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**Chemical vapour deposition of boron-carbon thin films from
organoboron precursors**

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Abstract

Boron-carbon (B_xC) thin films enriched in ^{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 the thin film. Chemical Vapour Deposition (CVD) of such films faces the challenge that the maximum temperature tolerated by the aluminium substrate is 660 °C and low temperature CVD routes for B_xC films are thus needed. This thesis presents the use of two different organoboron precursors, triethylboron $-B(C_2H_5)_3$ (TEB) and trimethylboron $-B(CH_3)_3$ (TMB) as single-source precursors for CVD of B_xC thin films.

The CVD behaviour of TEB in thermal CVD has been studied by both B_xC thin film deposition and quantum chemical calculations of the gas phase chemistry at the corresponding CVD conditions. The 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. A temperature window of 600 – 1000 °C for deposition of X-ray amorphous B_xC films with $2.5 \leq x \leq 4.5$ is identified showing good film density (2.40 – 2.65 g/cm³) which is close to the bulk density of crystalline B_4C , 2.52 g/cm³ and high hardness (29 – 39 GPa). The impurity level of H is lowered to < 1 at. % within the temperature window.

Plasma chemical vapour deposition has been studied using TMB as single-source precursor in Ar plasma for investigating B_xC thin film deposition at lower temperature than allowed by thermal CVD and further understanding of thin film deposition process. The effect of plasma power, total pressure, TMB and Ar gas flow on film composition and morphology are investigated. The highest B/C ratio of 1.9 is obtained at highest plasma power of 2400 W and TMB flow of 7 sccm. The H content in the films seems constant at 15±5 at. %. The B-C bond is dominant in the films with small amount of C-C and B-O bonds, which are likely due to the formation of amorphous carbon and surface oxidation, respectively. The film density is determined as 2.16±0.01 g/cm³ and the internal compressive stresses are measured to be < 400 MPa.

Preface

The presented licentiate thesis is written based on the collection of my knowledge and my research results during my Ph. D studies from September 2012 to November 2015 in the Thin Film Physics Division at the Department of Physics, Chemistry and Biology (IFM) at Linköping University. Understanding chemical vapour deposition of B_xC thin films using organoborons as single-source precursors is the aim of my research project. This project is in collaboration with the European Spallation Source (ESS), Lund, Sweden and financially supported by the ESS and the Knut and Alice Wallenberg foundation.

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 I wrote the manuscript.

Paper II

Trimethylboron as single-source precursor for boron-carbon thin film synthesis by plasma chemical vapour deposition

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

Manuscript in Final preparation

My contributions

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

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1. Introduction

1.1 Thin films

A thin film is a single or multiple layers of material(s) of which thickness ranges from fractions of nanometer (monolayer) to a few micrometers [1]. The earliest documented thin gold layers for decorative applications have a history of more than 5000 years. [2] Today, thin films are in wide use and have thus become an important area of material science. Optical coatings such as antireflective and UV protective coatings, hard and wear-resistant coatings for cutting tools and thin film electronic materials for microelectronics as well as energy harvesting technology, such as thin film batteries and solar cells, are 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 laboratory and industry. They are divided into two broad categories: chemical deposition and physical deposition depending on whether the process is primarily chemical or physical principles. In chemical vapour deposition (CVD), volatile precursor molecules are delivered into the reaction zone where they undergo series of reactions and form a layer of material on the substrate. [2] For further details on CVD, please see Chapter 2 of this thesis. In physical vapour deposition (PVD) atoms from a target material is released by evaporation or sputtering and deposited on a substrate by condensation. [2] The most common PVD techniques are sputtering and arc evaporation. However, CVD and PVD techniques are complementary techniques and usually utilized depending on the specific thin film deposition needs.

1.2 Neutron detectors

Neutrons are electrically neutral, thus they do not interact directly with the electrons in matter. Therefore, neutron-detecting mechanisms are based on indirect methods. A process for such a method begins when neutrons initiate releasing one or more charged particles by interacting with various atomic nuclei, the produced charged particles will ionize a gas, which in turn

generate electrical signals that can be processed by the detection system. [3][4] There are different types of neutron detectors such as Gas proportional detectors, Scintillation neutron detectors and semiconductor neutron detectors. The gas proportional detectors are the most common neutron detectors today. Among them, the ^3He gas-filled proportional detectors are very useful detectors due to the high neutron absorption cross-section and low sensitivity to gamma rays. In such a detector, the ^3He atom in the gas absorbs an incident neutron (n), one proton (p) and a tritium ion (^3_1H) are released in opposite directions with the simultaneous emission of γ -ray photons as shown in reaction (1)

The charged particles ionize the proportional counting gas (typically CF_4) and together with the liberated electrons can be detected as electrical signals. Unfortunately, in the past few years, the demands for ^3He gas have greatly exceeded than the supply, mainly due to U.S. Homeland security programmes. [5] This leads to an urgent need for alternatives to ^3He -based neutron detectors.

One possible replacement to ^3He for neutron detection is the isotope ^{10}B . ^{10}B has a relatively high (thermal) neutron 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 . The 10 % mass difference between the two isotopes makes the isotope separation relatively easy. [5] 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 (^7_3Li) and alpha (^4_2He) particles with certain kinetic energies in opposite directions according to reactions (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 (CF_4). Due to the bad oxidation resistance and

poor electrical conductivity of the 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 by its excellent thermal stability and chemical resistance [6], as well as the better conductivity than the 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 (ESS ERIC) will be the world's leading neutron spallation source for the study of materials. ESS was started 2010 in Lund, Sweden and it is a pan-European project involving participation of 17 countries in Europe. ESS has been conducting research on building $^{10}\text{B}_4\text{C}$ based solid-state neutron detectors and the estimated coating area of the $^{10}\text{B}_4\text{C}$ based instruments is 87 % of the total detector area of all instruments that will be built at ESS. [5][7][8] ESS will produce the first neutrons and bring the first seven instruments into operation in 2019. The full baseline suite of 22 instruments will be brought online by 2025.

1.3 Boron carbides

Boron carbide is an important ceramic with useful physical and chemical properties. It was discovered in the 19th century as a by-product of reactions for production of metal borides [9]. Boron carbide has a complex crystal structure where B_{12} icosahedra form a rhombohedral lattice unit linked through an inter-icosahedral chain along the longest diagonal of the rhombohedra as shown in Figure 1[10-13].

Figure 1. The atomic configuration of $B_{12}C_3$ ($B_{11}C$ -CBC). The grey and black spheres represent boron and carbon atoms, respectively, residing in the icosahedra and in the inter-icosahedral chain (figure is used with permission).

Therefore, its ideal chemical formula is nominally written as $B_{12}C_3$ instead of B_4C . However, based on studies, it is indicated that the incorporation of one or more C atoms into the B_{12} icosahedra results in stable single phase compounds in a large homogeneity range from 8 up to 20 at. % C concentration. [14]. Boron carbide is chemically inert and stable at high temperatures, moreover known as an excellent hard material after diamond and cubic boron nitride (c-BN). Thus it has attracted great interest as hard coatings in the cutting tools industry. In addition to the hardness, the high wear and impact resistance of boron carbide, as well as its lightweight has made it a very good candidate for bulletproof vests and tank armour applications. Boron carbide is naturally a p-type semiconductor and its band gap varies with composition and the degree of crystalline order. The estimated band gap is around 2 eV. [15]

In this thesis, B_xC thin films – films containing mainly boron and carbon atoms with B-C bonds, have been deposited by several CVD and PVD routes in both laboratory and industrial scale. [16-18] The PVD method is a line-of-sight deposition technique and while CVD is not to the same extent. CVD has been demonstrated to deposit well-defined, high quality single-phase boron carbide films [14]. To deposit boron carbide thin films for neutron detection applications, in this thesis I studied deposition of B_xC thin films in thermal and plasma CVD using organoborons as single-source precursor. Organoborons are advantageous compared to the conventional boron precursors; BCl_3 , BBr_3 and B_2H_6 , and carbon precursor; CH_4 , as their high reactivity allows for a CVD route at lower deposition temperature. [19] They also give non-corrosive by-products. This allows CVD of boron carbides on metallic substrates like Al. The most used organoborons are triethylboron, $B(C_2H_5)_3$ (TEB) and trimethylboron $B(CH_3)_3$ (TMB).

I introduce the methodologies of depositing B_xC films from TEB and TMB, and also present the investigated properties by characterizing them 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) and, Raman spectroscopy as well as nano-indentation.

2. Chemical Vapour Deposition

CVD is a film deposition method based on chemical reactions of vapour-phase precursor species, which occur both in the gas phase and on the substrate surface. 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. Usually, CVD processes are very complex and involve a series of gas phase and surface reactions. In Figure 2 a schematic picture of an overall CVD reaction during film growth is illustrated which includes several steps listed as follows [20]:

Figure 2. Transport and reaction processes in a CVD process.

- (1) Evaporation and transport of reagents (i.e., precursors) into the reactor;
- (2) Gas phase reactions of precursors in the reaction zone to produce reactive intermediates and gaseous by-products;
- (3) Mass transport of the reactants to the substrate surface;

-
- (4) Adsorption of reactants on the substrate surface;
 - (5) Surface diffusion to growth sites, nucleation and surface chemical reactions leading to film formation;
 - (6) Desorption and mass transport of maintaining fragments of the decomposition away from the reaction zone;

2.1 Precursor

Precursor molecules are molecules containing the element or elements that are necessary for the deposition of the thin film. Precursors employed in a CVD process can be inorganic or organic chemicals and also be in different phases including gas, liquid or solid. The input of precursors which are naturally occurring in gaseous state such as NH_3 as source of nitrogen [21][22], O_2 or CO_2 as source of oxygen [23][24] 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 commonly called ‘bubblers’ usually made of stainless steel. [25] 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 and carries the precursor vapour by passing through the liquid, and one outlet where 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. CVD precursors are an important aspect of the CVD technology as CVD is based on chemical reactions, therefore the chemical behaviour of precursors is very important. [26] The general requirements for CVD precursors are that they must be volatile, thermally stable during transport into the reactor and a lower decomposition temperature is also required. 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 cases, it is hard to find such a precursor that fulfils all requirements mentioned above. In such a circumstance, there could be ways that makes things work. As an example, the vapour pressure of the precursor is one of the parameter that determines the growth rate. The vapour pressure of any molecule is given by its temperature. Therefore, the temperature of liquid and solid precursors is controlled by e.g. keeping the bubbler in a well-controlled temperature bath.

2.2 CVD growth regimes

In CVD of thin films, the deposition temperature is very essential in order to determine the film growth rate. [20] 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 temperature ($1/T$) as given in Figure 3.

Figure 3. Three growth-regimes in a CVD process.

So, there are three deposition regimes, they are thermodynamics limited, gas-phase transport and kinetics limited regimes. At low temperatures, 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 named as kinetics limited 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 called mass-transport limited 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 regime. However, the importance of the three regimes alters when the pressure inside reactor changes. The higher pressure ($\sim 10^{-3}$ 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 ($\sim 10^{-4}$ mbar), by the desorption of ad-atoms, as well as the gas and substrate temperatures. [20]

2.3 Thermal CVD

CVD can be classified as thermal CVD, photo-assisted CVD or plasma CVD depending on the provided energy input such as heating, higher frequency radiation or plasma, respectively. [27] In this thesis, thermal CVD and plasma CVD will be discussed.

Thermal CVD or thermally activated CVD is a conventional CVD process in which thermal energy is used to activate chemical reactions in a hot wall or cold wall reactor. In a thermal CVD process, the thermal energy can be provided in the form of rf heating, infrared radiation or resistive heating. [28] According to the pressure range of the deposition process, thermal CVD can also be subdivided further into atmospheric pressure CVD (APCVD), low pressure CVD (LPCVD) or ultrahigh vacuum CVD (UHVCVD). [28][29] The pressure ranges for APCVD, LPCVD and UHVCVD processes usually are in a range of an atmospheric pressure, 0.1-13.3 mbar, and $<10^{-3}$ mbar, respectively.

The conventional thermal CVD uses 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. As its name implies the organometallic precursors contain organic compounds and metal atom in which at least one carbon atom of the organic compound bonds to the metal. [30]

2.3.1 Thermal CVD setup

The two types of reactors most frequently used in CVD processes are hot-wall reactor and cold-wall reactor. 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 4 is used for deposition of B_xC thin films. The reactor is a horizontally placed quartz tube in which a susceptor (hot zone) made of high-density graphite is placed close to gas inlet and heated inductively by a surrounded RF coil. In order to keep the quartz tube away from high temperature exposure, an isolation layer made of low-density graphite is added between the susceptor and quartz tube. The susceptor is also coated with a layer of protective coating that prevents out diffusion of impurities from graphite. Besides, the protective coating makes the susceptor tolerant at high temperature 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 4. A view of film deposition process with the hot-wall CVD reactor.

2.4 Plasma CVD

Plasma CVD is a form of CVD where the energy in a plasma is used as energy input 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 is 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. [31] The active species for the deposition must have sufficient lifetime to reach the substrate/film surface. 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. [32] Usually inert gases such as He and Ar, as well as N_2 gas can have relatively long lifetimes, thus used as plasma gases.

2.4.1 Plasma CVD setup

There are different ways of generating plasma, such as electrical discharge, radio frequency (RF) and microwaves (MW). The microwave assisted plasma CVD is a method in which high frequency microwaves (2.45 GHz) are used as energy source for generating the plasma.

However, the microwave sources for generating plasma have not been used as widely as other techniques, since the difficulties of constructing a simple and convenient experimental set-up and the difficulties to sustain plasma at low power. [33]

In this thesis, we modified an ASTEX microwave plasma CVD deposition system, which was previously used for diamond deposition. The microwave generator is equipped with a power supply with maximum output power of 2500 W as shown in Figure 5.

Figure 5. Schematic of microwave plasma CVD deposition system.

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 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. In addition, 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 and long life-time and high energy of the excited atoms. TMB has been employed as a single-source precursor for 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.

2.5 CVD chemistry

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 more complex than what is hinted in Figure 2. [2] 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. An understanding of the overall CVD chemistry provides tools for improving the process and the deposited thin film quality.

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 studied experimentally by changing deposition conditions and studying 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. [2] Moreover, quantum chemical calculation is also used to provide detailed gas phase chemistry models and thermochemical data for the gas phase species. [2]

3. Film Characterization Techniques

3.1 Scanning electron microscopy

Scanning electron microscopy (SEM) is a widely used imaging technique, which produces images by scanning a sample with a focused electron beam. The relatively faster and more convenient operation of the SEM compared to transmission electron microscopy (TEM) make it a fast method for examining microstructures and morphology.

SEM set up is composed of: Electron gun; Electron condenser lens; Scan coils; Objective lens; Detectors; Specimen as presented in Figure 6:

Figure 6. Schematic diagram of Scanning electron microscopy setup.

The resolution of SEM is dependent on the wavelength of electron beam, which is determined by the energy of electrons of 1-50 keV. 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 to the sample surface and generate signals such as secondary electrons, back scattered electrons and characteristic X-rays and cathodoluminescence. These detected signals can then be associated with the beam position and form an SEM image. Secondary electron imaging (SEI) is in most commonly use, in which the detected electrons are the emitted low energy electrons from atoms at and near to 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, thus can be used for compositional contrast. 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 causes poor resolution.

The SEM images in this thesis are 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 compared to thermionic gun even at lower acceleration voltage. Since both boron and carbon atoms are light elements, 5 kV excitation voltage is applied, SEI mode using an Inlens – high signal to noise ratio detector, is used to produced high-resolution cross-sectional SEM images.

3.2 X-ray reflectivity

X-ray reflectivity (XRR) is a non-destructive, surface-sensitive analytical technique for structural characterization of thin films and also provides layer periodicity of multilayers. The refractive index in solids is smaller than unity for x-rays, thus total internal 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. 7) while the oscillations and slope of the curve are determined by film thickness and surface roughness, respectively.

Figure 7. X-ray reflectivity scan of a sample deposited by plasma CVD.

XRR measurement can be done using an X ray diffractometer (XRD) in grazing incidence XRD geometry. In this thesis, a Philips X'Pert Pro MRD diffractometer equipped with a hybrid mirror monochromator and 2-bounce Ge 220 triple-axis crystal analyser has been used

for the XRR measurement. Film densities were determined by fitting the experimental data using X'pert reflectivity software.

3.3 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, polycrystal 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 (Thomson scattering). 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 in the Braggs law, eq. (4) and illustrated in Figure. 8.

$$n \lambda = 2d \sin \theta \quad (4)$$

Where n is an integer corresponding to the order of diffraction and θ is the angle between the incident beam and atomic plane (equal to half of 2θ).

Figure 8. Illustration of X-ray diffraction from atomic planes according to the Braggs law.

In Paper (I), θ - 2θ scans have been 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 scans the spacing of lattice planes parallel to the surface.

3.3.1 Stress measurement

Compressive stresses are calculated from measuring the curvature of substrates in high-resolution rocking curve geometry. The radius of substrate curvature is calculated using formula (5):

$$R \approx \frac{\Delta x}{\Delta \omega [\text{rad}]} \quad (5)$$

in which Δx is the distance between two measured positions x on the sample surface and $\Delta \omega$ is the small change between the peak positions of ω measured at the two x -positions. Lastly, compressive stresses are derived from the Stony equation:

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

t_f and t_s are film and substrate thickness, respectively. The biaxial modulus of substrate $M_s = E_s/(1-\nu)$ and E_s is elastic modules of substrate and ν poisson's ratio. In Paper (II), the internal compressive stresses formed in the films are determined using the same diffractometer used for the XRR measurement.

3.4 Time of flight elastic recoil analysis

Elastic recoil detection analysis (ERDA) is an ion beam analysis technique, which provides information about chemical composition and elemental depth profile of materials. The basic principle of ERDA is that as energetic ions (primary beam) in MeV range irradiate on a sample, atoms /ions are recoiled by the collision of an ion with the atoms in the sample. The

collision is assumed as two-body elastic collision and the transferred kinetic energy of the recoiled atom E_r can be described with eq. (7):

$$E_r = \left(\frac{4M_i M_r \cos^2 \beta}{(M_i + M_r)^2} \right) E_{i0} \quad (7)$$

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 , M_r can be derived from eq. (7).

However, the kinetic energy of recoils E_r can be changed with possible multiple scattering, 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 energy. In this thesis, all measurements have been done using 36 MeV Iodine ions as primary beam with a time of flight detector.

4. Summary of Results

4.1 Paper I

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

In Paper I we seek to obtain a better understanding of TEB as a single-source precursor for B_xC films in thermal CVD. We used a combined experimental and theoretical approach with both film deposition and quantum chemical calculations. We deposited films in two different atmospheres; H₂ and Ar within 700 -1200 °C and used also previously published results (400-600 °C) [17] to get a more complete picture.

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; temperatures in 800-1000 °C gave almost constant boron content and temperature above 1000 °C mainly resulted in carbon-rich films in both atmospheres (more pronounced in H₂ atmosphere). The incorporated hydrogen is temperature dependent and a temperature for out diffusion of the H (< 1 at. %) was found at around 700 °C. Films look dense in cross sectional SEM images (see Fig. 1 in Paper I) and the film density is determined as $2.42 \pm 0.05 \text{ g/cm}^3$ which is very close to density of bulk crystalline B₄C: 2.52 g/cm^3 [34] and the density of sputtered films 2.45 g/cm^3 [16]. XRD shows that no obvious crystalline boron-carbide phases have formed when films deposited below 1000 °C. Film hardness is varied from 29-39 GPa depending on the deposited boron content and formed compressive stresses, i.e., high boron content and high stress resulted in high hardness.

Based on our experimental findings and quantum chemical calculations, a gas phase chemical model for TEB consisting of two reaction types, β -hydride elimination and H₂ –assisted ethane (C₂H₆) elimination, is proposed. Based on the reaction products (also intermediate products, see Paper I), B(C₂H₅)₂H, B(C₂H₅)H₂, and BH₃ are considered to be the boron containing species for the film deposition while C₂H₄ is the main carbon containing species.

To conclude, TEB in a thermal CVD condition shows the feasibility of depositing boron-rich, amorphous, B_xC films with good density and low impurities on Si substrates.

4.2 Paper II

Trimethylboron as single-source precursor for boron-carbon thin film synthesis by plasma chemical vapour deposition

Paper I showed that the process temperature of thermal CVD of B_xC films (700 °C) is slightly beyond the melting point of substrates such as Al (melts at 660°C). Therefore we turned to plasma CVD to find a deposition route at lower temperature. Here we also chose to use TMB as a single-source precursor instead of TEB as it has higher B/H and B/C ratios, which should be beneficial when aiming for low H content and B-rich films.

The microwave plasma CVD system described in chapter 2 is used to deposit B_xC films using TMB on 100 mm diameter (100) oriented Si wafers. The temperature of the substrate is estimated to at least 300 °C due to the energetic bombardment of the substrate by the plasma. Two different sets of samples have been deposited at various deposition parameters.

The film composition is found to be dependent on both plasma power and TMB flow. The highest B/C ratio achieved was 1.9, when films are 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 15 ± 5 at. %. Film density is determined to 2.16 ± 0.01 g/cm³ and the measured internal stress in the films is < 400 MPa. A observed film delamination is related to a compressive stress in the films deposited with denser microstructures, while films deposited with columnar structure shows good adhesion. The B1s and C1s spectra from XPS show that B-C bond is dominant in the films; besides, C-C and small contribution from B-O are also observed. Raman spectroscopy shows that films contain amorphous carbon, which is considered the origin for C-C bond.

5. Future work

Paper (I) and paper (II) have presented CVD of B_xC thin films from two different organoboron molecules – TEB and TMB – using two different CVD methods – thermal and plasma CVD. The obtained results from both papers have shown good results in terms of high boron content than what has previously been published in the literature. [5] Paper (I) has also added to the general understanding of the CVD chemistry of organoborons. The results inspire us to go further with the explorations of these precursors.

It will be very interesting to explore TEB also in plasma CVD; our gas phase chemistry model points to a relatively easy unimolecular decomposition with the β -hydride elimination. Can this be used also in plasma CVD or will the highly reactive plasma chemistry favour other routes? Is it possible to deposit boron-rich films from TEB in plasma CVD as it is in thermal CVD? Can TEB in plasma CVD lead to low hydrogen content in the films?

Also for the TMB in thermal CVD, several questions have arisen such as: can TMB be used in thermal CVD given that the β -elimination path is not available for this molecule? Will a H_2 -assisted CH_4 elimination be seen in thermal CVD with TMB? In order to probe the deposition chemistry, optical emission spectroscopy (OES) will be used to study the plasma chemistry and how it is affected by change in the plasma CVD process parameters.

As the final goal of this project, $^{10}B_xC$ thin films should be fabricated using a ^{10}B enriched organoboron precursor and hopefully the feasibility of CVD films for neutron detection application will be tested in available prototype detectors at a neutron source facility. It can here be noted that TMB enriched in ^{10}B is commercially available while ^{10}B enriched TEB appears to be more of a challenge to acquire.

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