ/mol and 536 kJ/mol)²⁵⁸. sp²-BN films were deposited by CVD on graphite from reaction of BBr₃ and NH₃.²⁵⁹ The only report of CVD of BN using boron triiodide (BI₃) was to produce BN nanowires.²⁶⁰

As previously mentioned in Chapter 5, boron halides are non-flammable and non-explosive precursors. However, because of their high electronegativities, halogens form strong bonds to boron and tend to be incorporated in the deposited films. As for boron carbide CVD, the main issue with handling boron halides is the formation of highly poisonous gases and corrosive acids together with the formation of solid salts (*e.g.* NH₄Cl) which can be harmful to both the operator and the CVD tool. Interestingly, while safety concerns increase with decreasing size of the halogen, BI₃ is still the less explored amongst the boron halides precursors for BN CVD. Parasitic adduct formation (further detailed in Section 6.1.3) between the halide precursor and ammonia was also reported.²⁵⁷

6.1.3 Metalorganic CVD

The term metalorganic CVD (MOCVD) is used to describe a CVD process that uses organometallic precursors. As boron is not a metal, organoborons are not organometallics *per se*, but are often considered as such. In spite of being relatively strong, B – C bonds (448 kJ/mol) are weaker than B – F or B – Cl bonds. This should ease the release of the ligands and afford lower deposition temperature.

The most common organoboron employed for BN CVD is triethylboron (IUPAC: triethylborane, TEB, $B(C_2H_5)_3$). TEB has become a standard precursor for sp^2 -BN CVD^{3–5,64,65,77,103,110,111,177,261–270}. Amorphous and turbostratic films are usually obtained below 1200 °C.²⁶⁵ Epitaxial films are reported from the reaction of triethylboron and ammonia above 1200 °C (see References^{65,66,177} and **Paper V**).

Trimethylboron (IUPAC: trimethylborane, TMB, $B(CH_3)_3$) has been much less investigated as a boron source for BN deposition. One reason might have been safety concerns. Another reason might have been the fact that unlike TEB, TMB is not an efficient B-source at low temperatures is due to its slower kinetics of decomposition.^{25,28} $TM^{10}B$ was used to fabricate ^{10}BN -based neutron detectors⁴ and epitaxial growth of r-BN on sapphire is shown in **Paper III**⁶⁸. There are no reports of BN CVD from higher trialkylborons.

Trimethylborate ($B(OCH_3)_3$) was also used to deposit BN single layers²⁷¹ and t-BN on fibres²⁷², which may seem counterintuitive given the fact that B – O bonds (806 kJ/mol)²⁵⁸ have a higher dissociation energy than B – N bonds (398 kJ/mol)²⁵⁸.

Formation of organometallic-ammonia adducts tends to occur in MOCVD. This has been observed during the deposition of group 13-nitrides^{273,274}. This is due to an acid-base reaction between the organometallic (Lewis acid) and NH_3 (Lewis base). Such a reaction is known to occur between TEB and NH_3 , leading to a reduced growth rate²⁷⁵, although the lower stability of the adduct with respect to the separate precursors and higher barrier for ethane elimination suggests that the adduct-derived species should not disturb the deposition process itself²⁷⁶. A TMB: NH_3 adduct is also well known but is not stable above 15 °C.²⁷⁷ While it is ascertained that adduct formation in the gas phase plays a determinant role in MOCVD, it is rather unclear whether they are beneficial or detrimental to the deposition process in case of BN.

The ligands of metalorganic precursors, including organoborons, become prone to decomposition above 1200 °C. This was observed for with TEB where the B/C ratio is close to 0 for the highest susceptor

temperatures.²⁷ It is also one of the reason why MOCVD GaN and AlN are deposited below 1200 °C¹⁷⁴. Albeit easier to handle than diborane and halides, trialkylborons are both pyrophoric and corrosive and trialkylborates are flammable. In addition, TMB and trimethylborate are also toxic.

6.1.4 CVD of BN from single-source precursors

The most interesting single-source precursors for sp²-BN are ammonia-borane (AB, H₃BNH₃) and borazine (B₃H₆N₃, borazole) since H is the only heteroatom. AB is isoelectronic to the ethane molecule (H₃C-CH₃) while borazine is isoelectronic to benzene (C₆H₆). AB is a stable solid at standard condition while borazine is a liquid that must be kept cooled to avoid decomposition. Heating of AB induces dehydrogenation from 110 °C and polymerisation above 130 °C and turbostratic BN is formed above 1170 °C²⁷⁸. The pyrolysis of borazine is also known to induce polymerisation²⁷⁹. t-BN can be obtained from 800 °C^{280,281} and annealing of the product above 1400 °C leads to h-BN.²⁸¹

Most other single-source precursors for BN were initially developed as alternatives to diborane and boron halides for deposition of c-BN. Hence, while plasma CVD of these precursors have been extensively studied, there are fewer reports on pyrolysis and thermal CVD. It turned out that, albeit safer, thermal CVD of these precursors usually produced sp²-BN films.

Some of them are derivative of borazine: B-trichloroborazine (B-TCBA, B₃Cl₃H₃N₃), hexachloroborazine (HCBA, ₃Cl₆N₃), N-trimethylborazine (N-TMBA, B₃H₃(NCH₃)₃), B-trimethylborazine (B-TMBA, (BCH₃)₃H₃N₃), N-triethylborazine (N-TEBA, B₃H₃(NCH₂CH₃)₃) and N-tripropylborazine (N-TPBA, B₃H₃(NC₃H₇)₃) are simple examples from the literature. Amorphous sp²-BN films were deposited from B-TCBA even above 1100 °C^{282,283}, t-BN from HCBA at 900 °C²⁸⁴ and t-BN from N-TMBA between 980 and 1080 °C²⁸⁵. Interestingly, the pyrolysis of N-TEBA and N-TPBA yielded amorphous films whose EELS spectra were similar to B₄C²⁸⁶. The massive 5H,12H,19H-tris(1,3,2-benzodiazaborolo)borazine (C₁₈H₁₅N₆B₃) was found to give amorphous films with high carbon content.¹³¹

Another category of compounds are acyclic aminoboranes with boron bonded to three nitrogen atoms such as tris(dimethylamino)borane (TDMAB, B(N(CH₃)₂)₃) and triazaborabicyclodecane (TBBD, B(NHC₃H₂)₂N). TDMAB was used to deposit sp²-BN films from 700 to 1000 °C.¹⁰⁶

Finally, some can be described as adducts or complexes between an amine and a borane such as trimethylamine borane (TMAB, (H₃C)₃NBH₃),

triethylamine borane (TEAB, $(\text{H}_3\text{CH}_2\text{C})_3\text{NBH}_3$) or pyridine borane (PB, $\text{C}_5\text{H}_5\text{NBH}_3$). However, thermal CVD using TEAB or TMAB resulted in carbon-rich films which makes them less attractive for BN CVD,^{128,134,287,288} although the use of high NH_3 partial pressures allows to get close to stoichiometric BN.²⁸⁹

With the exception of borazine, there are no reports of BN epitaxy with single-source precursors, but this may change with the development of 2D materials and the regained attention of BN in this context.

6.2 Carrier gas

The carrier gases usually used for BN deposition are helium (He)²⁵⁶, argon (Ar)^{65,76,118,257,283,290}, dinitrogen (N_2 , nitrogen gas)^{4,65,101,118,253,269,281,291,292}, dihydrogen (H_2 , hydrogen gas)^{5,64-66,95,98,252,254,257,262,263,267,291,293} or mixtures of these gases^{65,95,103,259,294-296}. At low pressures (LPCVD), carrier gases are not needed.^{83,177,279,291} While noble gases such as Ar and He do not intervene in the deposition chemistry, they differ in their physical properties (*e.g.* thermal conductivity, molar masses, collision diameters) which has an influence on the transport of reactive species to the substrate. He is less common than Ar due to its higher price and is mostly used in earlier works. Unlike Ar and He, hydrogen gas tends to facilitate the decomposition of molecules in the gas phase and near the surface, takes care of impurities (*e.g.* Cl by forming HCl , CH_x by forming CH_4) and may also adsorb on surfaces. Finally, nitrogen gas is commonly used as an inert carrier gas in CVD, however care must be taken in the case of nitride deposition, as nitrogen is one of the two main products of ammonia decomposition (the other one being H_2).

There are few studies regarding the effect of carrier gas on BN epitaxy. Thermodynamics calculations showed that the use of H_2 in halide CVD allows to reduce the input of NH_3 needed to deposit BN.²⁹¹ Carminati *et al.* recently showed that the reaction between BCl_3 and H_2 leads to the formation of BHCl_2 which disturbs BN growth.²⁵⁷ Their films deposited in Ar showed better crystalline quality than those deposited in H_2 as seen from XRD and TEM. Finally, the preferential use of inert gas for BN halide CVD is supported by the epitaxial h-BN films deposited by Umehara *et al.* in an N_2 ambient.²⁵³ On the contrary, hydrogen is mostly used in the case of MOCVD. Chubarov *et al.* showed that H_2 should be used as a carrier gas in order to grow epitaxial r-BN by MOCVD.⁶⁵ Kim *et al.* also support that hydrogen is beneficial for the growth, as hydrogen is able to heal defects during growth.²⁶⁹

6.3 Substrates for sp²-BN deposition and epitaxy

There are four requirements on the substrates for sp²-BN epitaxy:

- Be stable around 1200 °C and preferably above 1600 °C
- Respect the symmetry of the lattice of BN
- Have a similar lattice parameter
- Have a similar negative thermal coefficient of expansion as BN at low temperature ($-2.7 \times 10^{-6} \text{ K}^{-1}$)²⁹⁷⁻²⁹⁹ or a positive thermal coefficient of expansion as small as possible

6.3.1 Silicon substrates

Silicon substrates have been extensively used in boron nitride CVD as they are of high technological interest. The Si(111) surface has a three-fold symmetry which would be ideal for both r-BN and h-BN epitaxy. The linear thermal coefficient of expansion of Si is $2.6 \times 10^{-6} \text{ K}^{-1}$.³⁰⁰ The relative lattice mismatch, as defined by: $\frac{a_{\text{film}} - a_{\text{substrate}}}{a_{\text{substrate}}}$ (with a_{film} and $a_{\text{substrate}}$ the in-plane lattice parameter of respectively the film and the substrate surface) is of -34.4 % but there is a “magic match” of 1.6 % for 3 BN cells over 2 Si cells.

Silicon remains one of the most challenging substrates for BN epitaxial growth which requires temperatures above 1200 °C. Most attempts to deposit films below 1200 °C without plasma resulted in amorphous or turbostratic films.^{94,98,101,102,109,118,257,265,281,295,301} As expected from a melting point of 1414 °C, silicon undergoes changes already at low temperatures. Regular monoatomic steps appear at the silicon (111) surface on the Si surface above 1000 °C upon annealing in H₂.^{302,303} Nitrogen from NH₃ is readily incorporated in the Si(111) subsurface above around 500 °C and the onset for nitridation is around 800 °C.³⁰⁴⁻³⁰⁹ The Si(111) surface reacts with hydrocarbons such as acetylene and ethylene to form SiC alloys from 600 °C and 700 °C, respectively.^{310,311} In **Paper IV**, we pre-treated the surface to reduce its reactivity towards C and N.

6.3.2 Sapphire substrates

Sapphire substrates ($\alpha\text{-Al}_2\text{O}_3$) are also of technological interest, as wafers up to 8 inches are commercially available. The melting point of $\alpha\text{-Al}_2\text{O}_3$

is around 2040 °C. α -Al₂O₃ has rhombohedral crystal structure which would make ideal α -Al₂O₃(0001) substrates for both h-BN and r-BN epitaxy. The relative lattice mismatch is of -47.4 %, which can be interpreted as 5.2 % mismatch for 2 BN cells on sapphire. Its in-plane thermal coefficient of expansion is about $8 \times 10^{-6} \text{ K}^{-1}$ (around 1000 °C).³¹²

Regarding its stability, hydrogen etches sapphire at high temperatures. Reported values for the etch rate are 3 nm/h at 1100 °C³¹³ and close to 100 nm/min at 1500 °C³¹⁴. α -Al₂O₃ reacts readily with NH₃ to form AlN_xO_y below 800 °C and polycrystalline AlN forms above 800 °C.³¹⁵ Epitaxial AlN can be obtained above 850 °C.³¹⁶ h-BN epitaxy was reported to grow directly on sapphire²⁵³ but controlled-nitridation was shown to improve sp²-BN nucleation on sapphire.^{64,270} A controlled nitridation of α -Al₂O₃(0001) allows for the deposition of twinned epitaxial r-BN^{64,65,68} with the out-of-plane epitaxial relationship:

$$\text{r-BN}[0003] \parallel \text{w-AlN}[0002] \parallel \alpha\text{-Al}_2\text{O}_3[0001]$$

and in-plane relationships:

$$\text{r-BN}[11\bar{2}0] \parallel \text{w-AlN}[11\bar{2}0] \parallel \alpha\text{-Al}_2\text{O}_3[10\bar{1}0]$$

$$\text{r-BN}[11\bar{2}0] \parallel \text{w-AlN}[11\bar{2}0] \parallel \alpha\text{-Al}_2\text{O}_3[\bar{1}010]$$

A few nanometres epitaxial h-BN can be found at the interface.^{67,317}

6.3.3 Graphite and graphene substrates

Graphite substrates would be the ideal substrate for sp²-BN heteroepitaxy: it has similar crystal structure, lattice parameter (relative lattice mismatch of 1.7 %) and sublimes between 2300 and 3500 °C at CVD conditions³¹⁸. The thermal coefficient of expansion of graphite is negative (minimum around $-1.4 \times 10^{-6} \text{ K}^{-1}$) below 400-500 °C and is around $1.0 \times 10^{-6} \text{ K}^{-1}$ above 1000 °C.³¹⁹

There have been few attempts to deposit sp²-BN on graphite^{252,259,281,291} and graphene. Most of the depositions on graphite render t-BN films below 2000 °C.^{252,281,291} A reason may be the quality of the graphite substrate which could be turbostratic as well.²⁸¹ The biggest issue with graphite is the similarity of the lattices that complicates the characterisation by XRD. Graphene substrates should have better quality than graphite substrates and easier to use in combination with XRD but should also be sensitive to etching. Growth of thick BN layers was attempted on epitaxial graphene on 6H-SiC but rendered t-BN films.²⁶² Recent works report epitaxy of a few layer BN on graphene.³²⁰⁻³²² Methane can be used to compensate for the etching of the graphene template.³²²

6.3.4 Silicon carbide substrates

Silicon carbide substrates (SiC), albeit expensive, are commercially available nowadays as wafer (up to 8 inches in diameter). The melting point of SiC is 2730 °C. The two most common polytypes are the hexagonal polytypes 4H- and 6H-SiC which are suitable for h-BN epitaxy but will inevitably induce twinning in the case of r-BN. The cubic polytype (3C-SiC) might be preferable for r-BN epitaxy but is less available. The relative lattice mismatch between BN and each polytype is of -18.7 %, but the unit cell of 4H-SiC and r-BN have similar c lattice parameter (10.096 and 10.000, respectively). The thermal coefficient of expansion is increasing significantly and almost linearly with the temperature: $\alpha_{11} = 3.2 \times 10^{-6} + 3.6 \times 10^{-9} T \text{ (K}^{-1}\text{)}$ for 4H-SiC³²³ (in-plane) and 3C-SiC³²⁴ and $\alpha_{11} = 3.2 \times 10^{-6} + 3.6 \times 10^{-9} T \text{ (K}^{-1}\text{)}$ for 6H-SiC³²⁵.

Graphitisation (by sublimation) improved nucleation but rendered t-BN films.²⁶² Chubarov *et al.* found that a proper ramping up in SiH₄-H₂ allows to deposit twinned, polytype-pure, epitaxial r-BN on 3C-, 4H- and 6H-SiC.^{66,67}

6.3.5 Metallic substrates

Metallic substrates have often been studied for sp²-BN epitaxy due to their catalytic action.²⁵⁵ Early works demonstrated the possibility of depositing thick and orientated sp²-BN films on nickel¹⁷⁷ and steel^{76,255}. With the growing interest in 2D materials, epitaxy of a monolayer, a few layer or clusters of sp²-BN was shown on Co³²⁶, Ni²⁹², Cu³²⁷, Cu-Ni alloy³²⁸, Ru³²⁹, Rh³³⁰, Ir³³¹ and Pt^{332,333}. The main drawbacks of metallic substrates are the lack of large single-crystal metals, and the limitation of the growth to one or a few layers sp²-BN as the catalytic action of the metal is impeded once the first BN layer is grown.

6.3.6 Zirconium diboride substrates

Zirconium diboride (ZrB₂) substrates, available in bulk and thin film form, gained attention in the field of 13-15 materials.³³⁴⁻³⁴³ ZrB₂ is a conductive ceramic with an electrical resistivity of $7.0 \times 10^{-6} \Omega \cdot \text{cm}$ ³⁴⁴ and with a high melting point (3245 °C). It has low absorption and high reflectivity around 5 and 6 eV³⁴⁵ which makes it an interesting substrate material for BN- and AlN-based UV devices. The relative lattice mismatch with

respect to the BN lattice is -21 % but this value can be reduced to -1.2 % by considering a mismatch of 5 BN cells over 4 ZrB₂ cells. The average in-plane thermal coefficient of ZrB₂ is $6.6 \times 10^{-6} \text{ K}^{-1}$ between 20 and 800 °C.³⁴⁶

We report r-BN epitaxy on ZrB₂ for the first time in **Paper V**. We observed the formation of interlayer with a cubic NaCl structure, often reported as ZrB_xN_{1-x} in the literature and of unknown composition. The epitaxial relationships were, out-of-plane:

$$r\text{-BN}[0001] \parallel \text{ZrB}_x\text{N}_{1-x}[111] \parallel \text{ZrB}_2[0001] \parallel 4\text{H-SiC}[0001]$$

and in-plane:

$$r\text{-BN}[11\bar{2}0] \parallel \text{ZrB}_x\text{N}_{1-x}[220] \parallel \text{ZrB}_2[11\bar{2}0] \parallel 4\text{H-SiC}[11\bar{2}0]$$

6.4 Status of BN epitaxy by CVD

Orientated sp²-BN film with respect to the surface substrate is usually reported. Besides the numerous studies focusing on the deposition and epitaxy of a few BN honeycomb layers, sp²-BN epitaxy of thicker layers was only demonstrated using BCl₃²⁵³, TEB^{65,66} and TMB (**Paper III**) as B-precursor and NH₃ as N-precursor. Epitaxial films were obtained from TEB on Ni(111)¹⁷⁷, 3C-SiC(111)⁶⁶, 4/6H-SiC(0001)⁶⁶, α-Al₂O₃(0001)^{65,68,253}, and ZrB₂(0001) substrates (**Paper V**). This clearly shows that there are still many unexplored paths for BN epitaxy whether in terms of chemistry (heavier boron halides, single-source precursors, other nitrogen precursors) and substrates (other orientations, other high-temperature substrates).

There are significant differences between the BN epitaxy from BCl₃ and from trialkylborons on α-Al₂O₃(0001). The halide process used N₂ as a carrier gas, unlike the MOCVD process that used H₂. While r-BN was the predominant phase deposited using TEB and TMB, h-BN seems to be deposited from BCl₃. The three precursors showed a similar temperature window, but the optimal temperature was found to be 1500 °C for TEB^{65,66}, 1400 °C for TMB (**Paper III**) and 1200 °C for BCl₃²⁵³. The morphological differences between them remains the most striking: the BN films deposited from BCl₃ presented a typical pebble-like structure as often reported, while BN crystals from TEB and TMB presented triangular crystals with sharp edges and a smooth surface but suffers from the competitive growth of a rough amorphous phase.³⁴⁷

Chapter 7: Plasma Chemical Vapour Deposition of Boron Carbonitrides

This chapter focuses on the plasma CVD of sp^2 -boron carbonitrides. The different approaches in term of precursor chemistry are reviewed in the context of this thesis. sp^2 - BC_xN_y films deposited by plasma CVD are usually not aimed to be epitaxial, therefore most studies are done using Si substrates. The commonest plasma in this context are radiofrequency (RF, 13.5 MHz) and microwave (MW, 2.45 GHz) plasmas, but some direct current (DC) discharges are found.

7.1. Different approaches for sp^2 -BCN thin films

7.1.1 Three-precursor approach

The three-precursor approach is the simplest and allows to have more control on the plasma composition¹¹⁹. The main drawback of using a precursor for each element is that they often contain heteroatoms (*e.g.* Cl) that can easily be incorporated in the films.³⁴⁸ The usual precursors are B_2H_6 or BCl_3 for B, a hydrocarbon (*e.g.* CH_4 , C_2H_6 , C_2H_4 , C_2H_2) for C and N_2 or NH_3 for N.^{119,136,141,147,149,348,349} Ar and H_2 are often used for dilution, Ar is sometimes added to stabilise the plasma discharge¹²⁰. BC_xN_y nanowalls were synthesised by microwave PACVD using BF_3 - CH_4 - N_2 - H_2 .¹⁶⁶

Using three separate precursors allows to deposit both binary and ternary compounds with various compositions.¹¹⁹ However, the few reported ternary compounds deposited at low temperatures ($< 650\text{ }^\circ\text{C}$) with this approach seem to have lower B content ($< 30\text{ at. } \%$) if diborane is used as a boron source^{119,136,149} and higher B content ($> 30\text{ at. } \%$) if BCl_3 or BF_3 is^{141,166,348,349}. At higher temperature ($> 900\text{ }^\circ\text{C}$) the composition of the films seems to be more dependent on precursor flows and sp^3 -hybridisation starts to occur.¹²³

7.1.2 N-coordinated boron precursors

This approach consists in using molecules with B-N bonds such as the ones presented in the previous chapter. As most of them contain carbon-based ligands, they can be used as single-source precursors for BC_xN_y films.

On the one hand, the composition of the film becomes constrained by the composition of precursor but, on another hand the deposition process can be tuned more easily by adding only one other precursor (most often N_2 , H_2 , NH_3 or CH_4).

The plasma decomposition of amine-borane adducts such as pyridine-borane and trimethylamine-borane yielded nitrogen-deficient films^{125,127,143}, carbon-rich at 250 °C¹²⁵ and boron-rich^{127,143} above 500 °C. Addition of H_2 , N_2 or CH_4 did not seem to affect the composition of the films^{125,127,143}; addition of NH_3 allowed to incorporate more N instead of carbon¹⁴³.

Another alternative are the triply coordinated precursors such as triazaborabicyclodecane (TDDB) and tris-(dimethylamino)borane (TDMAB), in which boron is bonded to three nitrogen atoms. TDDB was found to produce only carbon-rich films at 250 °C, even with the addition of nitrogen.¹²⁵ On the contrary, TDMAB- H_2 deposited boron-rich films (B/(C+N) ratio around 1) above 650 °C.³⁵⁰ Carbon tended to replace boron at increasing temperatures.³⁵⁰

The borazine derivatives with alkyl ligands N-TEBA^{148,239} and N-TMBA^{130,137,144,155,156,288,351} have been extensively studied to deposit sp^2 - BC_xN_y films. The films obtained with N-TMBA have usually low carbon content^{137,144}, unlike the ones deposited from N-TEBA.¹⁴⁸ The addition of NH_3 or N_2 renders the films N-rich (N/(B+C) ratio around 1), regardless of the alkyl ligands.^{129,137,144,148} The addition of H_2 has little effect to the composition of the films deposited from N-TMBA^{137,144} but reduces the carbon content of the film from N-TEBA between 200 and 700 °C.²³⁹

7.1.3 Use of C-N-containing co-reagent with B precursors

This approach was exclusively used in thermal CVD.^{121,139,352} It could be due to the fact that the focus of PACVD in the B-C-N system was strongly driven by the c-BN/diamond pair.

7.1.4 C-coordinated boron precursors

Another approach is to use C-coordinated boron precursor instead of N-coordinated ones. As the previous one, this approach was also unexplored. In **Paper VI**, we used TEB and N_2 to deposit sp^2 - BC_xN_y films in a

microwave PACVD. Both smooth films and nanosheets could be deposited depending on the growth conditions. We found that the films were boron-rich ($0.7 \leq B/(C+N) \leq 1$). The B/N ratio was found to be nearly constant at our experimental conditions and varies between 1.2 and 1.4.

Comparing with previous works, films with similar a composition as with TDMAB-H₂ at 650-750 °C and 800 W RF-power could be obtained at much lower temperature ($\sim 300^\circ\text{C}$, from plasma heating), without H₂ and with higher MW-plasma power (1500-2500 W).³⁵⁰ We could deposit BC_xN_y nanosheets with compositions similar to the ones reported by Qin *et al.*, but without the drawbacks of using BF₃ (safety concerns brought by the toxicity BF₃, F₂ and HF, reactor corrosion and F incorporation in the film) and H₂.¹⁶⁶

Chapter 8: Contribution to the fields

The focus on this thesis is on the development of the chemical vapour deposition (CVD) of high quality sp^2 -hybridised boron nitride (sp^2). As most of the chemistry investigated in this work is based on organoboron chemistry, the study of these precursors inevitably led to the study of the CVD of boron carbides and carbonitrides. The contribution to the fields can be divided three parts:

- Contribution to boron carbides thermal CVD
- Contribution to boron nitrides thermal CVD
- Contribution to boron carbonitrides plasma CVD

8.1 Contribution to boron carbide CVD

In **Paper I** we focused on the gas phase chemistry of trimethylboron (TMB). We pyrolysed TMB in H_2 and Ar ambient between 700 and 1200 °C and found that TMB is able to deposit B-C films with high B-content at high temperatures. The B/C ratio was found to be maximum ($B/C = 3$) at a susceptor temperature of 1000 °C and remains higher than for TEB²⁷ above this temperature for similar deposition conditions. As such, TMB allowed us to co-deposit boron carbide and graphite while mainly graphite (or boron-substituted graphite) could be obtained in previous work on TEB pyrolysis.²⁷ This indicated slower decomposition kinetics for the TMB molecule. Quantum chemical calculation showed that TMB primarily decomposes by α -H elimination of methane in both ambient. The bimolecular H_2 -assisted also occurs in hydrogen ambient.

In **Paper II**, we focused on the surface chemistry of TMB at 700 °C. We observed that the average growth rate decreases after a few tens of nanometres in H_2 , leading to film with similar thickness at 30-, 90- and 270-min depositions. Conversely, this was not observed in Ar. We observed that the apparent activation energy in H_2 was exceptionally high (342 kJ/mol *i.e.* 3.54 eV) and that the deposition rate decreased proportionally to $\lg(P_{H_2})$. To get some insight into this phenomenon we proposed several possible mechanisms and attempted to falsify our hypotheses:

- competitive etching
- self-termination

- competitive adsorption of passivating species originating from TMB
- competitive adsorption of hydrogen related species

The competitive adsorption of hydrogen related species is the only hypothesis that we could not falsify, hence it is the most likely to happen. This is also consistent with the desorption of hydrogen from graphite and boron-substituted graphite, that occurs in the range 625-825 °C.³⁵³ Finally, we used this phenomenon to deposit near-conformal a-B_xC films. It was possible to deposit a-B_xC films in DRAM structure of aspect ratio 60:1 in 60 min and to reach aspect ratios as high as 2000:1 in 120 min using LHAR structures from VTT. The morphology and B/C ratio of the films was similar to the films deposited in **Paper I**. It is worth noting that on the one hand that only a few carbides^{178,354,355} have been deposited by ALD, since self-terminated growth is usually achieved by C-containing ligands that are meant to be removed after the next pulse. On another hand, most conformal CVD processes are operated at much lower temperatures (100-250 °C) and total pressures (10-1000 Pa) than 700 °C and 5000 Pa.

In **Paper IV**, we made use of what we learn from the kinetics of TEB and TMB to deposit graphite-free rhombohedral boron carbide films. We observed in a previous work that at substrate temperatures of 1100 °C and above TEB mostly yields carbon-containing materials such as graphite and silicon carbide. The B/C ratio of the graphite layer was about 0.05 which is much lower than the B/C ratio of 0.17 of the precursor molecules, which was an indication that most of the boron was deposited at the inlet of the susceptor. By increasing the gas speed (by a factor 1.7) and the dilution ($P_{\text{TEB}} = 0.94$ Pa instead of $P_{\text{TEB}} = 3.21$ Pa), we promoted the deposition of rhombohedral boron carbide. Although it is thought to be stable in aggressive environment, we showed that boron carbide is etched by H₂ gas and by SiH₄ at 1300 °C.

Finally, we investigated the possibility of synthesising rhombohedral boron subnitrides and subcarbonitrides. Our attempts were unsuccessful, but our observations will be useful for future work. High temperature synthesis at 1500 °C using TEB and N₂-H₂ carrier gas mixture (ratio 1:10) led to the deposition of B₄C on 4H-SiC substrates and to conversion of the Al₂O₃ substrates into w-AlN with no trace of boron. Replacing N₂-H₂ by NH₃-H₂ (1:56) rendered sp²-BN and w-AlN.

Synthesis at 1250 °C using TEB and NH₃ and H₂ on a B_xC/AlN/Al₂O₃ substrate has led to the formation of a film with pebble-like morphology

that cracked and partially peeled off of the substrate. sp^2 -BN (000 l), AlN(0002) and r-B $_x$ C(0003) were detected by XRD. It was unclear whether N was incorporated in the boron carbide lattice or not. One must also note that the eventual formation of an amorphous phase is usually not considered in thermodynamic calculations in the B-C-N system^{116,117}.

PACVD using TEB-N $_2$ -Ar plasma was thought to be an alternative route, but the B/N ratio of the deposited film remained close to 1.3 regardless of the deposition conditions (see section 8.3).

Finally, the characterisation of these films was found to be difficult using XRD and FTIR due to the wide solubility range of rhombohedral B $_x$ C. Our conclusion is that quantitative analysis (*e.g.* XPS, AES, ERDA but not SEM-EDX or RBS) must be used to clearly differentiate the subnitrides and subcarbonitrides from boron carbides.

8.2 Contribution to boron nitride CVD and epitaxy

There are four main questions needed to be solved in order to deposit high quality epitaxial boron nitride films using organoboron chemistry:

- Reduction of impurity content, in particular carbon content
- Prevent the formation of the rough amorphous phase
- Reduce growth temperature
- Prevent r-BN crystal twinning

Some these issues are interdependent which complicate the task of solving them. The issues regarding carbon content and the formation of a competitive amorphous phase seem to be directly related to the chemistry we use. Reduce the growth temperature should always be the objective, as long as the crystalline quality of the films is not degraded. It would partly solve the problem with carbon incorporation (the less reactive methane (CH $_4$) becomes unstable with respect to acetylene (C $_2$ H $_2$) above 1200 °C)³⁵⁶ and it would allow us to explore many other substrates. On the long term, it would be beneficial in terms of cost and energy consumption. The problem with r-BN twinning comes from the lack of substrates with surfaces with a three-fold symmetry (*e.g.* cubic, rhombohedral) that are both high-temperature-resistant and lattice-match. All these issues have been addressed in different ways throughout this thesis.

In **Paper III**, we explore the possibilities to use TMB as a boron source for sp^2 -BN epitaxy. We deposited epitaxial r-BN on nitridated sapphire. The epitaxial relationship as obtained by XRD ϕ -scan and pole figure measurement were:

out-of-plane:

and in-plane:

We found that, as for TEB, epitaxy occurs in a small temperature window but that this window is centred at 1400 °C instead of 1500 °C. Furthermore, the TMB process is more flexible than TEB process and r-BN crystals are obtained for wide ranges of N/B ratios (321-1286) and total pressures (3000-9000 Pa). The deposition rate was found to be three times higher than with TEB at the same conditions. We attributed the decrease in optimal temperature, higher growth rate and increase of flexibility to the better matched kinetics of NH₃ with TMB, with respect to TEB. SiH₄ was also found to play an important role in BN epitaxy. Carbon and oxygen were the main impurities as determined by ERDA and were higher than when TEB. was used. The competitive growth of the amorphous phase was also observed.

It is worth mentioning that deposition using SiC substrates at 1400 °C were not successful, using either sides (Si-side 4H-SiC(0001) and C-side 4H-SiC(000 $\bar{1}$)), removing the oxide with HF or not, and with or without SiH₄ pre-treatment as in⁶⁶. The reason for this might be that the pre-treatment needs to be performed at higher temperature (*e.g.* 1500 °C). BN films deposited from TMB and NH₃ Si(111) substrates at 1300 °C were amorphous. The films deposited on bare $\alpha\text{-Al}_2\text{O}_3(0001)$ to make use of the symmetry of the surface in hope to reduce r-BN twinning yielded w-AlN and either a-BN or t-BN, hence supporting the conclusion of previous studies showing that controlled nitridation is a necessary step.

In **Paper IV**, we decided to use silicon as a substrate. The choice of silicon as a substrate limits the use of high temperatures due to its melting point (1414 °C) and reactivity towards C and N. As most thermal CVD processes performed directly on Si led to amorphous or turbostratic BN films and since pre-treatments are required to deposit on SiC and Al₂O₃ substrates, we decided to investigate the effects of pre-treating the silicon surface on BN deposition. We choose to use TEB as a boron and carbon source and NH₃ as nitrogen source for all experiments. The pre-treatments applied on Si(111) surface prior to BN deposition are listed below:

1. Nitridation, performed by 120 min exposure to NH₃ at 1300 °C
2. Carbidisation, performed by 3 s exposure to TEB at 1300 °C
3. Nitridation followed by carbidisation

Most surface pre-treatments were found to produce a-BN films. The exceptions were a few nitridation experiments that allowed us to co-deposit t-BN and 3C-SiC. We found that these experiments could be reproduced only if boron carbide was present on the chamber walls before BN deposition. We found that H_2 and SiH_4 could etch boron carbide and allow us to deposit t-BN, even without TEB.

Additionally, we performed surface pre-treatments that were not added to **Paper IV** for consistency reasons, but are, nevertheless, of scientific interest. These are listed below:

4. Nitridation of an a- B_xC buffer
5. Deposition on boron-substituted graphite buffer

An a- B_xC buffer was deposited at 910 °C on Si(100) by exposure to 0.67 sccm TEB for 1 min. This layer was nitridated in 469 sccm NH_3 for 10 min at 1350 °C. BN was then deposited using the same flows of TEB and NH_3 ($NH_3/TEB = 700$) with addition of 0.024 sccm SiH_4 . The H_2 flow and total pressure were kept to 4000 sccm and 50 mbar. XRD and FT-IR showed that the resulting BN film was t-BN. The most interesting feature of these films is that their morphology is pebble-like as often reported for films deposited from BCl_3 ^{253,257} or borazine²⁸¹ and the fibrous amorphous morphology was not visible (see Figure 8.1).

Fig. 8.1: Top view SEM of t-BN films deposited after deposition and nitridation of an a- B_xC buffer on Si(100).

The boron-substituted graphite buffer was deposited for 120 min on Si(100) using lower TEB partial pressure and twice as lower gas speed compared to reference²⁷. XRD, FTIR and XPS confirmed the formation of boron-substituted graphite (around 10 at.% B). The morphology of the buffer is shown in Figure 8.2(a) and is similar to the one observed in Reference²¹². A BN film was then deposited for 120 min at 1200 °C, 7000 Pa and $\text{NH}_3/\text{TEB} = 750$. FTIR showed the formation of sp^2 -BN but the XRD study was inconclusive due to the similarity of the lattices, which could hardly be distinguished if they are turbostratic. The surface morphology of the film is shown in Figure 8.2(b).

Fig. 8.2: Top view SEM of (a) graphitic buffer from TEB and (b) BN films deposited such a buffer on Si(100).

In **Paper V**, we decided to use zirconium diboride thin films as a substrate. The choice of ZrB_2 is logical regarding the potential applications of BN in the UV, as discussed in Chapter 6. We used the conventional precursors TEB and NH_3 at 1485 °C, 7000 Pa and $\text{NH}_3/\text{TEB} = 643$. We observed r-BN epitaxy with the following relationship to the substrate, out-of-plane:

$$\text{r-BN}[0001] \parallel \text{ZrB}_x\text{N}_{1-x}[111] \parallel \text{ZrB}_2[0001] \parallel 4\text{H-SiC}[0001]$$

and in-plane:

$$\text{r-BN}[11\bar{2}0] \parallel \text{ZrB}_x\text{N}_{1-x}[220] \parallel \text{ZrB}_2[11\bar{2}0] \parallel 4\text{H-SiC}[11\bar{2}0]$$

We also found that the nature of the interlayer is closer to ZrB than ZrN . The exposure to SiH_4 prior to growth was investigated. On the contrary, increasing exposure time to SiH_4 was found to reduce the formation

of the amorphous phase. When the surface coverage by the amorphous phase is reduced below 50 %, the carbon content at the surface was found to drop from 10 to 2 at. %. The drawback of using SiH₄ at 1485 °C is the formation of etch pits at the ZrB₂ surface.

Paper III, Paper IV and Paper V give some insight into the role of SiH₄ in BN CVD. It is clear that SiH₄ is a strong etchant of otherwise relatively stable materials such as B₄C and ZrB₂. This must be kept in mind when working with B-containing materials.

The case SiC might be different as SiH₄ is commonly used in SiC CVD to counterbalance H₂ etching by a so-called regrowth process. More importantly, even if the etching of BN by SiH₄ was found to be insignificant at 1300 °C, possible etching of BN by dihydrogen and silane above 1400 °C might occur.

8.3 Contribution to sp²-BC_xN_y plasma CVD

In **Paper VI**, we deposit amorphous sp²-hybridised BC_xN_y films by MW-PACVD using a TEB-N₂-Ar plasma. To our knowledge, there is no report of deposition of BC_xN_y films using C-coordinated boron precursors. By adopting a factorial-plan-like approach, we could observe the effects of the absorbed plasma power, total flow and N/Ar ratio on the growth rate, morphology and composition of the films.

The deposited films were boron-rich compared to most methods using separate precursors for B, C and N or using N-coordinated boron precursors. The B/N ratio of the films was somehow fixed between 1.2 and 1.4, while the B/C ratio could be varied between 1.4 and 5.9, as determined by XPS. The analysis of the chemical bonding structure of the films show that the films comprised essentially B-N bonds, and in a smaller amount, B-C and C-C bonds. This seems counterintuitive, considering the initial B/C ratio of the precursor (0.17) and the lower B/C ratios of a-B_xC films deposited from TEB-Ar plasma (up to 1.7 in MW discharge)³¹, but could be explained by the formation of CN radicals, which are known to be volatile from vapour phase deposition and etching in the C – N system.³⁵⁷⁻³⁶¹

Two kinds of morphology could be obtained: smooth films and nanowalls (NW). NW were the most common and their morphology varied with the deposition parameters. It is interesting to observe growth of NW at such low temperatures (300 °C ≤ T ≤ 400 °C), but it is consistent with the minimal deposition temperatures reported by Merenkov *et al.*¹⁶⁵ for BN NW deposition. The morphology of the NW could be varied from so-called

maze-like (*i.e.* straight interconnected nanowalls) to disordered single nanosheets to disordered nanosheets with ramifications (subsheets). Smooth films were obtained with two sets of conditions. The morphology of the smooth films deposited for plasma power of 2325 W, 238 sccm total flow and N/Ar = 13.3 could be explained by too low deposition temperatures as in¹⁶⁵, induced by cooling by high N₂ flow. This is consistent with the high growth rate and high oxygen content. The smooth films deposited for plasma power of 2325 W, 80 sccm total flow and N/Ar = 13.3 showed the lowest growth rates, high density and low oxygen content which is consistent with ion-bombardment induced densification (higher plasma power, high nitrogen concentration in the plasma and lower pressures). The smooth BCN films had lower C content and were found to have a variable dielectric constant that could be as low as 3.

Chapter 9: Outlooks

First, concerning the thermal chemical vapour deposition of boron carbides, the outlooks are mostly towards the optimisation and modification of the conformal α - B_xC process. The modification of the process could be done by adding minute amounts of TEB to increase the B/C ratio close to 1 or by doping with a methylated precursor (e.g. trimethyl aluminium, methyl amines) to obtain films with new properties without disturbing the deposition process.

Nowadays, crystalline rhombohedral boron carbide is of minor importance for any electronic or thermoelectric device applications but neutron detectors, and the main requirements for neutron detectors is on the B-content and sturdiness, rather than on crystallinity. Nevertheless, combining our findings regarding the deposition of halogen- and graphite-free r - B_xC (semiconductor) from TEB, the potential availability of a boron subnitride with metallic conductivity, and the availability of epitaxial boron subphosphide and subarsenide (both wide bandgap semiconductors) on SiC substrates, these boron-rich solids may gain some interest in the future.

While sp^2 -BN CVD has been widely explored, sp^2 -BN epitaxy remains a challenge. The biggest issue remains the competitive growth of a carbon-rich amorphous phase during r -BN growth by MOCVD. This is a serious obstacle to further investigations. We found that preparation of the surface already helped reduce the formation of the amorphous phase with respect to r -BN (e.g. **Paper V**), but this is also dependent on process parameters (as seen in **Paper III**). A more systematic study of the effects of process parameters is needed to attempt optimisation of the growth process.

Such an amorphous phase has not been reported in the case of halides CVD of BN, which usually leads to smoother morphologies. Therefore, it could be worth to investigate BN CVD using the less corrosive precursors BBr_3 and BI_3 in inert ambient (Ar and N_2). As they are easier to pyrolyse than BCl_3 , a more reactive source than NH_3 might be needed to match their kinetics.

Investigating the potential benefits of a more reactive nitrogen source is not only limited to halide CVD. Roth *et al.* showed that well crystallised h -BN could be deposited at 900 °C on Si using a amine-borane adduct and a remote N_2 microwave plasma.³⁶² The deposited films were polycrystalline, but this illustrates the possible benefits of using another nitrogen source. The most appealing precursors would be remote N_2 -plasma or hydrazine (N_2H_4). Being able to deposit films at temperature below 1200 °C

would be highly beneficial for BN growth, as it would increase the stability of hydrocarbon by-products such as methane and consequently drastically reduce carbon contamination. Furthermore, in **Paper III**, we found that the average growth rate is almost independent of the temperature. This is an indication that surface processes are not the limiting step in the range 1200-1485 °C. Although it might be the on the edge of the transport limited regime, a process that allows to deposit h- or r-BN slightly below 1200 °C is likely to yield epitaxial films if the right substrate is used.

Our work on ZrB₂ (**Paper V**) opens up option for a variety of substrates for sp²-BN, namely transition metal ceramics. Many metal borides, nitrides and carbides have high melting points and can be epitaxially deposited by sputtering on high-temperature substrates (e.g. sapphire, silicon carbide). However, one should focus on the ones that have interesting optical properties in the UV (particularly high reflectance) and that have a better lattice match to BN than ZrB₂.

Finally, the memory-effect-based deposition process on Si(111) allows to co-deposit orientated t-BN grains and epitaxial SiC crystals (**Paper IV**). Although the current process does not provide films with high crystalline quality, one must keep in mind that there is still room for optimisation and improvement: ammonia concentration, other etchants, total flow, pressure, temperature, substrate off-cut angle, composition of the material on the susceptor walls are a few examples of the parameters that can be played with. The memory effect that we brought to light should also be checked at higher temperatures, as BN etching by silane was not observed at 1300 °C, but the situation may be different at higher growth temperatures.

Regarding plasma deposited films, the most obvious thing to do would be to study the TMB-N₂-Ar plasma. Although the results may be similar to that of TEB-N₂-Ar, such a study would answer many more questions than expected, as the decomposition of the TMB molecule is not limited to α -hydride elimination but also occurs by collisions with electrons, photons, ions and excited neutrals. The B/C ratio of a-B_xC films deposited by low pressure RF-PACVD were higher for TMB than for TEB (0.59 for TMB against 0.22 for TEB)³⁶³ while the B/C obtained by MW-PACVD were similar (1.9 for TMB against 1.7 for TEB)^{29,31}. CH and C₂ were both detected in both microwave discharge. In the case of TMB forming CH seems quite straightforward while forming C₂ would require the collision of two C containing species. Such collisions would be reduced with the addition of N₂ due to the formation of CN. Intuitively, assuming that bigger molecules do not have a significant impact, TMB would allow to deposit BC_xN_y films that are closer to BN rather than with TEB at similar partial pressures.

Our experimental space was delimited by the capabilities of the chamber, with exception of the plasma power. It would be interesting to see the evolution of the composition of the films and of the plasma at lower plasma powers, maybe this will allow us to “unlock” the B/N ratio of our films. Finally, comparative experiments using TEB and TMB at different dilutions could help clarify the role of hydrogen in these deposition processes.

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