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CVD Chemistry of Organoborons for Boron-Carbon Thin Film Depositions

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Abstract

Boron-carbon thin films enriched with ^{10}B are potential neutron converting layers for ^{10}B -based solid state neutron detectors given the good neutron absorption cross section of ^{10}B atoms in thin films. The common neutron-transparent base material, Al (melting point $660\text{ }^{\circ}\text{C}$), limits the deposition temperature and the use of chlorinated precursors forming corrosive by-products such as HCl. Therefore, the organoborons triethylboron $\text{B}(\text{C}_2\text{H}_5)_3$ (TEB) and trimethylboron $\text{B}(\text{CH}_3)_3$ (TMB) are evaluated as precursors for CVD of B_xC films. In order to get a complete understanding of the CVD behaviour of these precursors for deposition of boron containing films, both thermal CVD and plasma CVD of B_xC films have been demonstrated. A gas phase chemical mechanism at the corresponding thermal CVD conditions is proposed by quantum chemical calculations while chemical mechanism in the plasma is suggested based on plasma composition obtained from Optical emission spectroscopy (OES).

The behaviours of TEB and TMB in thermal CVD are investigated by depositing B_xC films in both H_2 and Ar atmospheres, respectively. Films deposited using TEB within a temperature window of $600 - 1000\text{ }^{\circ}\text{C}$ are X-ray amorphous with $2.5 \leq x \leq 4.5$. The impurity level of H is less than 1 at. % above $600\text{ }^{\circ}\text{C}$. Calculations predict that the gas phase reactions are dominated by β -hydride eliminations of C_2H_4 to yield BH_3 . In addition, a complementary bimolecular reaction path based on H_2 assisted C_2H_6 elimination to BH_3 is also present at lower temperatures in the presence of hydrogen molecules. As for films deposited with TMB, dense, amorphous, boron rich ($\text{B/C} = 1.5\text{-}3$) films are obtained at $1000\text{ }^{\circ}\text{C}$ in both H_2 and Ar atmosphere. The quantum chemical calculations suggest that the TMB molecule is mainly decomposed by unimolecular α -elimination of CH_4 complemented by H_2 assisted elimination of CH_4 .

Plasma CVD of B_xC thin films has been studied using both TMB and TEB as single-source precursors in an Ar plasma at temperatures lower than that allowed by thermal CVD. The effect of plasma power, TMB/TEB and Ar gas flow, as well as total pressure on film composition and morphology are investigated. The highest B/C ratio of 1.9 is found for films deposited at highest plasma power (2400 W) and high TMB flow (7 sccm). The H content in the films stays almost constant at 15 ± 5 at. %. The B-C bonding is dominant in the films while small amounts of C-C and B-O exist, likely due to formation of amorphous carbon and surface oxidation. Film density is determined as 2.16 ± 0.01 g/cm³ and the internal compressive stresses are measured to be less than 400 MPa. OES shows that TMB is decomposed to mainly atomic H, C₂, BH, and CH. A plasma chemical model for decomposition of the TMB is constructed using a combination of film and plasma composition. It is suggested that the decomposition of TMB starts with dehydrogenation of the methyl groups followed by breakage of the B-C bonds to form the CH radicals. This bond breaking is at least partly assisted by hydrogen in forming the BH radicals.

When films are deposited using TEB flow of 5 and 7 sccm, the B/C ratio is found to be plasma power dependent while the carbon content is almost not affected. The highest B/C ratio of 1.7 is obtained at the highest power applied (2400 W) and attributed to better dissociation of TEB at higher plasma power. The H content in the films is within 14-20 at. %. The density of films is increased to 2.20 g/cm³ with increasing plasma power and attributed to a higher energetic surface bombardment during deposition. The oxygen content in the film is reduced to less than 1 at. % with increasing plasma power due to the densification of the films preventing surface oxidation upon air exposure. Plasma composition from OES shows that the TEB molecules are also dissociated mainly to BH, CH, C₂ and H. A plasma chemical model where the first ethyl group is split off by β -hydride elimination to form C₂H₄, which is further dehydrogenated to C₂H₂ and forms C₂ and CH is suggested. The BH species is assumed to be formed by the dehydrogenation of remaining ethyl groups and breakage of the remaining B-C bonds to form BH.

Populärvetenskaplig Sammanfattning

Tunna filmer av grundämnena bor och kol, där den absoluta merparten av boratomerna är av isotopen ^{10}B är potentiellt intressanta som neutronomvandlande skikt i fastfas-neutrondetektorer. Neutroner är som namnet antyder elektriskt neutrala och därmed väldigt svåra att detektera och måste därför omvandlas till laddade partiklar i en kärnreaktion. Isotopen ^{10}B har en ovanligt hög affinitet för att reagera med neutroner och skapa laddade partiklar. Neutrondetektorn måste konstrueras av ett neutrontransparent material och aluminium är ett relativt billigt, neutrontransparent material som dessutom är lätt att konstruera saker med. Dock smälter aluminium vid $660\text{ }^{\circ}\text{C}$ vilket sätter en övre gräns för deponeringsprocessen för bor-kol filmen. Det får inte heller skapas några korrosiva gaser vid deponeringsprocessen eftersom aluminiumet då förstörs. Ett av de vanligaste sätten att deponera en tunn film är CVD (chemical vapor deposition eller ungefär kemisk ångdeponering) där molekyler innehållande, i detta fallet bor- och kolatomer, får reagera i gasfasen och på ytan där den tunna filmen ska deponeras och skapa en tunn film via kemiska reaktioner. I denna avhandling studeras molekylerna trimetylbor (TMB), $\text{B}(\text{CH}_3)_3$, och trietylbor (TEB), $\text{B}(\text{C}_2\text{H}_5)_3$, i olika CVD-processer för bor-kol filmer. För att skapa en så god förståelse som möjligt för hur dessa molekyler beter sig i CVD har både termiskt- och plasmaaktiverade CVD-processer studerats. De deponerade filmerna har analyserats med avseende på atomärt innehåll och kristallina faser medan molekylernas kemi i gasfasen respektive plasmat har studerats med kvantkemiska beräkningar respektive optiska emissions mätningar. Resultaten har använts för att föreslå kemiska mekanismer för molekylernas nedbrytning till mera reaktiva fragment.

I termisk CVD deponerades B_xC filmer från både TEB och TMB i både väte- och argonatmosfär. TEB visade sig ha ett temperaturfönster för CVD på $600\text{--}1000\text{ }^{\circ}\text{C}$ och deponerade amorfa B_xC filmer med $2.5 \leq x \leq 4.5$ med mindre än 1 atomprocent väte i filmerna.

Kvantkemiska beräkningar visar att TEB främst bryts ner via β -hydrideliminering av C_2H_4 . I väteatmosfär finns även en komplimenterande H_2 -assisterad C_2H_6 elimineringsreaktion, främst vid lägre temperaturer. TMB visade sig kräva högre temperaturer för att deponera filmer och gav B_xC filmer med ett lägre borinnehåll, $1.5 \leq x \leq 3$. De kvantkemiska beräkningarna visar att TMB främst bryts ner via α -hydrideliminering av CH_4 .

I plasma CVD deponerades B_xC filmer vid lägre temperatur, ca $300\text{ }^\circ\text{C}$, dock med ett lägre borinnehåll; $x \leq 2$. En observerad trend var att högre plasmaeffekt gav högre borinnehåll. B_xC filmer deponerade med plasma CVD var alltid tämligen väterika med ett väteinnehåll på 15 ± 5 atomprocent. Kemiska bindningar mellan bor och kol dominerar i filmerna, dock med inslag av bor-syre och kol-kol bindningar som en följd av ytoxidering när provet togs ur deponeringskammaren respektive bildandet av amorft kol i filmerna. Optiska emissionsmätningar visar att TMB och TEB bryts ner till H , C_2 , BH , and CH fragment. Från detta föreslås att nerbrytningen av TMB i plasmat börjar med att väteatomer bryts loss varpå B-C bindningarna bryts för att bilda CH -radikaler. Troligen bryts åtminstone en B-C bindning av väteradikaler varpå BH -radikaler bildas. TEB molekylen föreslås brytas ner genom först en β -hydrideliminering där C_2H_4 bildas som sedan bildar C_2H_2 genom att två C-H bindningar bryts. C_2H_2 kan sedan bilda både C_2 och CH . TEB bryts vidare ner till BH genom ytterligare β -hydridelimineringar eller direkt brytande av B-C bindningar av plasmaradikaler.

Preface

The presented PhD thesis is written based on the collection of my knowledge acquired and research results obtained during my Ph. D studies from September 2012 to April 2017 in the Thin Film Physics Division at the Department of Physics, Chemistry and Biology (IFM) at Linköping University. The aim of my research project is to understand the CVD chemistry of organoborons for boron carbon thin film depositions. Much of the foundation for this work was laid during my first half of Ph.D. study, and thus my licentiate thesis (thesis No. 1741, 2016) “Chemical Vapour Deposition of Boron-Carbon Thin Films from Organoboron Precursors” forms the basis for some parts of this thesis.

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Included Papers

Paper I

Gas Phase Chemical Vapor Deposition Chemistry of Triethylboron Probed by Boron-Carbon Thin Film Deposition and Quantum Chemical Calculations

Mewlude Imam, Konstantin Gaul, Andreas Stegmüller, Carina Höglund, Jens Jensen, Lars Hultman, Jens Birch, Ralf Tonner and Henrik Pedersen

J. Mater. Chem. C, 3, 10898 – 10906 (2015)

My contributions

I did the film depositions together with one of the other authors. I did all film characterizations apart from ERDA and wrote the paper.

Paper II

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

Submitted

My contributions

I planned all experiments with my supervisor and did the depositions with one of the co-authors. I did all characterizations apart from ERDA and XPS. I analysed and summarized all experimental results and wrote the first draft of the manuscript.

Paper III

Trimethylboron as Single-Source Precursor for Boron-Carbon Thin Film Synthesis by Plasma Enhanced Chemical Vapour Deposition

Mewlude Imam, Carina Höglund, Jens Jensen, Susann Schmidt, I. G. Ivanov, Richard Hall-Wilton, Jens Birch, Henrik Pedersen

J. Phys. Chem. C, 120, 21990-21997 (2016)

My contributions

I planned and did all depositions and all characterizations apart from ERDA, XPS and Raman. I analysed and summarized all experimental results and wrote the paper.

Paper IV

Plasma CVD of Boron-Carbon Thin Films from Triethylboron

Mewlude Imam, Carina Höglund, Susann Schmidt, Richard Hall-Wilton, Jens Birch and Henrik Pedersen

Submitted

My contributions

I planned and did all depositions and all characterizations apart from ERDA, XPS. I analysed and summarized all experimental results and wrote the first draft of the manuscript.

Table of Contents

Acknowledgement.....	i
Abstract	iii
Populärvetenskaplig Sammanfattning	v
Preface	vii
Included Papers	ix
Table of Contents.....	xi
Chapter 1 Introduction.....	1
1.1 Thin Films	1
1.2 Neutron Detectors	2
1.3 Aim of the Research.....	4
Chapter 2 Boron Carbides	5
2.1 Overview of Boron Carbides	5
2.2 Structures of Boron Carbides	6
2.3 Boron-Carbon Thin Films	7
Chapter 3 Chemical Vapour Deposition	9
3.1 Precursor	10
3.1.1 Frequently Used Precursors for Boron Carbide Depositions.....	11
3.1.2 Single Source Precursors	11
3.1.3 TEB and TMB	12
3.2 CVD Growth Regimes	13
3.3 Thermal CVD.....	14

3.3.1	Thermal CVD setup.....	15
3.3.2	Gas Phase CVD Chemistry and Quantum Chemical Calculations	16
3.4	Plasma CVD.....	20
3.4.1	Plasma CVD setup.....	21
3.4.2	Plasma chemistry	22
3.4.3	Effects of Deposition Parameters on Film Deposition	24
Chapter 4	Characterization Techniques.....	27
4.1	Scanning Electron Microscopy	27
4.2	X-Ray Diffraction	29
4.3	X-Ray Reflectivity	30
4.4	Stress Measurement	31
4.5	Time of Flight Elastic Recoil Detection Analysis.....	32
4.6	X-Ray Photoelectron Spectroscopy	33
4.7	Optical Emission Spectroscopy.....	34
Chapter 5	Summary of Results.....	37
5.1	TEB and TMB in Thermal CVD.....	37
5.2	TMB and TEB in Plasma CVD.....	38
Chapter 6	Future Work.....	41
References		43
Paper I		49
Paper II		83
Paper III		111
Paper IV		121

Chapter 1 Introduction

1.1 Thin Films

A thin film is normally a single or multiple layers of material(s) of which thickness ranges from fractions of nanometer (monolayer) to a few micrometers. Even though there is no such a clear cut definition that everyone agrees upon, this range given above is most interesting and most relevant to the vast majority of the thin film researches, which can be attributed to the unique properties of this sort of materials that differ substantially from bulk materials [1]–[3].

The history of thin film related craftsmanship is rather long standing. The earliest documented thin gold layers for decorative applications have a history of more than 5000 years [4]. Today, thin films are in wide use not only in various conventional applications, but also in many emerging advanced technological applications, and thus thin films research have become an important area of material science. Optical coatings such as antireflective and UV protective coatings, hard and wear-resistant coatings for cutting tools, thin film electronic materials for microelectronics, as well as new generation energy technologies, such as thin film supercapacitors / batteries and solar cells, are some interesting thin film applications among many others.

Thin film deposition processes are the heart of thin film technology. Thin film deposition techniques have been developed for many years in the laboratories and industries. They are generally divided into two broad categories: chemical vapour deposition (CVD) and physical vapour deposition (PVD), depending on whether the process is designed primarily on chemical principles or physical principles. In CVD, volatile vapour-phase species, specifically known as precursor molecules, are delivered into the reaction zone where they undergo series of chemical

reactions and form a layer of material on the substrate [5]. CVD techniques will be introduced in more detailed manner in Chapter 3 of this thesis. Knowledge about the reaction mechanisms and routes are crucial in high quality film depositions. In PVD, on the other hand, chemical reactions are not involved or do not play a major role in the process. Atoms or molecules from a target material are released by evaporation or sputtering and transported through vacuum or plasma to a substrate, where vapour phase species can be deposited onto it by adsorption and condensation. Some common PVD techniques are vacuum evaporation deposition, sputtering deposition, ion plating and molecular beam epitaxy [6]–[8].

CVD processes, compared to PVD, are normally more complex. They often deal with multiple flows of precursors, which undergo more intricate gas phase and surface reactions, to the extent that only overall reactions can be summarized. Moreover, the safety issues in the handling and storage of many reactants and products in CVD processes are also to be concerned, due to their toxic or corrosive nature. But PVD processes have their own disadvantages too. They are highly directional in terms of deposition geometry, and thin films tend to have lower uniformity and conformity on the substrate. PVD is usually slower than CVD for thicker films too.

However, CVD and PVD techniques are complementary techniques and utilized depending on the specific thin film deposition requirements, such as film composition, thickness, structure, cost and time limitations, etc. Both have been continuously developed during the past decades, resulting many versatile systems and variations, and some systems have even merged their advantages, utilizing two techniques in hybrid systems [9][10].

1.2 Neutron Detectors

One of the applications of thin films is to use them as neutron converting layer in solid state neutron detectors, which is the main intended use of the films studied in this thesis. Neutrons do not interact directly with the electrons in materials since they are electrically neutral. Therefore, unlike many other particle detectors, neutron-detecting mechanisms must count the neutrons by making use of indirect methods. A typical process for such a method is: when neutrons interact with various atomic nuclei, they release one or more charged particles as the product of the interaction; the produced charged particles will then ionize certain surrounding gas, which in turn generates electrical signals that can be processed by the detection hardware and software system. There are different types of neutron detectors such as gas proportional counter detectors, scintillation detectors and semiconductor detectors. The gas proportional

counter detectors are the most common neutron detectors today and based on the principle mentioned above. Among them, the ^3He gas-filled proportional counters are widespread detectors due to the high neutron absorption cross-section and low sensitivity to gamma rays. In such a detector, once a ^3He atom in the gas absorbs an incident thermal neutron (n), one proton (p) and a tritium ion (^3H) are released in opposite directions [11] with the simultaneous emission of γ -ray photons, as expressed in Equation (1):

The charged particles ionize the proportional counting gas (e.g. CF_4) and together with the liberated electrons can be detected as electrical signals. Unfortunately, in the past few years, the demands for ^3He have greatly exceeded than the supply, mainly due to U.S. Homeland security programmes [12], [13]. This leads to an urgent need for alternatives to ^3He -based neutron detectors.

One possible replacement to ^3He for neutron detection application is the boron isotope ^{10}B . ^{10}B has a relatively high thermal neutron (wavelength $1.8 \text{ \AA}$) absorption cross-section – 70 % of the cross-section of ^3He . Moreover, boron is naturally abundant and contains 20 % of ^{10}B and 80 % ^{11}B . Boron with more than 97% ^{10}B enrichment is commercially available in large amount [14], [15]. The 10 % mass difference between the two isotopes makes the isotope separation relatively easy [12]. The ^{10}B containing neutron detectors are based on the neutron absorption of ^{10}B atoms inside few microns-thick ^{10}B containing thin films deposited on neutron transparent substrates, e.g., Al or Si. The nuclear reaction results in releasing of Lithium ions (^7Li) and alpha (^4He) particles with certain kinetic energies in opposite directions according to Equation (2) and (3) [at different probability]:

Depending on the escape probability, some of the released charged particles can escape from the thin film and be detected in a detecting gas (e.g. CF_4 , Ar, CO_2) where they get ionized. Due to the bad oxidation resistance and poor electrical conductivity of elemental boron, the most stable compound of boron - $^{10}\text{B}_4\text{C}$ has been studied as the neutron converting thin layer for neutron detectors due to its excellent thermal stability and chemical resistance [16], as well as

the better conductivity than elemental boron. The basic principle of the thin solid film based new generation neutron detectors is similar to ^3He gas detectors except that the used neutron converting material is a thin solid layer of $^{10}\text{B}_4\text{C}$ (on a base material like Al) instead of ^3He gas.

The European Spallation Source ERIC (ESS) will be the world's leading neutron spallation source for the study of materials. The ESS company was started 2010 in Lund, Sweden and it is a pan-European project involving participation of 17 European countries. ESS has been conducting research on building $^{10}\text{B}_4\text{C}$ based solid-state neutron detectors and the estimated total coating area for the planned ^{10}B based-detectors covers 87 % of the total detector area of all instruments that will be built at ESS [12], [17], [18]. ESS will produce the first neutrons and bring the first instruments into operation in 2020. The full baseline suite of 16 instruments will be brought online by 2025.

1.3 Aim of the Research

The purpose of this research is to study the CVD Chemistry of organoborons for boron-carbon thin film depositions, which will be the fundamental knowledge in production of the potential neutron converting layers for ^{10}B -based solid-state neutron detectors.

The chosen organoboron precursors, triethylboron $\text{B}(\text{C}_2\text{H}_5)_3$ (TEB) and trimethylboron $\text{B}(\text{CH}_3)_3$ (TMB), are used as single-source precursors for CVD of boron-carbon (B_xC) thin films. By introducing methodologies of experiments carried out using these two precursors respectively in thermal CVD and Plasma Enhanced CVD, and characterization of the deposited films (with characterization tools such as scanning electron microscopy (SEM), Time-of-Flight elastic recoil detection analysis (ToF-ERDA), X-ray reflectivity (XRR), X-ray diffraction (XRD), X-ray spectroscopy (XPS), Raman spectroscopy, as well as nano-indentation), we aim to provide further experimental insight into this approach, including e.g. proper materials and setup preparations, better experiment parameters and quality of the films regarding proposed application. Together with the theoretical quantum chemical calculations by partners, some complex intermediate reactions and products in the CVD processes can be probed effectively.

Chapter 2 Boron Carbides

2.1 Overview of Boron Carbides

Boron carbide is an important ceramic with remarkable physical and chemical properties. It is one of the most inert and stable compounds that resists chemical and thermal attacks very well (melting point higher than 2700K). Discovered in the 19th century as a reactions by-product during the production of metal borides, boron carbides have since been gradually attracting more and more research interests. Pioneers in preparation of boron carbides identified first B₃C and B₆C compounds, then decades later into 20th century the B₄C stoichiometric formula was discovered and first commercially produced by R.R. Ridgway in electric arc furnace using dehydrated boric acid and coke in a process similar to the silicon carbide production [19][20], which can be expressed in an overall reaction Equation (4).

Boron carbide powders can also be obtained by magnesium reduction of dehydrated boric acid in graphite furnace [20]. However, these two routes are quite inefficient in terms of raw material utilization and it is troublesome to mill the products and eliminate metal impurities using acids to get highly purified boron carbide further down in the practice. To get highly condensed boron carbide from powders, they must be sintered in difficult methods too. CVD routes are good alternatives to the previous methods in order to get highly purified single-phase boron carbides. There are many different gas mixtures to choose from for different technical setups in CVD of boron carbides with different resulting stoichiometries and properties, which have already been well summarized in [21] and references therein.

Applications development of boron-carbides also kept the same pace with research understandings of the productions, structures and properties of them. Even though there are still plenty of controversies about the detailed pictures at the fundamental level, its widespread usage nowadays can be found in many industries: being the third hardest material (with Vickers hardness of 38 GPa) after diamond and cubic boron nitride (c-BN) while having a lower manufacturing cost truly make it a wise choice for wear resistant and hard materials / components, for example coating for cutting tools, lightweight bulletproof vests and tank armour applications; high Seebeck coefficient ($\sim 300 \mu\text{VK}^{-1}$) at high temperature making boron carbide highly relevant for thermo-electric applications; thanks to its high neutron absorption cross section, it has become one of only a few choices for nuclear reactor neutron absorption applications and neutron detectors; it is also used in chemical applications like metal matrix composites reinforcements, evaporating boats and so on [20].

2.2 Structures of Boron Carbides

Boron carbides have complex crystal structures: with the aid of neutron and X-ray diffraction examinations, the crystal lattices are often identified to have a rhombohedral unit cell structure (D_{3d}^5 - $R\bar{3}m$ space group), where eight twelve-atom icosahedra (normally denoted as $B_{11}C$) locating at vertices and linked through an inter-icosahedral three-atom chain along the longest diagonal of the rhombohedra (normally denoted as -C-B-C-) form a lattice unit as shown in Figure 1 [20], [22]–[25]. Therefore, its ideal chemical formula is nominally written as $B_{12}C_3$ instead of B_4C .

However, the exact atomic configuration of boron and carbon atoms within icosahedra and inter-icosahedral chain are technically hard to figure out, as a result of their similar atomic form factor for x-ray diffraction and similar nuclear scattering cross-section for neutron diffraction [25]–[28]. It is indicated in many sources that boron-carbide compounds with configurational disorders, such as incorporation of one or more C atoms into the B_{12} icosahedra or substitution of boron or carbon for one another in diagonal chain, can exist in large homogeneity range with broad C concentration range from 8 up to 20 at. % [20], [21].

Boron carbide with stoichiometry B_4C is naturally a p-type semiconductor and its band gap varies with stoichiometry and the degree of crystalline order. One research group reported its band gaps ranging from 0.48 eV to 2.09 eV while stoichiometry ranges from $B_{4.3}C$ to $B_{11}C$ in different studies. Considering these values, it seems that boron carbide band gap is relatively

small compared to other semiconductor ceramics [29][30]. But interestingly, it is also reported that with the increase of applied stress on the material (> 60 GPa), some phase transitions can happen and thus causing boron carbide to become wide band gap (> 3.1 eV) semiconductor and optically transparent material [31].

Figure 1 The atomic configuration of ground-state B_4C (B11C-CBC). The grey and black spheres represent boron and carbon atoms, respectively, residing in the icosahedra and in the inter-icosahedral chain. Figure is adapted from [26] with permission.

2.3 Boron-Carbon Thin Films

In this thesis, boron-carbon (B_xC) thin films refer to films containing mainly boron and carbon atoms with B-C bonds. B_xC films have been deposited by several CVD and PVD routes in both laboratory and industrial scale [32]–[34]. The PVD method is a line-of-sight deposition technique and CVD is not to the same extent. CVD has been demonstrated to deposit well-defined, high quality single-phase boron carbide films [21]. As mentioned before, to deposit boron carbide thin films I studied depositions in thermal and plasma CVD using organoborons as precursors. Organoborons are advantageous compared to the conventional boron precursors BCl_3 , BBr_3 and B_2H_6 , and carbon precursor CH_4 , not only because they can provide both boron

and carbon atoms in a single stream, but also their high reactivity allows for a CVD route at lower deposition temperature [35]. They also generate non-corrosive by-products. This allows CVD of boron carbides on metallic substrates like Aluminium. The most used and common organoborons are TEB and TMB, so naturally those are ideal starting point for us, given our goal to develop reliable techniques for producing neutron detector materials in large quantity.

Chapter 3 Chemical Vapour Deposition

CVD of thin films are complex processes based on a series of chemical reactions of vapour-phase precursor species, which occur both in the gas phases and on the substrate surfaces. It is possible with CVD techniques to deposit films of uniform thickness with low porosity not only on flat substrates but also on complex shaped substrates. In Figure 2, a schematic view of an overall CVD reaction during film growth is illustrated which includes several steps listed as follows [7]:

Figure 2. Schematic of transport and reaction processes in CVD. Adapted after [48].

- (1) Evaporation and mass transport of reagents (i.e., precursors) into the reaction zone;
- (2) Gas phase reactions in the reaction zone to produce film precursors and gaseous by-products;
- (3) Mass transport of the film precursors from gas phase to the substrate surface;
- (4) Adsorption of film precursors on the substrate surface;
- (5) Surface diffusion of precursors to growth sites, nucleation and surface chemical reactions leading to film formation;
- (6) Desorption of film precursors or other volatile species and mass transport of by-products away from the reaction zone;

3.1 Precursor

In CVD, precursor molecules are molecules containing the element or elements that are necessary for the deposition of the thin film. Precursors employed can be organic or inorganic chemicals, which can be in different phases including gas, liquid or solid. The precursors which are naturally occurring in gaseous states, such as NH_3 as source of nitrogen [36], [37], O_2 or CO_2 as source of oxygen [38], [39] and others, are directly inserted into the reactor. A Mass flow controller (MFC) is used for controlling the flow rate. Volatile liquid precursors, like organoborons such as triethylboron (TEB), triethylgallium (TEGa) and trimethylgallium (TMGa), are kept in special containers called ‘bubblers’ commonly made of stainless steel [7]. The bubbler is usually maintained in a temperature-controlled bath in which the vapour pressure of the liquid can be adjusted by controlling the temperature of the bath. The bubbler has one inlet where the carrier gas (H_2 , Ar or N_2) is introduced to carry the precursor vapour by passing through the liquid and one outlet, there the carrier gas and the precursor vapour is transported to the reactor. An electrical pressure controller (EPC) is used to adjust the downstream pressure of the precursor, which is associated to the precursor flow rate. Solid precursors such as trimethylindium (TMIn) are also used as precursors by means of evaporation.

CVD precursors are an important aspect of the CVD technology as CVD is based on chemical reactions, therefore the insight into chemical behaviour of precursors is very valuable [40]. The general requirements for CVD precursors are that they must be volatile, thermally stable during transport into the reactor and having a lower decomposition temperature. Except the precursor volatility and stability, the chemical purity, the low incorporation (or high volatility) of by-

products and compatibility with co-precursors are also important requirements. But, in most of the cases, it is hard to find such a precursor that fulfills all requirements mentioned above. In such a circumstance, there could be ways that make things work. As an example, the vapour pressure of the precursor is one of the parameters that determines the growth rate. The vapour pressure of any molecule is given by its temperature. Therefore, the temperatures of liquid and solid precursors are controlled by e.g. keeping the bubbler in a well-controlled temperature bath.

3.1.1 Frequently Used Precursors for Boron Carbide Depositions

Typical CVD of boron carbides involves high temperature reactions of precursors: hydrocarbons (e.g. CH_4) and boron chlorides (e.g. BCl_3) or boron hydrides (e.g. B_2H_6) [41]. The high temperature requirements and chlorinated by-products are not suitable for deposition on Al substrates. Low temperature plasma CVD at 400 °C using nido-pentaborane (B_5H_9) or nido-decaborane ($\text{B}_{10}\text{H}_{14}$) with CH_4 is another possible way [42]. But pentaborane and decaborane rich in ^{10}B are still hard to find. Using nido-2,3-diethyldicarbahexaborane, $(\text{CH}_3\text{CH}_2)_2\text{C}_2\text{B}_4\text{H}_6$, under synchrotron light induced CVD can also selectively deposit boron carbon films [43].

3.1.2 Single Source Precursors

Single source precursors for CVD contain all the desired element in the thin film. Hence, they enable simplified gas delivery systems (they often also avoid toxic and expensive mixture processes happening in multi-source CVD), better film homogeneity, and avoiding incorporating much of the unwanted elements otherwise will be present in other sources. They generally require lower deposition temperatures. The disadvantages of single source precursors are, however, that they tend to have lower vapor pressure than multiple source precursors for individual elements, so that the delivery processes and deposition speed are slower [44][45]; their individual elements ratio are predetermined and less tunable than multiple source precursors, resulting normally narrower range for the stoichiometry [46].

Compared with the conventional precursors, single source precursors are less investigated in CVD of boron carbide thin films. Thus, we have chosen TEB and TMB as single source precursors in our research to examine and explore this relatively new option.

3.1.3 TEB and TMB

Figure 3. Molecular structures of (a) Triethylboron - $B(C_2H_5)_3$ - TEB and (b) Trimethylboron - $B(CH_3)_3$ - TMB.

TEB and TMB are all colorless, pyrophoric, toxic and highly reactive organoborons. Their molecular structures are shown in Figure 3. TEB is a liquid at room temperature with a boiling point of 95°C , while TMB is a gas at room temperature with boiling point of -20.2°C .

The vapour pressure of TEB ($P_{\text{vap.TEB}}$) and TMB ($P_{\text{vap.TMB}}$) can be calculated respectively as a function of temperature $T(\text{K})$ using Equation (5) and (6) [47]. TEB flow into the reactor, Flow_{TEB} (sccm), is calculated using Equation (7), where P_{total} is the total pressure in the bubbler, which is controlled by the EPC, and $\text{Flow}_{\text{Ar carrier}}$ (sccm) is the gas flow of Ar carrier.

$$\log_{10}(P_{\text{vap.TEB}}) = 7.812 - \frac{1814}{T} \quad (5)$$

$$\log_{10}(P_{\text{vap.TMB}}) = 6.1385 - \frac{1393.3}{T} + 1.75 \log_{10} T - 0.007735T \quad (6)$$

$$\text{Flow}_{\text{TEB}} = \frac{P_{\text{vap.TEB}}}{P_{\text{total}} - P_{\text{vap.TEB}}} \cdot \text{Flow}_{\text{Ar carrier}} \quad (7)$$

3.2 CVD Growth Regimes

In CVD of thin films, the deposition temperature is very essential to determine the film growth rate [7][48]. The effect of the substrate temperature on the film growth rate is usually studied experimentally by plotting the growth rate (log scale) as a function of reciprocal of temperature ($1/T$) as illustrated in Figure 4. This type of graph is called Arrhenius plot.

Figure 4. Three growth-regimes in a CVD process. Adapted after [7], [48].

There are three distinct deposition regimes as shown above, they are thermodynamics limited, gas-phase transport limited and kinetics limited regimes. In low temperature range, there is not enough thermal energy to dissociate all precursor molecules, resulting in low mobility of ad-atoms on the substrate surface. In this regime, the growth rate increases with increasing temperature, therefore it is named as kinetics limited or kinetics controlled regime. When the temperature increases further, the dissociation of precursors and mobility of ad-atoms become nearly independent of temperature and the film growth rate is mainly controlled by the mass transport of the precursors, thus it is called mass-transport limited or diffusion controlled regime. At even higher temperatures, due to increasing desorption of ad-atoms from the growth surface, the growth rate tends to decrease, so the regime is named as thermodynamics limited or desorption regime. However, the importance of the three regimes alters when the pressure inside reactor changes. At higher pressure ($\sim 10\text{-}10^3$ mbar), kinetics and mass transport both play important role. At lower pressures (< 1.3 mbar) film growth is controlled by surface

reactions, at very low pressures ($< 10^{-4}$ Torr or $\sim 10^{-4}$ mbar), by the desorption of ad-atoms, as well as the gas and substrate temperatures [7], [48].

Figure 5. Example Arrhenius plot from CVD of boron carbon thin films using TMB as single source precursor in H_2 atmosphere.

Figure 5 is an example of Arrhenius plot using data from thermal CVD of boron carbon thin films using TMB as single source precursor in H_2 atmosphere. Starting from the right side of the plot to the left, one can roughly see that three regimes are present: (c) region up until $T = 1073\text{K}$ corresponds to kinetics limited regime; (b) region having smaller slope corresponds to mass transport limited regime; (a) region from $T = 1173\text{K}$ to higher temperatures corresponds to desorption regime. However, only a few data points are used here, so the accuracy and usefulness of Arrhenius plot in this series of experiments are very much discounted.

3.3 Thermal CVD

CVD can be classified based on the provided energy input for the reaction zone, such as thermal CVD with heating input, photo-assisted CVD with higher frequency radiation input or plasma enhanced CVD with plasma energy input [7]. In this thesis, thermal CVD and plasma CVD will be discussed.

Thermal CVD or thermally activated CVD is a common CVD process in which thermal energy is utilized to activate chemical reactions. The reactor can be further classified as hot wall or cold wall reactor. The thermal energy can be provided in various methods, of which most widely

used ones are RF heating, infrared radiation and resistive heating [49]. According to the pressure range of the deposition process, thermal CVD can be also subdivided into atmospheric pressure CVD (APCVD), low pressure CVD (LPCVD) or ultrahigh vacuum CVD (UHVCVD) [49], [50]. The pressure ranges for APCVD, LPCVD and UHVCVD processes usually are around one atmospheric pressure, 0.1-13.3 mbar, and $<10^{-3}$ mbar, respectively.

The conventional thermal CVD uses mostly inorganic chemical precursors and involves rather high deposition temperatures. Therefore, the metal organic CVD (MOCVD) is developed as a relatively low temperature CVD technique using volatile organometallic precursors. By definition, the organometallic precursors contain organic compounds and metal atoms in which at least one carbon atom of the organic compound bonds to the metal atom [51].

3.3.1 Thermal CVD setup

Hot-wall reactor and cold-wall reactor are both frequently used in CVD processes. In the hot-wall reactor, the substrate and reactor wall are heated uniformly with a tube furnace surrounding the reactor or by RF induction. In the case of cold-wall reactor, the heat source (RF induction or high radiation lamps) only heats the substrate holder.

In this thesis, a hot-wall CVD system as shown in Figure 6 is used for deposition of B_xC thin films. The reactor is a horizontally placed quartz tube in which a susceptor (a heated component) made of high-density graphite is placed close to gas inlet and heated inductively by a surrounded RF coil. An isolation layer made of low-density graphite is set between the susceptor and quartz tube to reduce the high temperature exposure onto the tube. The susceptor is coated with a layer of protective SiC coating that prevents out diffusion of impurities from graphite. Besides, the protective coating makes the susceptor tolerant to high temperatures and corrosive environments that might happen during deposition process. The vacuum level of the reactor is 10^{-6} mbar achieved with a turbo molecular process pump prior to deposition and the total pressure in the reactor during film deposition is kept at 50 mbar by throttling the process pump.

Figure 6. A view of film deposition with the hot-wall CVD reactor.

3.3.2 Gas Phase CVD Chemistry and Quantum Chemical Calculations

As shown in Figure 2, thin film growth process by CVD involves several types of chemical and physical processes, both in the gas phase and on the surface. CVD chemistry is often much more complex than what is hinted in Figure 2 [5]. A good understanding of the CVD chemistry in the gas phase is also a prerequisite for an understanding of the CVD surface chemistry, as one must understand which species are available for the surface chemistry. It is only through grasping overall picture of CVD chemistry that one can provide effective strategies for improving the process and the quality of deposited thin film.

Experimental studies of the CVD chemistry in real time is often very challenging as reactive species will be lost when sampling gas and the relatively high pressure prevents most experimental surface science techniques. Therefore, the CVD chemistry is typically studied experimentally by changing deposition conditions and characterizing the deposited films. CVD chemistry is also typically modelled: methods such as thermochemical and quantum chemical calculations are used to predict the possible gas phase and surface chemistry in a CVD process. One good example is a proposed understanding of a CVD process for SiC, in which the gas phase and surface chemistry have been probed by thermochemical calculations for several years [5]. Quantum chemical calculation is also used to provide detailed gas phase chemistry models and thermochemical data for the gas phase species[5].

Quantum chemical calculations, which involve quantitative calculations and qualitative modelling based on quantum theories for chemical processes, nowadays are much more common and accepted methods in chemical research compared to decades ago: with many well developed specific strategies, schemes and models, as well as constantly increasing computational power, these calculations are very powerful means to make fundamental discoveries and complement the understandings of experimental findings and data.

In quantum mechanics theory, all information of interest in a system can be provided by the wave function Ψ of the system in focus. By solving time-dependent Schrödinger equation - Equation (8) or its time-independent version – Equation (9), one can describe microscopically subatomic, atomic, molecular systems or even macroscopic system. The Hamiltonian H is the energy operator which can extract potential and kinetic energies from wave function Ψ .

$$H\Psi = i\hbar \frac{\partial \Psi}{\partial t} \quad (8)$$

$$H\Psi = E\Psi \quad (9)$$

However, the Schrödinger equations are impractical to solve with analytical solutions at the moment for generally all systems unless they are extremely small systems. The reason is they are many body systems involving huge number of particles and even larger amount of interactions between them, thus resulting infinite amount of calculation difficulties. The practical way to start with is to introduce approximations. First, in most of the cases stationary ground state are of main importance to us, and for those cases solving time-dependent Schrödinger equation can be reduced to solving corresponding time-independent form; Second, because of large mass differences between nuclei and electrons, approximation called Born-Oppenheimer approximation can be made [52]; Then in almost all ab initio methods, introduction and applying of symmetry and a basis set can further reduce the complexity and computational difficulties [53]; Hartree-Fock Theory [54]–[56], Møller-Plesset Many-Body Perturbation Theory [57], Coupled Cluster Theory [57], Density Functional Theory (DFT) [58], [59] can be chosen and used depending on the considerations of the effects that these approximations have on the cost and accuracy during calculations. The investigated molecular structures in this study were optimized on the DFT level using the Generalized Gradient Approximation (GGA) functional PBE [60]. The reader is referred to the mentioned references

here and the included papers for more details and backgrounds that are out of reach for this thesis.

Based on our experimental results which characterizing films deposited under various conditions and quantum chemical calculations, we have better understandings of the elementary gas phase reactions of TEB and TMB in thermal CVD, which is summarized below.

In the case of TEB: β -hydride elimination of ethylene (C_2H_4) is the most favorable reaction type in terms of thermodynamic values and constitutes the major decomposition channel of TEB, both in Ar and H_2 atmospheres. This type of reaction was reported to occur at 300 °C [35], and at higher temperatures the other ethyl groups could further be eliminated to form BH_3 [33]. The quantum chemical calculations agreed with this suggestion. Kinetic Monte Carlo (KMC) simulations based on Gibbs reaction energies (ΔG) and barriers ($\Delta G^\ddagger$) for computed reactions show that in both Ar and H_2 atmosphere a fast decrease of reactant TEB with increase of temperature will happen and intermediate product $B(C_2H_5)_2H$ and $B(C_2H_5)H_2$ and product BH_3 dominate the gas phase. At low temperatures H_2 assisted ethane (C_2H_6) elimination reactions are also one major decomposition channel in H_2 atmosphere. But this type of elimination can be ignored at higher temperatures. The carbon contents in the deposited films are most probably originating from C_2H_4 formed in the β -hydride elimination processes or C_2H_2 formed in H_2 elimination from C_2H_4 [61]. In the studied temperature range, these hydrocarbon species are likely to have very low reactivity at lower temperatures, which gradually increases with temperature, and give rise to higher carbon content in the films when temperature reaches 1000 °C. This is one explanation for the observed low carbon content in low temperature depositions despite of B/C ratio being 1/6 in TEB molecule. Figure 7 below are used in included Paper I to show product distribution derived from KMC simulations under CVD conditions for H_2 and Ar atmosphere at varying temperatures.

Figure 7. Product distribution derived from KMC simulation under CVD conditions for varying temperatures. (a) simulation of full reaction catalogue with H_2 assisted elimination reactions, i.e. in H_2 atmosphere; (b) simulation of full reaction catalogue without H_2 assisted elimination reactions, i.e. in Ar atmosphere; See Table 1 and Figure 8 in included Paper I for reaction details.

In the case of TMB: After examining all the thermodynamically allowed unimolecular decomposition reactions of TMB in Ar atmosphere at 800 °C with quantum chemical investigations, it is apparent that the most likely decomposition pathway is the abstraction of methane (CH_4) in α -H elimination reaction. Another gas phase reaction channel most probable is the loss of C_2H_4 to form H_2BCH_3 , and further decomposition to HBCH_2 via loss of H_2 . However, this pathway has quite high barriers and are strongly endergonic. In H_2 atmosphere, other than the abstraction of CH_4 in α -H elimination as a decomposition pathway with lowest barrier, H_2 assisted reactions have to be considered, since a larger number of reactions are energetically accessible, as shown in Figure 8. H_2 assisted CH_4 elimination has a considerably higher thermodynamic driving force (the middle arrow vs. top arrow in Figure 8). Moreover, H_2 assisted CH_4 elimination of H_3CBCH_2 to HBCH_2 , $\text{HB}(\text{CH}_3)_2$ to H_2BCH_3 , H_2BCH_3 to BH_3 are also thermodynamically favored in comparison to the unimolecular pathway. Methane is likely not very active in CVD at lower deposition temperatures, but has a higher reactivity at higher temperatures. As a summary of the above, in Ar atmosphere, H_3CBCH_2 is the major film forming species at lower temperature, resulting lower B/C ratio, and will incorporate more and more H_2BCH_3 species at higher temperature (> 900 °C), resulting higher B/C ratio; in H_2 atmosphere, other than the same pathway in Ar atmosphere, there are H_2 assisted additional

elimination reactions with negative Gibbs free energies, which add $\text{HB}(\text{CH}_3)_2$, H_2BCH_3 , and BH_3 to the film forming species. These H_2 assisted decomposition pathways are active at low temperatures and getting even more active with the increase of temperature. These can explain why films deposited in H_2 atmosphere have higher B/C ratio and it can get even higher at high temperatures. In both Ar and H_2 atmosphere, the drop in B/C at 1100°C compared to 1000°C can be ascribed to higher reactivity of CH_4 at higher temperatures, allowing it to deposit more carbon to the film.

Figure 8. Scheme of most probable gas phase reactions of TMB and decomposition products in H_2 atmosphere with Gibbs reaction energies (ΔG) and barriers ($\Delta G^\ddagger$) in kJ/mol for CVD conditions $T=800^\circ\text{C}$ and $p=50$ mbar (Structures investigated were optimized on DFT level using GGA functional PBE and def2-TZVPP basis set).

3.4 Plasma CVD

Plasma CVD is a form of CVD where the energy in a plasma is used to promote chemical reactions. The main purpose/advantage of this method is to reduce the deposition temperature by replacing thermal energy with plasma energy. In this process, the chemically active species for the film growth are formed as a result of inelastic collision of precursor molecules with ionized or excited atoms and electrons in the plasma. Then the active species are transported to

the substrate surface and form a layer of material. The plasma can also provide energy to the substrate surface via energetic particle bombardment [7]. The active species for the deposition must reach the substrate/film surface within their lifetime. This is to some degree controlled by the plasma gas: general considerations for the plasma gas in plasma CVD is that it should be chemically inert with respect to the precursors and reactor materials and that its excited particles should have considerable life time and energy to dissociate precursor molecules[7]. Usually inert gases such as He and Ar, as well as N₂ gas can have excited particles with relatively long lifetimes, thus used as preferable plasma gases.

3.4.1 Plasma CVD setup

There are different ways of generating a plasma, such as using arcs, electron beams, flames, radio frequency (RF) and microwaves (MW) [62]. The microwave assisted plasma CVD is a method in which high frequency microwaves (2.45 GHz) are used as energy source for generating plasma, where the degree of ionization typically varies from 10^{-4} to 10^{-3} [63]. However, the microwave sources for generating plasma have not been used as widely as other techniques, due to the difficulties of constructing a simple and convenient experimental set-up along with the difficulties to sustain plasma at low power [7].

In this thesis, we modified an ASTeX microwave plasma CVD deposition system, which was previously used for diamond deposition. The schematic view of the whole system is shown in Figure 9 (adapted from [64]).

Figure 9. Schematic of microwave plasma CVD system.

The microwave generator is equipped with a power supply with maximum output power of 2500 W. The generated microwave is channelled through a T- shape three-way circulator waveguide to the top of the deposition chamber, which is a quartz glass dome. The inner diameter of the chamber is 14 cm, and the diameter of the graphite sample holder is 12 cm, which is neither heated, biased nor grounded. The microwaves penetrate the quartz glass and ignite the plasma. The quartz dome is cooled by compressed air to minimize microwave reflection due to loss of microwave permeability at high temperature in the quartz. Microwaves reflected back into the waveguide are directed into a water-cooled dummy load. A three-stub tuner is used to control and minimize the reflected power. The background pressure inside the deposition chamber is 10^{-5} mbar obtained by a turbo molecular pump. A dry rotary pump is used to keep a constant gas flow/pressure during the process.

Ar gas is used as plasma gas given its inertness, long life-time and high energy of the exited atoms. In two series of experiments, TMB and TEB have been employed, respectively, as single source precursor for providing both boron and carbon atoms. TMB is in gas phase at atmospheric conditions, which made the precursor delivery process easier as well as the flow controlling process. TEB is liquid at room temperature and thus require installation of an additional bubbler system using Ar carrier gas to deliver the precursor vapour into the reaction chamber, as shown in Figure 9. TEB bubbler bath temperature is kept to 26.4 ± 0.4 °C with thermostat. TEB vapor pressure of 76 mbar and TEB flow are calculated and set to experiment value using Equation (5) and (7).

3.4.2 Plasma chemistry

The most motivating advantage of using plasma to activate reactions in CVD is that the substrate and ambient temperature can be kept relatively low compared to thermal CVD. The new reaction pathways would be accessible via abundant electron transfers between gas species. The main types of chemical reactions of importance for plasma CVD are well summarized in Figure 10, which is adapted after [65]. Plasma electrons, excited neutral and positive ionic plasma species can activate precursor molecules via excitation, dissociation and ionization processes.

Figure 10. Summary of the important plasma chemical reactions in plasma CVD. X_2 denotes a diatomic precursor and A denotes plasma gas species. Reactions written here are for summary purpose, thus are not only limited to diatomic precursor molecules. Figure is reproduced after original figure in [65].

To study plasma chemistry in our experiments, specifically the composition of the plasma during CVD which consists of ionized and excited species, as well as dissociated radicals from precursor molecules, Optical Emission Spectroscopy (OES) measurements are made. The results for TMB precursor show that: Ar species are mainly excited Ar atoms (Ar I); decomposition products of TMB are dominated by BH, CH, atomic H, and C_2 molecules, with trace of C_3 , but no presence of B or CH_3 ; CH- and BH are the most likely film depositing species in the plasma, while at higher plasma power C_2 and C_3 clusters will mostly account for carbon content in the films; changing precursor flow or plasma power will mainly change the intensity of the precursor related emission lines without any lines appearing or disappearing; almost all Ar I lines are more intense than any of the other emission lines in the plasma. Our proposed possible reactions are listed in Paper III (see Equation 5 to 8 therein). The OES measurement results for TEB precursor show something similar to findings in TMB case: the plasma mainly consists of excited Ar atoms, H, C_2 , BH and CH species, which are essentially the same species found in TMB decompositions in Ar plasma CVD; BH, CH and to certain extent C_2 are most

likely the film forming species. Our proposed possible reactions are listed in Paper IV (see Equation 6, 11 and 12 therein).

3.4.3 Effects of Deposition Parameters on Film Deposition

Normally deposition parameters in a microwave plasma CVD system include plasma power, plasma gas flow, precursor gas flow, total pressure and substrate temperature. It should be noted that like some other systems [66], in our system the substrate temperature cannot be controlled independently of plasma power, gas flow and other parameters. So here we discuss mainly effects of plasma power, precursor flow and pressure on film deposition.

In plasma CVD using TMB: The films deposited at higher plasma power (2400 W) and higher TMB flow (7 sccm) appear to be more porous in a total pressure range of 1.3 ± 0.3 mbar. This is associated with observed high deposition rate under these parameters as a combined effect of high flux of film forming species and low adatom mobility due to the low substrate temperature. Changing TMB flow and plasma power alter the film elemental composition when Ar flow are kept the same: with lower TMB flow (5 sccm) samples are C-rich regardless of plasma power, while with higher TMB flow (7 sccm) samples become B-rich if power settings are above 1400 W. Under these conditions, increasing power settings will cause C content decreasing and B content increasing steadily. This suggests that higher TMB flow will provide larger supply of boron species, especially at high power range. Apart from that, increasing plasma power resulted in slight decrease in H content, which is more effective at lower TMB flow (5 sccm) compared to higher flow (7 sccm). O contaminations in the films is also found to be power dependent by showing a steady decrease with increasing plasma power at both low and high TMB flows. The significant drop in O content in the films is attributed to the increased densification of the films preventing surface oxidation. However, all deposited films look porous in the pressure range mentioned above. It is believed that a lower concentration of precursors (supersaturation) should lead to deposition of less porous films at the same temperature, based on the well-known CVD structure/property/process relationships [67]. Indeed, film morphology and density, as well as B/C ratio are improved by lowering the TMB partial pressure and total pressure (by increasing pumping speed) while TMB flow and plasma power are kept at the set points (TMB at 7 sccm and plasma power 2400 W) where film elemental compositions are best according to the afore-mentioned experiments. However, delamination and surface cracks also developed with increasing of Ar flow (>20 sccm) at high

plasma powers. This is due to increased number of energetic plasma species bombarding the film resulting increased level of compressive stresses.

In plasma CVD using TEB: The deposition rate is dependent on both the precursor flow and plasma power. Increasing TEB flow results in thickness increase that is related to the higher concentration of film depositing species in the plasma. But as for correlation with plasma power, deposition rate increases when plasma power increases within low power range (700 W – 1500 W) and tends to decrease at high power (2400 W) due to the energetic surface bombardment as discussed above. B/C ratio in the deposited film increases with increasing plasma power, and have higher ratio in the films deposited with lower TEB flow under the plasma power settings studied. The slightly low B/C ratio for films deposited with high TEB flow is likely due to the lack of plasma energy for further decomposition of precursor molecules.

Chapter 4 Characterization Techniques

4.1 Scanning Electron Microscopy

Scanning electron microscopy (SEM) is a versatile and widely used imaging technique with the capability to magnify a sample 20 to 130000 times with high resolution [68], which produces images by scanning a sample surface point-by-point with a focused electron beam and detecting the secondary and backscattered electrons at each point. The relatively faster and more convenient operation of the SEM compared to transmission electron microscopy (TEM, another electron microscopic technique utilizing primary electrons transmitted through materials) make it a handy method for examining microstructures and morphology of various materials.

One typical SEM apparatus is composed of electron gun, electron condenser lens, scanning coils, objective lens, detectors and specimen stage, as schematically illustrated in Figure 11. The resolution of SEM is dependent on the wavelength of electron beam emitted from a thin (cathode) tip, which is determined by the energy of electrons (in the range of 1-50 keV) after accelerated by applied voltage. With the highest electron energy and optimal operating conditions a resolution better than 1 nm can be achieved.

Electron beam interacts with atoms at or near the sample surface and generates signals from secondary electrons, back scattered electrons, characteristic X-rays and cathodoluminescence. These signals can then be detected and recorded sequentially according to electron beam scanning position, thus can give information about the surface topography and provide material as well as local surface charge information [69].

Figure 11. Schematic diagram of Scanning electron microscopy setup.

In practice, secondary electron imaging (SEI) is the most common mode, in which the detected electrons are the emitted low energy electrons from shallow atoms at surface, therefore used to produce surface imaging. On the other hand, the back-scattered electrons (BSE), which are elastically scattered back by the heavy nuclei in the sample, usually have higher energy than secondary electrons, can be used for compositional contrast. The quantification of chemical composition using BSE is based on that back scattered electrons per primary electron is compositionally sensitive [70]. Characteristic X-rays, emitted when electron beam excites one inner shell electron, which subsequently causes de-excitation of another high-energy electron to fill the empty shell, can be a fingerprint of a specific element, so they are used to identify the composition and the distribution of composition. Detection of X-rays is usually called energy dispersive (X-ray) spectroscopy (EDS or EDX).

Samples for SEM should be vacuum compatible and electrically conductive to produce high-resolution SEM images. For biological and non-conductive samples, the surface needs to be coated by thin metal film and grounded to avoid charge accumulations on the surface, which cause poor resolution.

The SEM images in this thesis were prepared using a LEO 1550 Gemini SEM with a field emission gun (FEG) as an electron source, where electrons are emitted from a thin tip to which several kV is applied. The advantage of this type of electron gun is on its superior brightness, even at lower acceleration voltage, compared to thermionic gun. Since both boron and carbon atoms are light elements, 5 kV excitation voltage was applied, SEI mode using an Inlens – high signal to noise ratio detector, to produce high-resolution cross-sectional SEM images.

4.2 X-Ray Diffraction

X-ray diffraction (XRD) is a non-destructive, fast and efficient technique to examine phase composition and structural information about single crystal, poly crystal and amorphous materials. When monochromatic X-rays impinge on a material surface, the incident X-rays are elastically scattered by the electrons of the surrounding atoms. Therefore, the scattered X-rays have the same wavelength λ as the incident X-rays. The constructive interference occurs when the scattered X-rays are in phase after scattering by the lattice planes. The diffraction condition for a group of atomic planes with interplanar spacing d is described with Braggs law in Equation (10) and illustrated in Figure 12:

$$n\lambda = 2d\sin\theta \quad (10)$$

where n is an integer corresponding to the order of diffraction, and θ is the angle between the incident beam and the atomic plane.

Figure 12. Illustration of X-ray diffraction from atomic planes according to the Bragg's law.

In this thesis, θ - 2θ scans were performed in a Philips 1820 Bragg-Brentano diffractometer to study film crystallinity using Cu-K α radiation. In a θ - 2θ scan, rotating sample and detector with respect to the incident beam simultaneously changes the incidence angle θ and the diffracted angle 2θ at a ratio of 1:2. The θ - 2θ scan thus records data for a certain group of lattice planes parallel to the surface.

4.3 X-Ray Reflectivity

X-ray reflectivity (XRR) is a non-destructive, surface-sensitive analytical technique for structural characterization of thin films and can also provide layer periodicity of multilayers. The refractive index in solids is smaller than unity for x-rays and total external reflection occurs at very small incidence angle. When the X-rays are incident onto the sample surface, the reflected X-rays at the surface and at the interfaces between layers in a film stack or between film and substrate interfere, giving rise to interference fringes that provides information about thin films/multilayers. The density of the film is related to the critical angle (as shown in Figure 13) while the oscillations and slope of the curve are determined by film thickness and surface roughness, respectively.

XRR measurements can be done using an XRD equipment in grazing incidence XRD geometry with θ - 2θ scan mode. When the incidence angle θ is smaller than the critical angle θ_c for total reflection, total external reflection occurs, and the detected reflected X-ray intensity are close to original incidence intensity; when the incidence angle θ is larger than θ_c , the detected intensity of reflected X-ray rapidly decreases. The density of the film is then determined from the critical angle. In this thesis, we used a Philips X'Pert Pro MRD diffractometer equipped with a hybrid mirror monochromator, 2-bounce Ge 220 triple-axis crystal analyzer and a Panalytical Empyrean MRD diffractometer with hybrid mirror and parallel plate collimator. Film densities were determined by fitting the experimental data using X'pert reflectivity software.

Figure 13. X-ray reflectivity scan of a sample deposited by plasma CVD.

4.4 Stress Measurement

Compressive stresses were calculated from measuring the curvature of substrates in high resolution rocking curve geometry using a Philips X'Pert Pro MRD diffractometer. The radius of substrate curvature is calculated using Equation (11):

$$R \simeq \frac{\Delta x}{\Delta \omega [\text{rad}]} \quad (11)$$

in which Δx is the distance between two measured positions x_1 and x_2 on the sample surface and $\Delta \omega$ is the small difference between peak positions ω_1 and ω_2 . Lastly, compressive stresses are derived from the Stony equation in Equation (12):

$$k = \frac{1}{R} = \sigma_f t_f \frac{6}{M_s t_s^2} \quad (12)$$

where t_f and t_s are substrate and film thickness respectively. The biaxial modulus of substrate M_s is given by Equation (13):

$$M_s = \frac{E_s}{1 - \nu} \quad (13)$$

where E_s is elastic modulus of substrate and ν is Poisson's ratio.

4.5 Time of Flight Elastic Recoil Detection Analysis

Elastic recoil detection analysis (ERDA) is a technique that provides information about chemical compositions and elemental depth profile of materials. The basic principle of ERDA is that as a beam of mono-energetic ions (primary beam) in the MeV energy range irradiates on a sample, atoms /ions on the sample are recoiled in a forward direction by the impact from ions, energies of which are detected with detector system. The collision is assumed as two-body elastic collision and the transferred kinetic energy of the recoiled atom E_r can be expressed as Equation (14):

$$E_r = \left(\frac{4M_i M_r \cos^2 \beta}{(M_i + M_r)^2} \right) E_{i0} \quad (14)$$

Where M_i and M_r are the mass of primary ion and recoiled atom/ion, respectively. The E_{i0} is the initial kinetic energy of primary ion and β is the recoil angle. With the given E_{i0} , M_i and the fixed detection angle β , measuring E_r and inserting these values into Equation (14) can give us the value of M_r .

However, the kinetic energy of recoil E_r is also dependent on possible multiple scattering, the surface roughness and the depth of the recoils into the sample. The Time-of-Flight-ERDA (ToF-ERDA) is a method to identify elements in which the measured velocity of recoils is used to distinguish particle masses possessing an equal amount of energy.

When using heavy ions in the primary beam, ERDA can provide depth profiling for all elements, including H [71]. One drawback, though, of ERDA measurements using heavy ions is that

irradiation may cause damage to the sample [72]. In this thesis, all ERDA measurements was carried out using 36 MeV iodine ions as primary beam with a time of flight detector.

4.6 X-Ray Photoelectron Spectroscopy

X-ray Photoelectron Spectroscopy (XPS) is one of the most frequently used spectroscopy for material chemical analysis. It is best suited for the material surface (top layers within 1 -10 nm thickness into the sample) compositional and chemical bond structural analysis.

The physics of the photoelectron spectroscopy is as follows. A core level electron initially bound to an atom in the material can be ejected out of material surface upon receiving the energy of an impinging photon if the energy is large enough; the energy of the original photon is thus transferred into three parts: one part overcoming electron binding energy ($E_{B.E.}$) to free the electron from atomic nucleus attracting force; one part to account for work function of spectrometer ϕ_s ; one part into kinetic energy ($E_{K.E.}$) of the photo electron that detected by the spectrometer. Electron binding energies of core level electrons are determined by specific atoms and specific binding states, thus can give compositional information about sample. All elements except H and He (their low photoelectron cross sections and lack of core electrons are not suitable for detection by XPS) are detectable, provided that their atomic percentage in material sample are greater than 0.05 at. % [73]. So knowing X-ray photon energy $h\nu$ and work function ϕ_s , by measured $E_{K.E.}$, one can calculate electron binding energy $E_{B.E.}$ by Equation (15):

$$E_{B.E.} = h\nu - E_{K.E.} - \phi_s \quad (15)$$

XPS uses detection data to draw out a spectrum, in which the number of the electrons detected are plotted vs. corresponding binding energy values. Each detected element gives a group of characteristic XPS peaks at characteristic binding energies. The peaks or spectral lines are identified and noted by the core shell from which the photoelectron was emitted [74]. The number of the electrons at a certain energy is directly proportional to the relative amount of the element in the sample material.

Using XPS surface analysis technique normally requires an ultra-high vacuum environment to increase the mean free paths of photons and electrons. The sample should be solid and electrically conducting material. In cases of insulating materials, charge neutralizing equipment needs to be used. In this thesis, a X-ray photoelectron spectroscopy (XPS, Axis UltraDLD,

Kratos Analytical, Manchester, UK) using monochromatic Al ($K\alpha$) X-ray radiation ($h\nu = 1486.6$ eV) was performed.

4.7 Optical Emission Spectroscopy

Optical Emission spectroscopy (OES) analysis has been a widely implemented, fast, non-intrusive, technique to characterize plasma, which requires only moderate and inexpensive spectroscopic equipment and a high transparency optical window in the plasma reactor [75], [76]. Due to its versatility, OES has been used for different purposes and applications such as investigating electron temperatures, electron densities, electron energy distribution functions in low temperature plasmas and gas phase chemistry in plasma CVD [77]–[79].

In a plasma, both atomic and molecular species can be excited by electrons or photons. When they are de-excited to lower energy states by emission of photons, OES can be used to measure the wavelengths of the photons emitted. The wavelength λ of a particular photon emitted is determined by its energy, which is directly related to the energy difference between the electronic states of the photon emitting atomic or molecular species. Since the energy difference between two states are characteristic for each species and states they are in, OES can be used as a “fingerprint” reader for identifying plasma species excitation states. Semi-quantitative measures of concentrations of species can also be made by comparing spectral line intensities [80].

Figure 14. Example of OES spectra of Ar and TEB plasma. (a) the full range scan showing mainly emission lines from excited Ar atoms while (b) a zoom in of the range 375–675 nm showing emission lines related to the TEB decomposition products. Note that these two spectra have different intensity scales.

In this thesis, plasma composition was diagnosed using spectrometer Mechelle Sensicam 900 (by the Multichannel Instruments) in a wavelength range from 200 – 1100 nm with a spectral resolution $(\lambda/\Delta\lambda)_{FWHM}$ of 900. In Figure 14, three overlapping OES spectra taken at 700W, 1500W and 2400W plasma powers contain emission lines from Ar-TEB plasma. As shown in (b), emission lines related to TEB are mainly from H, CH, BH and C₂ species.

Chapter 5 Summary of Results

5.1 TEB and TMB in Thermal CVD

In Paper I and II, an understanding of the CVD chemistry for triethylboron (TEB) and trimethylboron (TMB) as a single-source precursor for B_xC thin film deposition in thermal CVD were studied by using a combined experimental and theoretical approach with both film deposition and quantum chemical calculations. Films deposited on (100)-oriented Si substrates in H_2 and Ar atmospheres respectively, within 700 -1200 °C were characterized and discussed together with the previously published results for TEB (400 -600 °C) [33].

When TEB was used as single-source precursor within the whole temperature range (400-1200 °C), boron content was increased with increasing temperature up to 700 °C where the highest B/C ratio of 4.5 was obtained; up to 1000 °C boron content was almost constant (77 ± 5 at. %) and temperatures above 1000 °C mainly resulted in carbon-rich films in both atmospheres (more pronounced in H_2 atmosphere). The incorporated hydrogen was temperature dependent and temperature for on-set of out diffusion of the H (< 1 at. %) was found at around 700 °C. Films looked dense in cross sectional SEM images (Figure. 1 in Paper I) and film density was determined as 2.42 ± 0.05 g/cm³ which is very close to the bulk density of crystalline B_4C : 2.52 g/cm³ [81] and the density of sputtered films 2.45 g/cm³ [32]. XRD showed that no obvious crystalline boron-carbide phases formed in films deposited below 1000 °C.

Based on our experimental findings and quantum chemical calculations, a gas phase chemical model for TEB consisting of two reaction types, β -hydride elimination of ethylene (C_2H_4) and H_2 -assisted ethane (C_2H_6) elimination, was proposed. Based on the reaction products (also intermediate products, see Paper I), $B(C_2H_5)_2H$, $B(C_2H_5)H_2$, and BH_3 are considered to be the

boron containing species for the film deposition while C_2H_4 is the main carbon containing species.

Film deposition using TMB as single-source precursor resulted in much lower deposition rates at 700 °C and lower B/C ratios within 700-900 °C (Figure 2 and 3 in Paper (II)) in both atmospheres compared to films deposited using TEB. This indicates that TMB is not as reactive as TEB at temperatures below 1000 °C, which is more pronounced for films deposited in Ar atmosphere by showing relatively low B/C ratio than films deposited in H_2 . However, the highest B/C ratio of 1.5 and 3 were obtained at 1000 °C in both Ar and H_2 atmospheres, respectively. Above 1000 °C, a decrease in B/C ratio was noticed. Based on the experimental results and quantum chemical calculations of gas phase reactions, it was concluded that the gas phase chemical mechanism for TMB is dominated by unimolecular α -H elimination of CH_4 to form H_2CBCH_3 in Ar atmosphere. As the temperature increases (> 900 °C), further decomposition of H_2CBCH_3 to H_2BCH_3 is expected to lead to higher B/C ratios in the films. In H_2 atmosphere, other than the unimolecular α -H elimination of CH_4 , a H_2 -assisted CH_4 -elimination to $HB(CH_3)_2$ with slightly higher energy barrier is available and could explain the high B/C ratio in the films. On the other hand, further decomposition path of $HB(CH_3)_2$ to B/C-rich species such as H_2BCH_3 and BH_3 can also explain the higher B/C ratio for films deposited in H_2 compared to films deposited in Ar. The decrease in B/C ratio in the films deposited in both atmospheres at 1100 °C can be attributed to a higher CVD reactivity of CH_4 at higher temperatures.

5.2 TMB and TEB in Plasma CVD

Low temperature CVD processes for deposition of B_xC films using TMB and TEB as a single-source precursor in Ar plasma was demonstrated. When films deposited with TMB-Ar plasma, film composition was found to be dependent on both plasma power and TMB flow. The highest B/C ratio of 1.9 was achieved as films were deposited at high plasma power (2400 W) and high TMB flow (7 sccm) at a total pressure of 0.3 ± 0.05 mbar. The hydrogen content in the films was slightly high (15 ± 5 at. %) due to the low substrate temperature (estimated to be ~ 300 °C). Film density was determined to be 2.16 ± 0.01 g/cm³. An observed film delamination was related to high compressive stress in the films deposited with denser microstructures while films deposited with columnar structure showed better adhesion with stress level less than 400 MPa. The B1s and C1s spectra from XPS showed that B-C bond is dominant in the films; besides, C-C and small contribution from B-O are also observed. Raman spectroscopy showed that

decrease in Ar (plasma) gas flow lowered amorphous carbon formation in the films, which is considered the origin of C-C bond. The Optical emission spectra (OES) showed that emitted lines from the decomposition products of TMB (Fig. 10 in Paper III) in the plasma were mainly from atomic H, BH, CH and C₂. It was suggested that the TMB molecule decomposed by dehydrogenation of the methyl groups likely assisted by excited Ar atoms/thermal energy in the plasma, followed by breakage of the B-C bonds to form [•]CH radicals where at least one B-C was broken by a [•]H radical to form the [•]BH radical. C₂ was suggested to form either by combination of two [•]CH radicals or by further dehydrogenation of [•]CH radicals followed by combination of atomic carbons. Based on the plasma and the film composition, it was proposed that CH and BH are most likely the film forming species.

As for films deposited using TEB flow of 5 and 7 sccm, the boron content in the films was found plasma power dependent while the carbon content was almost not affected. The highest B/C of ratio 1.7 was achieved at the highest power applied (2400 W) for both TEB flows. The hydrogen content in the films was within 14-20 at. %. A similar trend for oxygen content in the film (reduced to <1 at. %) with increasing plasma power to the one observed for films deposited with TMB was obtained and associated with the densification of the films, which could prevent post deposition oxidation. The density of films was increased to 2.20 g/cm³ with increasing plasma power and attributed to a higher energetic bombardment during deposition. Plasma composition from OES showed that the TEB molecules were also decomposed mainly to BH, CH, C₂ and H. Based on the film and plasma composition, a plasma chemical model, where the first ethyl group is split off by β -hydrogen elimination to form C₂H₄, which is further dehydrogenated to C₂H₂ and forms C₂ and CH, was suggested. The BH species is assumed to be formed by the dehydrogenation of remaining ethyl groups and breakage of the B-C bonds to form BH.

Chapter 6 Future Work

The four papers summarized above presented CVD of B_xC thin films from two different organoboron molecules – TEB and TMB – using two different CVD methods – thermal and plasma CVD. Paper (I) and (II) presented the feasibility of depositing dense, boron rich films with low impurity levels, as well as added to the general understanding of the gas phase CVD chemistry of organoborons. Thus, as a promising application for thermally deposited B_xC films, $^{10}B_xC$ thin films should be fabricated using ^{10}B enriched organoboron precursor for neutron detection application. It can be noted here that TMB enriched with ^{10}B is commercially available while ^{10}B enriched TEB appears to be more of a challenge to acquire.

On the other hand, Paper (III) and (IV) demonstrated promising results for low temperature CVD of B_xC films and suggested plasma chemistry for the decomposition/dissociation of TEB and TMB in Ar plasma. However, the high hydrogen incorporation in the films due to the low substrate temperature might be problematic for neutron detection application to some extent. Therefore, one possible way of reducing the high hydrogen content in the films is by intentionally heating the substrate during film deposition to diffuse out the hydrogen. Moreover, as it is discussed in Paper (I) and (II), the TEB and TMB resulted in boron-rich films in H_2 atmosphere compared to in Ar due to the assistance of hydrogen molecules for the better decomposition of TEB and TMB. Thus, it can be an interesting experiment to use H_2 plasma or H_2 -Ar plasma instead of pure Ar to see if this route can make a difference in plasma chemistry and film composition.

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