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Chemical Vapour Deposition of sp^2 Hybridised Boron Nitride

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Cover images – Scanning electron microscope micrographs of sp^2 -BN; front – triangular feature characteristic for r-BN, and back – disordered sp^2 -BN.

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Abstract

The aim of this work was to develop a chemical vapour deposition process and understand the growth of sp^2 hybridised Boron Nitride (sp^2 -BN). Thus, the growth on different substrates together with the variation of growth parameters was investigated in details and is presented in the papers included in this thesis. Deposited films of sp^2 -BN were characterised with the purpose to determine optimal deposition process parameters for the growth of high crystal quality thin films with further investigations of chemical composition, morphology and other properties important for the implementation of this material towards electronic, optoelectronic devices and devices based on graphene/BN heterostructures.

For the growth of sp^2 -BN triethyl boron and ammonia were employed as B and N precursors, respectively. Pure H_2 as carrier gas is found to be necessary for the growth of crystalline sp^2 -BN. Addition of small amount of silane to the gas mixture improves the crystalline quality of the growing sp^2 -BN film.

It was observed that for the growth of crystalline sp^2 -BN on c-axis oriented α - Al_2O_3 a thin and strained AlN buffer layer is needed to support epitaxial growth of sp^2 -BN, while it was possible to deposit rhombohedral BN (r-BN) on various polytypes of SiC without the need for a buffer layer. The growth temperature suitable for the growth of crystalline sp^2 -BN is 1500 °C. Nevertheless, the growth of crystalline sp^2 -BN was also observed on α - Al_2O_3 with an AlN buffer layer at a lower temperature of 1200 °C. Growth at this low temperature was found to be hardly controllable due to the low amount of Si that is necessary at this temperature and its accumulation in the reaction cell. When SiC was used as a substrate at the growth temperature of 1200 °C, no crystalline sp^2 -BN was formed, according to X-ray diffraction.

Crystalline structure investigations of the deposited films showed formation of twinned r-BN on both substrates used. Additionally, it was found that the growth on α - Al_2O_3 with an AlN buffer layer starts with the formation of hexagonal BN (h-BN) for a thickness of around 4 nm. The formation of h-BN was observed at growth

temperatures of 1200 °C and 1500 °C on α -Al₂O₃ with AlN buffer layer while there were no traces of h-BN found in the films deposited on SiC substrates in the temperature range between 1200 °C and 1700 °C. As an explanation for such growth behaviour, reproduction of the substrate crystal stacking is suggested. Nucleation and growth mechanism are investigated and presented in the papers included in this thesis.

Populärvetenskaplig sammanfattning

Bornitrid (BN) är ett väldigt intressant material för många forskare eftersom det har väldigt spännande egenskaper och kristallstrukturer väldigt lika kristallint kol. Det elektriska bandgapet har visat sig vara stort (~ 6 eV) och dessutom särskilt väl lämpat för konstruktion av ljusdioder, speciellt eftersom det kan modifieras genom dopning. Om man skulle kunna göra ljusdioder av BN skulle dessa sända ut ljus med en våglängd på cirka 220 nm alltså den typen av ultraviolett ljus (UV) som ozonlagret filtrerar bort från solen. Av sådana ljusdioder skulle man sedan kunna göra vita ljusdioder genom att använda en luminofor, vilket är ett material som absorberar UV-ljus och sedan sänder ut vitt ljus, men ännu mera spännande skulle det vara att använda ljusdioderna för vattenrening då denna typ av UV-ljus dödar bakterier. Eftersom BN bildar samma kristallstrukturer som kol, så är den grafitlika, sp^2 -hybridiserade formen av BN mycket intressant att använda tillsammans med grafen. Beräkningar har visat att om man använder sp^2 -BN som substrat till grafen så kommer man åt större del av de förutspådda materialegenskaperna för grafen än om man använder andra substrat.

Syftet med detta arbete har varit att utveckla en syntesprocess för tunna filmer av sp^2 -BN med tillräckligt hög kvalitet för att kunna börja utforska alla möjligheter med BN, för detta har en teknik som kallas chemical vapour deposition (CVD) har använts. Principen för CVD är att gaser innehållande de atomer man behöver för filmen, i detta fall bor och kväve, får reagera med varandra vanligtvis vid hög temperatur, och bilda en film, i detta fall av BN. Syntesprocessen för BN filmer har studerats på olika kristallina ytor, vid olika temperaturer med olika koncentrationer av utgångsgaserna. Den kemiska sammansättningen och den kristallina strukturen hos de syntetiserade filmerna har analyserats för att fastställa de optimala syntesbetingelserna för BN filmer för optoelektroniska tillämpningar.

Preface

This work concludes 4.5 years PhD studies on the growth and characterisation of BN thin films.

The thesis gives a brief overview of the family of boron nitride compounds, attractive properties of sp^2 -BN, historic overview and the ways how to synthesize sp^2 -BN. Experimental techniques that were employed in this work for the deposition and the characterisation of sp^2 -BN films are discussed in sufficient details for understanding of the experimental results. Publications included into the thesis present findings related to the deposition of sp^2 -BN and ways to tailor quality of the deposited layers. The papers are summarised and major results are shortly described in the chapter “Summary of the work”.

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List of publications included into the thesis

Paper 1:

Epitaxial CVD growth of sp^2 -hybridized boron nitride using aluminum nitride as buffer layer.

Mikhail Chubarov, Henrik Pedersen, Hans Högberg, Vanya Darakchieva, Jens Jensen, Per O. Å. Persson, Anne Henry. Phys. Status Solidi RRL **5**, 397–399 (2011).

Paper 2:

Growth of High Quality Epitaxial Rhombohedral Boron Nitride.

Mikhail Chubarov, Henrik Pedersen, Hans Högberg, Jens Jensen, Anne Henry. Cryst. Growth Des. **12**, 3215–3220 (2012).

Paper 3:

On the effect of silicon in CVD of sp^2 hybridized boron nitride thin films.

Mikhail Chubarov, Henrik Pedersen, Hans Högberg, Anne Henry. CrystEngComm **15**, 455 – 458 (2013).

Paper 4:

Chemical vapour deposition of epitaxial rhombohedral BN thin films on SiC substrates.

Mikhail Chubarov, Henrik Pedersen, Hans Högberg, Zsolt Czigány, Anne Henry. CrystEngComm **16**, 5430 – 5436 (2014)

Paper 5:

Polytype pure sp^2 -BN thin films as dictated by the substrate crystal structure

Mikhail Chubarov, Henrik Pedersen, Hans Högberg, Zsolt Czigány, Magnus Garbrecht, Anne Henry. Submitted for publication

Paper 6:

Nucleation and initial growth of sp^2 -BN on SiC and α -Al₂O₃.

Mikhail Chubarov, Henrik Pedersen, Zsolt Czigány, Hans Högberg, Sven G. Andersson, Anne Henry. Manuscript in final preparation

My contribution to the papers

Paper 1:

I took part in the planning of the work and participated in the deposition experiments. I performed XRD measurements and participated in the discussion of the experimental results. I prepared the first draft of the paper and finalised according to the comments from the co-authors.

Paper 2:

I have planned row of experiments, performed the films growth and the X-ray diffraction measurements, analysed experimental data and participated in the discussions of the results. I prepared the first draft of the paper and finalised it according to the comments from the co-authors.

Paper 3:

I have planned all the experiments, deposited the films, performed X-ray diffraction and FTIR measurements, analysed the experimental data and participated in the discussions of the results. I wrote the first draft of the paper and finalised it according to the comments from the co-authors.

Paper 4:

I did all the planning for all experiments, done the films deposition, performed X-ray diffraction and SEM measurements, analysed experimental data and participated in the discussions of the results. I prepared the first draft of the paper and finalised it according to the comments from the co-authors.

Paper 5:

I have planned and conducted the row of experiments, including the films deposition, X-ray diffraction measurements and critical thickness calculations,

the analysis of the experimental data and I have participated in the discussions of the results. I prepared the first draft of the paper.

Paper 6:

I have planned and made the row of growth experiments and characterised samples with X-ray diffraction, SEM and XPS measurements. I did the analysis of the experimental data and participated in the discussions of the results. I wrote the first draft of the paper and finalised it according to the comments from the co-authors.

List of publications not included into the thesis

On the effect of water and oxygen in chemical vapor deposition of boron nitride.

H. Pedersen, **M. Chubarov**, H. Högberg, J. Jensen, A. Henry. *Thin Solid Films* **520**, 5889–5893 (2012).

Characterization of Boron Nitride Thin Films.

M. Chubarov, H. Pedersen, H. Högberg, S. Filippov, J.A.A. Engelbrecht, J. O'Connel and A. Henry. *Pacific Rim Conference on Lasers and Electro-Optics, CLEO - Technical Digest* art. no. 6600222 (2013)

Boron nitride: A new photonic material.

M. Chubarov, H. Pedersen, H. Högberg, S. Filippov, J.A.A. Engelbrecht, J. O'Connel, A. Henry. *Physica B* **439**, 29–34 (2014)

Growth of Boron Nitride layer on SiC

M. Chubarov, H. Pedersen, H. Högberg, M. Garbrecht, Z. Czigány, S. G. Andersson, A. Henry. *Materials Science Forum*

Determination of stacking in boron nitride by K-edge X-ray absorption spectra: measurements and first-principles calculation.

W. Olovsson, **M. Chubarov**, A. Henry, M. Magnusson

Manuscript in final preparation

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1. Introduction

The group 13-nitrides have many interesting properties especially as a promising system for semiconductor optoelectronic devices working in the blue and ultraviolet regions. Significance of the materials system is highlighted by the Nobel Prize in Physics awarded to Isamu Akasaki, Hiroshi Amano and Shuji Nakamura “*for the invention of efficient blue light-emitting diodes which has enabled bright and energy-saving white light sources*” in 2014. Today they mainly involve GaN, AlN, InN and their alloys. However boron nitride (BN), which is the least investigated group 13-nitride material, gathers researchers’ interest due to its interesting properties and close similarities to carbon. Boron nitride can exist in two forms with sp^2 -hybridised or sp^3 -hybridised atomic orbitals of B and N.

BN in the sp^2 -hybridised form is analogous in crystalline structure to graphite. It has outstanding properties such as high electrical resistance when undoped, a band gap of ~6 eV, low dielectric constant and stability at high temperatures and in chemically aggressive environments. Furthermore, it is reported that sp^2 -BN can be doped p- and n-type that is necessary for electronic applications. In addition, due to the similarities to carbon, and especially having close lattice constants to graphite, it is suitable for use as a dielectric substrate for the growth of graphene. Thus it is a promising material for various applications, such as optical devices in the UV-range, insulating coatings and substrate for graphene. There are several attempts to grow hexagonal BN (h-BN) using various techniques where most of the works on chemical vapour deposition (CVD) of sp^2 -BN reports on the growth of turbostratic BN (t-BN) that does not possess out of plane ordering. Nonetheless, some works show growth of crystalline sp^2 -BN and even report devices based on this material. However, quality of the CVD deposited material is expected to be low and further exploration of the growth behaviour is necessary to obtain device-ready material.

This thesis gives an overview of the boron nitride growth and characterisation field and presents results achieved during the work on development and understanding of the growth behaviour of sp^2 -BN. In addition specific characterisation techniques are described which are the most relevant for this study.

2. Boron Nitride

Figure 1. Crystal structures of boron nitride. (a) – rhombohedral, (b) – hexagonal, (c) – wurtzite and (d) – cubic.

Boron (B) and nitrogen (N) can form a compound material BN that is isoelectronic to C [1] where these three elements are the closest neighbours in the 2nd period of periodic table. Atomic orbitals in the BN compound can be sp^2 or sp^3 hybridised forming sp^2 -hybridised (sp^2 -BN) or sp^3 -hybridised bonds (sp^3 -BN) [2]. In sp^2 -BN each atom possesses 3 strong in-plane bonds formed by sp^2 hybridised orbitals (hybridisation of the 2s orbital with two of the 2p orbitals) and one weak out-of-plane π bond of van der Waals type formed by one pure 2p orbital [3]. With such bonds hybridisation BN forms solid that is similar to graphite and can be found in the amorphous (a-BN), turbostratic (t-BN), rhombohedral (r-BN) (Figure 1a) and hexagonal (h-BN) (Figure 1b) phases [4]. In sp^3 -BN each atom possesses 4 equally strong and equally space separated bonds formed by sp^3 hybridised orbitals (hybridisation of the 2s orbital with all three of the 2p orbitals). In this case BN is found to have wurtzite (w-BN) (Figure 1c) and cubic (c-BN) (Figure 1d) crystal structures [5]. While there is demand to obtain pure sp^3 -BN, no such material has been synthesised yet and all layers contain sp^2 -BN inclusions. There is another type of

structure defined for BN – explosive BN (e-BN); that is observed when sp^3 - and sp^2 - hybridisations are mixed in the solid material and there are no distinct boundaries between sp^2 -BN and sp^3 -BN phases [6, 7]. Lattice constants, crystal symmetries and positions of the atoms in the unit cell for common BN polytypes are summarised in the Table 1.

Table 1. Crystal structures, lattice parameters and atomic coordinates of common BN crystals.

Polytype	Space group	Lattice constants	Atomic coordinates
r-BN	160	$a=2.504 \text{ \AA}$ $c=10.000 \text{ \AA}$	B: $\frac{1}{3}, \frac{2}{3}, 0; 0, 0, \frac{1}{3}; \frac{2}{3}, \frac{1}{3}, \frac{2}{3}$ N: $0, 0, 0; \frac{2}{3}, \frac{1}{3}, \frac{1}{3}; \frac{1}{3}, \frac{2}{3}, \frac{2}{3}$
		$a=3.633 \text{ \AA}$ $\alpha=40.31^\circ$	B: $0, 0, 0$ N: $\frac{1}{3}, \frac{1}{3}, \frac{1}{3}$
h-BN	194	$a=2.504 \text{ \AA}$ $c=6.656 \text{ \AA}$	B: $\frac{1}{3}, \frac{2}{3}, 0; 0, 0, \frac{1}{2}$ N: $0, 0, 0; \frac{1}{3}, \frac{2}{3}, \frac{1}{2}$
w-BN	186	$a=2.550 \text{ \AA}$ $c=4.215 \text{ \AA}$	B: $0, 0, 0; \frac{1}{3}, \frac{2}{3}, \frac{1}{2}$ N: $0, 0, \frac{3}{8}; \frac{1}{3}, \frac{2}{3}, \frac{7}{8}$
c-BN	216	$a=3.615 \text{ \AA}$	B: $0, 0, 0; 0, \frac{1}{2}, \frac{1}{2}; \frac{1}{2}, 0, \frac{1}{2}; \frac{1}{2}, \frac{1}{2}, 0$ N: $\frac{1}{4}, \frac{1}{4}, \frac{1}{4}; \frac{1}{4}, \frac{3}{4}, \frac{3}{4}; \frac{3}{4}, \frac{3}{4}, \frac{1}{4}; \frac{3}{4}, \frac{1}{4}, \frac{3}{4}$

Two crystal structures formed by sp^3 -BN are similar in properties to diamond where c-BN is found to be the second hardest material after diamond but does not react with ferrous materials as diamond. These properties make this material attractive for development as coating material for metal cutting tools. In addition, c-BN can be doped for both p- and n- type conductivity that is desirable for the electronic applications. This is in contrast to diamond where n-type doping is still problematic [8, 9, 10].

For BN with sp^2 hybridised bonds, two crystalline structures are usually observed – h-BN and r-BN. But in addition to these two crystals there are also less ordered forms of sp^2 -BN – a-BN and t-BN. a-BN is completely disordered material and is unstable in the atmosphere due to the fact that it reacts with water to form boron

oxides and hydroxides [11]. t-BN on the other side has some degree of order – basal planes are parallel to each other, but there is no ordering between the basal planes (rotational disorder) and spacing between them is larger than for h- or r-BN and is not well defined [12]. Thus, this structure is observed in X-ray diffraction (XRD) measurements causing broad peak at lower 2θ angles compared to 0002 or 0003 peaks of h- or r-BN. Additionally, XRD peak originating from (hki0), where h or k is not equal to zero, will be visible with a long tail at higher 2θ angles [13].

The rest of this thesis is solely devoted for the sp^2 -BN, its deposition, properties determination and quality improvement.

2.1. Properties and applications of sp^2 -BN

sp^2 -BN possesses various properties that in combination make this material suitable for many applications and thus an interesting material for the investigation and development of the routes for its synthesis.

There are many studies (theoretical as well as experimental) dealing with the determination of the sp^2 -BN properties where special attention is devoted to the the band structure (band gap and its properties). However, there is no certainty in the width of the band gap and if it is direct or not – these are important properties for the future development of this material. Table 2 summarises some of the theoretical works presented in the literature.

Table 2. Theoretical calculations presented in the literature that report on h-BN bandgap properties.

Model	Band gap, eV	Property	Reference
DFT-LDA	4.03/3.40/3.43	Indirect/direct/indirect	14
FLAPW	4.5	Direct	15
LDA	3.3 – 4.2	-	16
DFT-LDA	4.28 – 5.8446	Direct	17

Similar trends are also observed for the experimental investigations of the sp^2 -BN. There are some works reporting that h-BN possesses a direct band gap of around 6 eV where each work reports different values of the band gap. Table 3 summarises band gap properties derived from the experimental data by different authors.

Table 3 Experimental results presented in the literature that report on h-BN bandgap properties.

Method	Band gap, eV	Property	Reference
Luminescence excitation spectroscopy	5.96	Quasi-direct	18
Fluorescence excitation spectra	4.02	indirect	19
Cathodoluminescence	5.97	direct	20

Such deviation of the band gap value in the experimental work could be an issue of the composition of the film. It was shown that the band gap of h-BN can be varied by adding C into the film and thus forming ternary alloy $\text{BN}_{1-x}\text{C}_x$ [21]. Thus, to experimentally determine the band gap of $\text{sp}^2\text{-BN}$, high purity and high crystalline quality samples must be prepared.

There are reports presenting experimental evidences of the direct band gap of h-BN [18, 20, 22] and some theoretical calculations of the h-BN band structure also predict that it has a direct band gap. Thus, it is likely that the material has direct band gap of around 6 eV. In addition, it was shown that h-BN has higher luminescence efficiency than AlN [23]. Thus h-BN could be employed as a deep UV emitter and detector competing with AlN.

For the realisation of a deep UV emitter or detector, p- and n-type doping must be possible to obtain for a material. There are not many reports on the doping possibilities of $\text{sp}^2\text{-BN}$, nonetheless both p- and n-type semiconducting $\text{sp}^2\text{-BN}$ is presented and characterised [24, 25]. As a n-type dopant for $\text{sp}^2\text{-BN}$ sulphur (S) found to be suitable [24]. However, common group 13-N n-type dopant silicon (Si), is found to be a deep donor that needs temperature of 800 °C to be activated and thus is not suitable for room temperature applications [26]. Similarly as for 13-nitrides, Mg has been successfully employed as a p-type dopant for BN [27]. Additionally, activation energy of the Mg acceptor in $\text{sp}^2\text{-BN}$ was determined to be $\sim 31\text{meV}$ and found to be lower than that of Mg in AlN (510 meV) [27]. Therefore, it makes $\text{sp}^2\text{-BN}$ even more attractive for deep UV applications.

$\text{sp}^2\text{-BN}$ is an intrinsic dielectric that exhibits a low dielectric constant, seen from the low refractive index of 1.65 parallel to the c-axis and 2.05 in the perpendicular

direction, and a high breakdown field of ~ 4.4 MV/cm [28, 29, 30]. These properties make this material suitable for applications as a dielectric material in high speed and high power electronics.

Due to the high neutron capture cross section of ^{10}B isotope, compounds containing boron and thus also BN are recognised to be suitable candidates to use as materials for neutron detectors [31]. Fabrication and characterisation of such devices based on h-BN have been reported in the literature and proposed to be suitable for replacing ^3He gas based neutron detectors [32].

Chemical and thermal stabilities are other factors making this material to be attractive for other applications [33]. These properties of the $\text{sp}^2\text{-BN}$ make it a good candidate for use in harsh environments as a dielectric material or as a semiconducting material when appropriate doping of the material is done.

Because of the close similarities to graphite; weak out-of-plane π bonds and basal plane atomic structure similar to that of graphite with lattice constant $a=2.504$ Å that is close to graphite lattice constant $a=2.464$ Å, $\text{sp}^2\text{-BN}$ is shown to be an excellent insulating substrate for graphene. It was shown that due to the weak interaction between graphene and the $\text{sp}^2\text{-BN}$ substrate, the properties of the graphene are close to the theoretically predicted values [34]. This fact led to a huge interest for the development of the large area $\text{sp}^2\text{-BN}$ and ways to deposit or transfer large area graphene on to the $\text{sp}^2\text{-BN}$ [35, 36, 37, 38]. Device fabrication and characterisation employing graphene- $\text{sp}^2\text{-BN}$ heterostructures have been reported in the literature, showing promising performance [39, 40, 41]. However, large area, defect-free graphene and $\text{sp}^2\text{-BN}$ are still challenging [42].

The mechanical and thermal properties of $\text{sp}^2\text{-BN}$ are determined by its crystal structure and bonds anisotropy. Due to the weak out-of-plane π bonds and strong in-plane σ bonds $\text{sp}^2\text{-BN}$ exhibits high strength of basal planes (strong intraplanar bonding) while basal planes can be easily separated by scotch tape (weak interplanar bonds) like for graphite. Thermal conductivity of $\text{sp}^2\text{-BN}$ is also strongly anisotropic – 390 W/m K in plane ($\perp$ c-axis) and 2 W/m K out of plane ($\parallel$ c-axis) [43]. Another phenomenon encountered in the $\text{sp}^2\text{-BN}$ due to the weak interaction between the basal

planes is the negative in-plane linear thermal expansion coefficient that is also characteristic for graphite [44].

The properties of this interesting material make it hard to find a suitable substrate for the epitaxial growth of high quality crystalline sp^2 -BN but make it highly desirable to achieve epitaxial thin films of this material.

3. Chemical Vapour Deposition

Figure 2. Simplified scheme of CVD reactor employed for sp^2 -BN growth

Chemical vapour deposition (CVD) is a technique employed for the deposition of thin films of different materials on any substrate. Films deposited by CVD can exhibit different crystallinities ranging from amorphous to single-crystal thin films depending on the growth temperature, substrate material and its crystallinity, precursors and their concentrations in the carrier gas and also on the carrier gas as well as its pressure.

For the deposition of thin films, the choice of suitable precursors is important. Such precursors could be NH_3 as source of nitrogen [45, 46], O_2 or CO_2 as source of oxygen [47, 48], metal chlorides or metalorganics as sources of metals like Ti ($TiCl_4$), B (trimethyl boron (TMB), BCl_3), Ga (triethyl gallium) and other [49, 50, 51]. The requirements for the precursor are volatility, for an easy delivery of the precursor to the reaction cell, and reactivity (thermally decomposes to chemical species ready for the film deposition by chemical reaction with other precursors or just deposition in case of single element thin films) at the growth temperature. The purity of the precursors is another factor that plays a role in the CVD of thin films, especially for electronic applications.

Figure 2 shows a simplified scheme of the CVD reactor used in the current study for the deposition of sp^2 -BN and illustrates basic working principle of CVD reactor.

The reaction cell consisting of a graphite susceptor or just a sample holder can be heated inductively by the radio frequency (RF) coil or by a resistive heater. Precursors (NH_3 and Triethyl boron (TEB)) are diluted by the carrier gas (H_2 in this work) and are

led to the reaction cell where they are reacting forming thin film on the substrate ($\text{sp}^2\text{-BN}$ on $\alpha\text{-Al}_2\text{O}_3$ or SiC substrates). NH_3 has a considerable vapour pressure at room temperature and is thus delivered into the gas system from a gas bottle. TEB (liquid) on the other hand has a low vapour pressure at reasonable temperatures ($-20 - 40^\circ\text{C}$) and is thus bubbled by the carrier gas and led to the reaction cell. Bubbling of the carrier gas through a liquid precursor allows for a more rapid evaporation that ensures vapour pressure to be constant and close to a saturated vapour pressure of the liquid in the bubbler (at constant pressure and temperature). This setup ensures delivery of a reasonable amount of precursor into the reaction cell. In order to adjust concentration of the precursors in the carrier gas and adjust their flow speed, mass flow meters are employed. Electronic pressure controller together with the temperature controlled bubbler bath ensures a constant pressure and temperature of the bubbler for constant flow of precursors vapour to the reactor.

Adjusting the flows of precursors and carrier gas enables control of the precursor ratio and their concentrations in the gas mixture that allow for the manipulation of supersaturation. Supersaturation level of the precursors allows controlling both morphology and crystallinity. If the supersaturation is low there will be no growth; then by increasing it the growth will pass stages of epitaxial growth, growth of rough films, formation of nanostructures on the substrate surface, growth of polycrystalline films and finally, at high supersaturation levels, gas-phase nucleation will be observed. According to that, the level of supersaturation should be adjusted and controlled at a certain level depending on the desired morphology of the film.

The temperature during the growth of thin films in CVD is another important parameter for the growth. The basic consideration for the choice of a growth temperature is that it should be high enough to dissociate (pyrolyse) the precursors and ensure reasonable mobility of the adatoms on the substrate surface but low enough to avoid decomposition of the growing compound and allows sufficient time for adatoms on the substrate to “meet” other adatoms and form stable nuclei [52]. Thus, it can be summarised in a three growth regimes that can be experimentally determined by observing the growth rate dependence on the temperature (Figure 3) [53]. At low

Figure 3. CVD growth regimes

temperatures, the thermal energy is insufficient to effectively dissociate the precursors and the mobility of the adatoms on the substrate surface is low that leads to low growth rate that increases with increasing temperature; this regime is called kinetics limited regime. When the temperature is high enough to dissociate precursors and adatom surface mobility is sufficient, the growth rate is nearly independent of the temperature and limited by the amount of the precursors supplied to the growth cell; this is the mass transport limited regime. The third regime is called thermodynamics limited regime and is observed when the temperature is too high that desorption of adatoms dominates and they do not have enough time on the surface to form stable nuclei. In this regime a decrease of the growth rate is observed with increasing temperature.

At the optimum growth parameters (supersaturation and temperature) formation of the film can be illustrated as follows (Figure 4)[53]:

- Precursors transport to the reaction cell;
- Precursors dissociation and gas phase reactions;
- Transport of modified precursors to the substrate surface;
- Precursors adsorption on the substrate surface;
- Precursors diffusion on the substrate surface and surface reactions;

- Island nucleation/Step flow growth or desorption;
- Desorption of volatile by-products in case of film formation.

3.1. Epitaxy

Figure 4. Illustration of the precursors transport, reactions and film growth in CVD.

Epitaxial growth is a special case of the thin film deposition on to a substrate where the deposited film has a crystalline structure and a certain crystallographic orientation with respect to the substrate crystal called epitaxial relation (relation of epitaxy). The epitaxial growth of a film on a monocrystalline substrate implies formation of a monocrystalline thin film or film with grains where all grains have the same orientation on top of the substrate. Figure 5 illustrates an epitaxial relation of the h-BN to w-AlN that can be written as $(0001) \text{ h-BN} \parallel (0001) \text{ w-AlN}$ and $[10\bar{1}0] \text{ h-BN} \parallel [10\bar{1}0] \text{ w-AlN}$ ((0001) planes of both crystals are parallel to each other and $[10\bar{1}0]$ directions in both crystals are also parallel to each other).

Figure 5. Illustration of epitaxial growth of h-BN on w-AlN with epitaxial relation of (0001) h-BN $\parallel$ (0001) w-AlN and [10 $\bar{1}$ 0] h-BN $\parallel$ [10 $\bar{1}$ 0] w-AlN

The growth of epitaxial thin films helps to utilise various properties of a material. Such properties are, for example, when the crystal structure of the deposited material does not belong to the centrosymmetric crystal class and piezoelectric properties are of interest or when electric properties are important and negatively affected by grain boundaries. Epitaxy is a way to produce thin films with strictly defined crystal orientation (relation of epitaxy), to reduce number of grain boundaries and improve mobility of the charge carriers and resistivity of resulting film. Thus, epitaxial growth is highly desirable for the deposition of thin films and better utilisation of the unique properties of the material under consideration due to superior electronic properties compared to polycrystalline thin films of the same material.

3.2. Precursors

Compounds containing chemical elements that are necessary for the growth of thin films with desired composition are called precursors. Precursors employed for the growth of thin films are an aspect of the CVD technology that must be investigated before the actual growth experiments are conducted. The main requirements for the precursors are [53]:

- Volatility;
- Stability at storage temperatures;
- Chemical purity;
- Low incorporation (high volatility) of by-products;
- Decomposition at adequate growth temperature (higher than storage temperature);
- Compatibility with other precursors used.

However, in most cases, all these criteria cannot be fulfilled and compromise should be found. Volatility of the precursor (vapour pressure) is a parameter that determines the growth rate and should be high enough to ensure reasonable growth rate. In case if the vapour pressure of the precursor is low at room temperature, it can be increased by increasing its temperature or vice versa. This is done for metalorganic precursors that are stored in bubblers for more precise control of the vapour pressure keeping them at constant temperature. The limitation for increasing vapour pressure is decomposition temperature of the precursor. In addition, if the temperature of the precursor is set to be higher than the ambient temperature, heating of the gas lines should be considered to avoid condensation.

Chemical purity and low incorporation of by-products are critical for the properties of deposited films. If, for example, a semiconductor material for optoelectronic applications is deposited, impurities incorporated into the film could form defect levels in the band gap and serve as recombination centres for charge carriers and influence the optical properties. But if the problem of the incorporation of impurities is present and there is no way to make more pure precursor or use another,

additional volatile additives can be introduced that would remove unwanted impurities leaving no residues in the film.

Decomposition of the precursor should happen at adequate temperatures so it neither decompose at the temperatures that it is held at nor at too high temperature that desorption of the adatoms from the substrate dominates reducing growth rate or even prohibiting it. There is a way to overcome problem with too high decomposition temperature leaving growth temperature reasonably low by introducing assistance like plasma, hot filament, laser etc. The problem with decomposition temperature being close to storage temperature could be solved by in-situ preparation of the precursor.

Precursors employed for the deposition of compound material should be compatible to each other. This means that precursors do not react rapidly by forming adduct that are stable at growth temperature. This will reduce or even prohibit growth of the film and can negatively affect the reactor if a solid adduct is formed. Nevertheless, precursors can be delivered to the reaction cell separately, allowing them to mix only in the reaction cell or in close proximity to it.

3.3. Reactor

The reactor employed for the deposition of sp^2 -BN in this work is a hot-wall chemical vapour deposition (CVD) system. Figure 2 represents, in a simplified way,

Figure 6. Reaction cell of the CVD reactor used for sp^2 -BN deposition.

the gas panel of the reactor and Figure 6 illustrates the growth cell.

The hot-wall design of the reaction cell means that floor, walls, and ceiling of the reaction cell are heated that allow for more homogeneous temperature distribution and better dissociation of precursors [54]. The reaction cell is heated by inducing current in the high density graphite susceptor by a coil connected to a radio frequency generator (Figure 6). To protect the quartz tube from the high temperature susceptor a low density graphite isolation is installed between them (Figure 6). To avoid formation of an adduct due to a reaction between the precursors, they can be delivered separately and being allowed to mix only 10 cm before entering reaction cell (susceptor (hot zone)). This is fulfilled by separated delivery of one of precursors using separate quartz gas liner (Figure 2, Figure 6).

The used susceptor has a protective coating in order to reduce out diffusion of the unwanted impurity elements from the low purity graphite as well as for it to withstand high temperature in chemically aggressive environment that present in the reaction cell during growth.

To remove water adsorption in the reactor, which is the main source of oxygen that is not desirable to be present in the reactor during growth, the system was evacuated to a vacuum of about 10^{-7} mbar prior the growth and during stand-by of the system[11].

4. Characterisation

4.1. X-rays

X-rays play an important role in modern materials science for materials characterisation. As an X-ray sources, x-ray tubes and synchrotron radiation are used. The work principle of the x-ray tubes will be discussed below. The characterisation of materials by X-rays includes diffraction, reflection, composition measurements and others. In this work X-ray radiation was employed for diffraction (X-ray diffraction (XRD)) measurements to investigate crystalline structure and for composition measurements using X-ray photoelectron spectroscopy (XPS). These techniques are described in details in the corresponding sections below.

X-rays are electromagnetic radiation with a wavelength on the order of 10^{-10} m i.e. 1 Ångström (Å). Radiation with such wavelength can be acquired by bombarding a target with high energy electrons to obtain deceleration radiation together with a characteristic X-ray radiation that is specific for each chemical element. The deceleration radiation is produced due to the deceleration of the electrons in the material. The same physical principle is used in synchrotrons to produce X-rays, where charged, accelerated particles emit electromagnetic radiation. The characteristic radiation is obtained when the core shell electron of the element is excited by the incoming electron (ionisation of the element) and followed by the de-excitation of the electron from the upper shells (allowed by the selection rules) and emission of the energy in a form of photon with energy equal to transition energy. The characteristic radiation will only be present if the incoming electron energy is higher than the ionisation energy of the element. Simple schematic of the process of emission of X-rays is depicted in Figure 7.

Figure 7. Illustration of X-ray generation

In this work, X-ray tubes with a copper (Cu) anode are used. Figure 8a shows atomic levels of the Cu atom and allowed electron transitions when an electron from the 1s orbital is excited and Figure 8b shows the X-ray emission spectrum from Cu

Figure 8. Cu (a) atomic levels diagram indicating allowed transitions when electron from K shell (1s orbital) is excited and (b) X-ray emission spectrum for 8, 25 and 50 kV electrons [55]

irradiated by 8, 25 and 50 kV electrons [55]. When the electrons are accelerated by a field of 8 kV before hitting the Cu target, only the deceleration radiation is visible since the energy of electrons is insufficient to excite electrons from the 1s level that lies 8.98 keV below the vacuum level and that is the minimum energy necessary to excite electrons from the 1s level of Cu. When the energy of the incoming electrons is higher than the ionisation energy, lines characteristic for each element will appear on the background of the deceleration radiation spectrum. The minimum wavelength of the deceleration radiation is given by the energy of the incoming electrons and can be calculated:

$$\lambda_{\min} = \frac{hc}{E_{\text{kin}}}, \quad (1)$$

where h is the Planck's constant, c the speed of the light in vacuum and E_{kin} the highest kinetic energy of the incoming electrons.

The discussion of X-ray generation above was devoted to the emission from Cu, however in general this discussion is valid for any element containing at least 3 orbitals – elements starting with boron in periodic table.

4.1.1. XRD

“Reciprocal space never lies”

Hans Högborg

The X-ray diffraction relies on the fact that X-rays can be reflected (coherently scattered) by the atoms in the crystal, and since the wavelength of the X-rays is comparable to the distance between the atoms (and atomic planes), diffraction of the

Figure 9. Illustration of the X-ray diffraction from two atomic planes according to Bragg's law.

X-rays can be observed. The simple way to describe diffraction of the X-rays on the crystal is to employ Bragg's law:

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

where n is the diffraction order, λ the X-ray wavelength, d the distance between atomic planes and θ the diffraction angle. Simple illustration of the X-ray diffraction on the crystal according to the Bragg's law is shown in Figure 9.

A more correct way to treat and predict diffraction from a crystal is to use the structure factor. This accounts not only for the diffraction caused by scattering from 2 planes but also considers the distribution of the atoms in the plane to take care for the phase difference between diffracted beams from many atoms within the family of planes (same distance) in the crystal. If the structure factor is equal to zero, there will

be no diffraction from such planes. The structure factor can be obtained by calculations using [56]:

$$F = \sum_{n=1}^N f_n e^{2\pi i(hu + kv + lw)}, \quad (3)$$

where f_n is atomic scattering factor, N number of atoms in the unit cell, u, v, w positions of the atoms in the unit cell and h, k, l Miller indexes of the planes in the crystal.

Another way to describe X-ray diffraction which is more complicated, however more clear for interpretation, is the observation of the X-ray incoming ($\bar{k}_0$) and diffracted ($\bar{k}$) wave vectors together with the reciprocal crystal. In this case, as it can also be seen from the structure factor, scattering vector ($\bar{q}$) that is the difference between incoming and diffracted wave vectors should be equal to the crystal reciprocal lattice vector ($\bar{r}$) in order to observe the diffraction [57]. This is illustrated (figure 10) and expressed as follows:

$$\begin{aligned} |\bar{k}_0| &= |\bar{k}| = \frac{2\pi}{\lambda} \\ |\bar{r}| &= \frac{2\pi}{d_{hkl}} \\ \bar{q} &= |\bar{k}| - |\bar{k}_0|, \quad (4) \\ |\bar{q}| &= \frac{4\pi}{\lambda} \sin(\theta) \\ |\bar{q}| = |\bar{r}| &\Rightarrow \lambda = 2d_{hkl} \sin(\theta) \end{aligned}$$

Figure 10. Illustration of the incoming, diffracted X-rays with a wavevector $\vec{k}$, X-ray scattering vector $\vec{q}$ and diffraction angle θ on the left figure and same vectors with a 2D reciprocal lattice.

Due to all the considerations described above, X-ray diffraction finds its use in crystallography as a powerful tool for characterisation of solid materials. In this work XRD was employed to characterise grown samples by, first – observing formation of the crystalline material (XRD in Bragg-Brantano geometry), then determination of the crystalline structure and epitaxial relation of the grown crystal to the substrate employed for the growth (Pole figure measurements, XRD measurements of asymmetric planes and glancing incidence XRD). Figure 11 illustrates the diffractometer setup with the angles that can be controlled. The Bragg-Brentano geometry was developed for XRD measurements on powder samples where small

Figure 11. Illustration of diffractometer angles. $\vec{k}_0$, $\vec{k}$, $\vec{q}$ and $\vec{n}$ are incoming X-ray wave vector, diffracted X-ray wave vector, scattering vector and surface normal, respectively. Angle 2θ is the angle between the incoming beam and the scattered beam. ω is the angle between the incoming beam and its projection on to the sample surface plane. ϕ is the rotation around the surface normal. χ is the angle between the surface normal and the X-ray scattering vector. The refraction plane is defined by the incoming and diffracted beams.

crystals have a random orientation leading to the reciprocal space of the crystal to consist of spheres instead of points like in the case of single crystal. Nonetheless, this technique is sufficient for the observation of crystallinity and determination of the orientation for the deposited films. In such geometry there is no control for ϕ angle (random), ω is equal to θ and χ is zero. Thus, measurements in such geometry are also called θ - 2θ scans. In this case scattering vector is perpendicular to the sample surface (collinear to surface normal). Thus, only planes that are parallel to the sample surface will contribute to the diffraction pattern. Figure 12 shows a typical diffraction pattern recorded in the Bragg-Brentano geometry for a BN layer deposited on α - Al_2O_3 substrate with an AlN buffer layer. Peaks that originate from (000 l) of these materials are visible indicating c-axis orientation of all three crystals.

Pole figure measurements are conducted by fixing 2θ angle for a plane of the crystal under investigation and measuring ϕ scans at various χ angles in the range from 0° to 90° . This allows to observe whether peaks from the plane present at corresponding inclination angles χ or in-plane disorder are present in the film by

Figure 12. XRD pattern of a crystalline BN deposited on α - Al_2O_3 with AlN buffer layer. Peaks originating from (000 l) planes are visible suggesting C-axis orientation of the substrate, buffer layer and BN film. The weak peaks around 45° are coming for the sample holder and the sharp step at 40° is due to the Ni filter employed for suppression of Cu K_β emission.

observing a ring at a χ angle corresponding to the planes under investigation. Such measurements allow the determination of the crystalline structure of the film, its in-plane ordering and, when similar measurements are done for the underlying substrate planes, epitaxial relation between the film and the substrate can be assessed.

When c-axis orientation is observed in the θ - 2θ scan and supported by the ω -scan (2θ -constant, $\chi=0$, ϕ -random) Pole figure measurements could be simplified to the simple ϕ -scan at desired χ and 2θ angles that will give the same information regarding crystal structure and epitaxial relation.

Glancing incidence XRD is an option that allows observing ($hk0$) planes when h and/or k are not equal to 0. Measurements in this geometry are similar to the measurements in Bragg-Brentano geometry with the difference that the χ angle is close but not equal to 90° to avoid total external reflection of the X-rays. This, in a similar manner as Pole figure measurements and investigation of asymmetric planes allows determining in plane ordering and crystal structure of the film. This technique is helpful when thin samples are under investigation where X-ray diffraction from the asymmetric planes is negligibly low due to the low volume of the material being illuminated by the X-rays and due to the low scattering of the X-rays given by low electron density of the material that is the case for BN. Such measurements are performed in this work to investigate crystalline structure of the BN at the early stages of the growth. In addition correlation with data obtained by the transmission electron microscopy (TEM) showed that probing films that are only about 40 Å thick is possible.

XRD measurements in Bragg-Brentano geometry were used as a primary tool for the investigation of the crystalline quality of the deposited films and results are reported in **Papers 1, 2, 3 and 4**. Pole figure measurements are presented in **Papers 1 and 2**. Measurements of the asymmetric planes by XRD are performed in the studies presented in **Papers 4, 5, and 6**. Results of glancing incidence XRD are presented in **Papers 5 and 6**.

4.1.2. XPS

X-ray photoelectron spectroscopy (XPS) is a technique suitable for compositional measurements and the determination of the chemical bonding in the material under investigation. The work principle of the technique is the illumination of the sample by X-rays, excitation of the core electrons to the vacuum and observation of the kinetic energy of excited electrons. Thus, by knowing the excitation energy ($h\nu$), the instrument's work (Φ) function and measuring the electrons' kinetic energy (E_{kin}) it is possible to determine electrons binding energy (E_b) using the following equation [58]:

$$E_b = h\nu - E_{kin} - \Phi \quad (5).$$

Figure 13 illustrates the XPS work principle where one electron from a 1s level is excited to the vacuum. The advantage of the XPS over other techniques capable to determine chemical composition, like Rutherford backscattering (RBS), elastic recoil detection analysis (ERDA), secondary ion mass spectrometry (SIMS) and Energy or wavelength dispersive X-ray spectroscopy (WDX or EDX), is the possibility to determine chemical bonds between the elements present in the sample. This is due to

Figure 13. Work principle of XPS. Electron from the 1s level is excited and its kinetic energy E_{kin} is measured. By knowing the instrument's work function and the excitation energy it is possible to determine the electron binding energy.

Figure 14. X-ray photoelectron spectra of boron 1s electrons. Contributions for elemental B (188.6 eV) and B bind to N (190.4 eV) are observed.

the fact that the energy of the atomic orbitals is affected when an element is bonded to other element and in this case equation 5 can be modified as:

$$E_b = h\nu - (E_{kin} + \Delta E) - \Phi \quad (6),$$

where ΔE is the chemical shift.

In addition, XPS has high sensitivity (0.1 – 1 at%) and is surface sensitive technique since the kinetic energy of the electrons is usually low to escape from the volume of the sample. Thus, this technique was employed to observe formation of the sp^2 -BN after short growth experiments of 1 – 10 minutes. Figure 14 shows the 1s peak of boron where contributions from two peaks are observed; one peak is positioned at 190.4 eV and another at 188.6 eV. The later, according to the instruments database, is associated to elemental boron and contribution at 190.4 eV is from B bonded to nitrogen [59].

XPS was utilized to determine formation of sp^2 -BN in study presented in **Paper 6**.

4.2. *Electron Microscopy*

The advantage to use electron microscopy (EM) instead of optical microscopy is the fact that electrons can be accelerated to a high energy that will lead to a wavelength which is shorter than the wavelength of the visible light. Such reduction of the wavelength enables the observation of fine features of the sample that are not visible (resolved) in optical microscopy. The wavelength (λ) of the electrons can be calculated by using de Broglie's equation:

$$\lambda = \frac{h}{\sqrt{2m_e E_{kin}}} \quad (7),$$

where h is Planck's constant, m_e mass of the electron and E_{kin} kinetic energy of the electron. For example, de Broglie's wavelength of the electrons accelerated to energy of 5 keV is 0.17 Å.

Similarly to optical microscopy, in EM an illumination source is necessary with high brightness to reduce the exposure time to obtain an image. There are various approaches to produce electrons; one is to use low work function metal or alloy, heat it and use it as a cathode, and another approach is use of field emission guns. Both groups have their advantages and disadvantages for certain applications. Electrons in the gun are accelerated to certain energy, leave the gun and enter a lens system that conditions the beam in a way required for the desired measurement.

Thus, EM is more desirable to use when fine features of the sample are of interest. Below two geometries employed in this work for studying microstructure of the sample are described in more details and are scanning electron microscopy (SEM) and transmission electron microscopy (TEM).

4.2.1. SEM

The work principle of the scanning electron microscope (SEM) is similar to that of an optical microscope where the difference is that a focused electron beam is scanned across the surface and backscattered and thus the secondary electrons are detected [60]. The signal from the detector is then associated with the beam position and an image can be formed. The image in SEM is an intermixture of the surface topography and elemental composition – sharp features will backscatter more electrons than flat regions and will appear more bright in the image; areas where heavy elements are present (higher atomic number) will scatter electrons more effectively and will also appear more bright in the image. This consideration is valid for the backscattered electrons (BSE) and the imaging. If the imaging is conducted using secondary electron (SE) detector, contrast in the image depends only on to the topography of the sample. The energy of secondary electrons that are forming an image is usually chosen to be below 50 eV, while backscattered electrons have energy from 50 eV up to the energy of the incoming electrons. In SE mode the information is mainly acquired from the surface due to the low escape depth of the low energy electrons detected in this mode, while in BSE mode high energy electrons can escape from higher depth, resulting in the contribution to the image from the “bulk” of the sample. Illustration of the SEM setup is presented in Figure 15. Electrons emitted from the electron gun are accelerated by an anode by electric field that is usually in the range of 0 – 60 kV. After this acceleration, they are focused on to the sample surface by a magnetic lens and are scanned by the scan coil over the surface of the sample. Backscattered or secondary electrons are then detected by a corresponding

Figure 15. Scanning electron microscope setup.

detector. The signal from this detector and the control of the scan coil are then used to restore the image.

The advantage of using SEM over optical microscope is that electrons accelerated to energy of 5 keV, as discussed above, have a wavelength of $0.17 \text{ \AA}$ that allows resolving surface features which have a size in the nanometer range. It is even suggested that SEM can have a resolution better than 1 nm [61]. In addition to that, the depth of field (height range in which the sample is in focus and clear image is visible) in SEM is higher than in optical microscope and at the same magnification which can be up to 3 orders of magnitude higher.

The sample preparation for SEM, typically, does not require special procedure; however samples must meet the requirement to be vacuum compatible. This means that samples should not evaporate in the vacuum chamber of the SEM instrument since the operation range for SEM is at the pressure of 10^{-6} mbar and lower. Special care should be taken when measuring electrically insulating samples, since it will lead to the charging of the sample by the electrons and no image of the surface will be acquired. This can be overcome by lowering down the electron accelerating voltage or by covering the sample with thin metallic film. Covering a sample with a thin metal film, however, can complicate the interpretation of the surface structures. Figure 16

Figure 16. SEM image of a BN sample covered by thin metal film with intention to increase the conductivity of the sample and reduce its charging effect [62]

shows a SEM image obtained from a BN sample that was coated with thin metallic film to increase conductivity and avoid charging [62]. Nanosised particles visible over the whole sample are found to be related to the droplets of the deposited metal that can be wrongly interpreted as the features related to the sample under investigation.

In this current work SEM was used at a low acceleration voltage of 5 kV and the samples were not covered by any metal to avoid surface contamination and simplify interpretation of the structures observed on the surface.

Results obtained employing SEM are presented in **Papers 1, 2 and 6.**

4.2.2. TEM

Transmission electron microscopy (TEM) is very similar to optical microscopy conducted in the transmission mode when transparent samples are used. The difference from SEM and optical microscope is the energy of electrons that is on the order of 100 keV that result in the wavelength in the picometer range [63]. In this case for electrons de Broglie's wavelengths calculation in the equation (7) relativistic corrections must be applied. Thus, using such short wavelength it is possible to obtain atomic resolution in TEM, however good quality electromagnetic lenses are also necessary to properly condition the electron beam. In most of TEM instruments the resolution limiting factors are the electromagnetic lenses due to strong aberrations.

Figure 17. TEM setup [64].

Figure 18. TEM micrograph of h-BN deposited on α -Al₂O₃ substrate with AlN buffer layer. By observing atomic positions, it is possible to determine the crystal structure of sp²-BN.

The sample preparation for TEM is a critical part of the process since the specimen must be electron transparent to acquire a good image of the microstructure. Thus, in TEM the sample is illuminated by a parallel electron beam (microprobe mode) that is conditioned by condenser lenses, transmits through the sample, passes objective lens, intermediate lens and is projected on to the fluorescent screen by the projector lens. This sketch is a simple description of the TEM setup and is illustrated in Figure 17 [64].

In this thesis, TEM was done to observe microstructure of selected sp²-BN samples and investigate the stacking sequence of the sp²-BN basal planes for crystal structure determination. Figure 18 shows a TEM micrograph of h-BN deposited on α -Al₂O₃ (not visible) with AlN buffer layer. Stacking sequence of the basal planes can be observed leading to a conclusion that h-BN is formed (presented in **papers 5 and 6**). TEM micrographs are presented in **Papers 1, 4, 5 and 6**.

4.3. Ion beam analysis

The interaction of high energy ions with a material includes many aspects such as surface modification, ion implantation, sputtering and/or elemental analysis. In the current work ion beam analysis techniques for determination of the sample composition were employed. These techniques are elastic recoil detection analysis (ERDA) and secondary ions mass spectrometry (SIMS).

Depending on the energy of the incoming ions (projectiles), different processes could be observed and this is the main difference between SIMS and ERDA that will be discussed below.

Ions for use in the ion beam analysis are generated by ionisation of the neutral atoms and accelerating them to a desired energy. The two energy regions that are usually separated, where different ion interaction with materials is observed, are energy region of keV and MeV. Ions with keV energy have a low penetration depth and yield sputtering of surface atoms of the material under investigation. For MeV ions interaction with the sample occurs in a different way – due to the high energy, ions have higher penetration depth and can be backscattered and can also create a recoil. There are more processes acquiring when ions interact with the material, but these, discussed above, are commonly used in ion beam compositional analysis of the material.

4.3.1. ERDA

Elastic recoil detection analysis (ERDA) is an ion beam technique that utilises MeV ions which interacting with the material produce recoils of elements present in this material. These recoils are afterwards analysed to obtain information of elemental composition, concentration of elements in a sample and elemental depth profile [65]. Elemental composition and concentration are extracted by analysing the mass of the recoils and amount of recoils with the same mass whereas the depth profile is acquired by analysing energy of the recoils with the same mass and amount of such recoils

reaching a detector. This technique allows analysis of elements starting with H and up to the last stable element U of the periodic table. For better mass separation, sensitivity and depth resolution, the projectile mass should be much higher than mass of the element being analysed since kinematic factor and yield are proportional to the projectile mass.

In this work ERDA was conducted using 32 MeV iodine ions as projectiles and time-of-flight detector. Results are presented in **Paper 1**.

ERDA is a thus powerful technique for compositional analysis of samples however its sensitivity is limited to a level of 0.1 at% and if higher sensitivity is needed, as for example for analysis of the dopants in semiconductor materials SIMS is the technique of choice.

4.3.2. *SIMS*

In SIMS the sample material is sputtered and the sputtered ions are then analysed. The mass of ions and their flux are the parameters under interest for obtaining composition and concentration of elements in the sample [66]. However, in comparison to ERDA where the concentration can be calculated from the flux of ions, pre-set values like projectile mass and energy and measurement angle and other parameters that are known, in SIMS calibration using standards with known concentration of elements inside should be used to obtain concentration of elements in the sample. Depth profile in SIMS is obtained using sputtering rate that is also dependent on the material and must be determined separately. Preferential sputtering of some elements in the compound will complicate the determination of the depth concentration of the elements. All these facts complicate data analysis to obtain concentration of the elements and their depth profiles compared to the more simple ERDA, however sensitivity of this SIMS technique is better, typically in the range 10^{12} to 10^{16} atoms/cm³ ($\sim 10^{20}$ for ERDA), depending of the elements analysed and ions used for sputtering.

In this work SIMS was conducted by Evans Analytical Group (EAG) by employing Cs^+ ions and collecting negative ions. These SIMS measurements were done to determine the concentration of Si in the films and the sensitivity for the Si is 10^{16} atoms/cm³.

Results obtained employing this technique are presented in **Paper 3**.

5. History of BN

Boron nitride has a long research history starting with the first reported synthesis of BN and description of its chemical properties by W. H. Balmain in 1842 [67]. Since this time BN has attracted researchers interest, however the efforts to develop and characterise this interesting material were not sufficiently high to achieve high quality thin films like it happened with, for example, GaAs, GaN or SiC.

Many attempts were made to characterise synthetic BN but most of them are dated with the beginning of the 20th century. There were numbers of studies on the determination of the crystalline structure of sp^2 -BN, but the first to determine and establish the correct crystalline structure of sp^2 -BN that is used nowadays and is called hexagonal BN (h-BN, Fig. 1b) was R. S. Pease in 1950 [68]. The other crystalline phase of sp^2 -BN, r-BN, was first discovered by A. Herold *et al.* in 1958 [69]. Interesting is that the next study on r-BN phase was conducted 23 year later by T. Ishii *et al.* [70]. In 1966 Geick *et al.* measured infrared and Raman spectroscopy and found that the observed lines in those spectra were in agreement with the crystal lattice proposed by Pease [71, 68]. In 1963, J. Thomas *et al.* reported on the formation of t-BN and transformation of it into the ordered form of sp^2 -BN – h-BN by heat treatment at 1800 °C [72]. The term “turbostratic” was adopted from the graphite material system where such structure is reminiscent of a lack of interplanar ordering of the basal planes. Such graphite structure was studied in detail by B. E. Warren employing XRD [12]. Thus, characteristics of such structures are well known and such description can be applied to other layered materials as BN.

Early works on the characterisation of BN mainly include optical characterisation of the material with photoluminescence (1920), cathodoluminescence (1925), electroluminescence (1956) and reflectance [73, 74, 75]. Such luminescence investigations showed many bands in the blue and near UV region, but the near bang gap luminescence was not observed [75]. Nevertheless, the width of the band gap was estimated to be not lower than 5.5 eV by the Larach *et al.* analysing reflectance data [75]. Later Baronian has reported on the determination of the band gap and refractive index of BN deposited by CVD and has compared the results with what has been reported in the literature at that time (1972) [76]. It was reported that BN films

deposited from the ammonia and boron trichloride (BCl_3) in a temperature range from 600 to 900 °C exhibited a band gap of 5.8 – 5.9 eV and a refractive index of 1.9 – 2 [76]. Later in 2004, K. Watanabe *et al.* by using high pressure/high temperature approach produced high purity h-BN single crystals with mm size and showed that h-BN has a direct band gap of 5.971 eV while previous experimental and theoretical studies had contradicting information on the nature and width of the band gap 3.6-7.1 eV [77].

First attempts to grow sp^2 -BN employing CVD were conducted in the middle of the 20th century while it is hard to identify the pioneering work due to the unavailability of the referenced materials. One of the first notes on formation of the BN from gaseous sources is found in the US Patent filed in 1955 [78]. The patent did not covered CVD growth of BN but formation of the BN from the normally solid and liquid precursors at room temperature that were heated up to react forming solid BN and gaseous by-products. The work that the firsts reports on CVD of sp^2 -BN from diborane (B_2H_6) and ammonia (NH_3) is done by M. J. Rand in 1968 [79] and refers to a book from 1966 [80] and a company progress report from 1965 [81] for the details on CVD of BN from boron trichloroborazine, and BCl_3 and NH_3 . Thus, we can assume that the period 1950-60s could be the starting point for sp^2 -BN CVD. First growth experiments of sp^2 -BN by using organic group 13 precursor – triethyl boron (TEB, $\text{B}(\text{C}_2\text{H}_5)_3$) was done by K. Nakamura in 1986 [82]. Since then growth of sp^2 -BN in many cases was done by employing ammonia and TEB likely due to the easier handling compared to B_2H_6 or BCl_3 .

6. Growth of sp^2 -BN

During last two decades many researchers directed their efforts to the investigation of the growth, characterisation and further improvement of the sp^2 -BN deposition process in order to obtain thin films that would be suitable for various applications. However, growth of sp^2 -BN has been found to be challenging and many difficulties are encountered that hamper the development of this material. Currently, the problem with the growth of sp^2 -BN is the development of a stable process leading to the growth of epitaxial crystalline sp^2 -BN while most of the studies report on the formation of t-BN or even a-BN [83, 84, 85, 86]. Deposition of such structures is easily observed by techniques used for the structural investigations such as XRD and TEM [83, 87]. In XRD formation of t-BN can be confirmed by the observation of the peak that corresponds to diffraction from two nearest basal planes. For the case of crystalline sp^2 -BN this XRD peak is observed at a 2θ angle in the range 26.71° - 26.75° and for t-BN this peak is found at a lower values that characterise degree of disorder [88] (see Figure 12). Thus, t-BN differs from crystalline sp^2 -BN by the spacing between basal planes and that also can be observed in TEM. Usually when a material shows characteristic XRD associated to t-BN at around 26.3° or even lower, in TEM it is not possible to observe basal planes and determine spacing between them (Figure 19). As reasons for growth of such structure insufficient temperature and high growth rate are listed in the literature. At the early days of the sp^2 -BN growth K. Nakamura observed a change of the c-axis lattice constant from XRD with respect to a temperature and by the extrapolation of the experimental data, suggested that for the growth of sp^2 -BN that would have c-axis lattice constant similar to that of bulk h-BN, a growth temperature of 1500°C is necessary [82].

Figure 8. TEM image showing 6H-SiC substrate, ordered (crystalline) sp^2 -BN in green rectangle and t-BN in red rectangle.

In my study, and by analysing information available in literature it was found that high growth rate leads also to formation of t-BN while at a slower growth rate, and when the precursors concentration is lowered keeping their ratio and other parameters the same, r-BN can be formed [89].

Such growth behaviour suggests low adatom mobility on the substrate surface that requires either an increasing temperature to increase mobility or a reduction of growth rate to increase the time for adatoms to find and occupy a correct site.

Exfoliation of the deposited film is another problem often observed for sp^2 -BN films [90]. This phenomenon is likely due to the difference in in-plane linear thermal

expansion coefficients between substrate and film. As it was discussed above (section 2.1.), h-BN exhibits negative in-plane linear thermal expansion coefficient, while all materials commonly used as the substrates for CVD growth do not have such behaviour. Thus, while during cool-down to room temperature after growth the substrate shrinks, the c-axis oriented sp^2 -BN film expands laterally. Such behaviour of the substrate-film system will lead to an accumulation of stresses in the film and the weak π -bonds between the basal planes will allow stress relaxation through the exfoliation.

CVD is not the only way taken for the deposition of sp^2 -BN. There are various reports on deposition of sp^2 -BN thin films employing physical vapour deposition (PVD) techniques that mainly result in t-BN deposition [91]. Like in CVD, the same substrates are employed for deposition of sp^2 -BN by PVD. Metallic substrates are also employed for the deposition of sp^2 -BN by both CVD and PVD where thickness of sp^2 -BN is limited to about 10 basal planes of sp^2 -BN. One of such growth studies is mentioned in a section below where deposition of different crystal structures of sp^2 -BN is discussed [92]. Growth technique yielding formation and control of different crystal structures of sp^2 -BN on differently prepared Ru substrate is the reactive magnetron sputtering [92].

6.1. Growth on metals

To circumvent the problem associated to the high growth temperature and lattice mismatch, transition metal substrates have been employed. Due to the catalytic activity of the surfaces of these metals reduction of the growth temperature is possible. Metals commonly employed for the deposition of sp^2 -BN are Cr, Fe, Ni, Cu, Ru, Rh, Pd, Ir, Pt [93, 94, 95, 96, 97, 98]. As already mentioned due to the low growth temperature thickness of the ordered sp^2 -BN is limited to a few basal planes, usually not more than 10 [99]. Another characteristic feature of the sp^2 -BN deposited on the transition metals is the formation of triangular islands on the surface [100]. Hexagonal shape of the sp^2 -BN islands has been also observed when a special care for the preparation of the smooth Cu substrate surface has been taken [101].

In addition to the surface morphology dependence on the substrate preparation, it was observed that monolayer of graphene on the surface of Ru substrate promotes formation of r-BN while h-BN grows directly on the Ru surface [92].

Growth of sp^2 -BN on the metallic substrates is found to be promising for the integration of sp^2 -BN with graphene and growth of their heterostructures for applications in nanoelectronics based on the graphene [102, 103, 104].

6.2. CVD of sp^2 -BN

For the deposition of BN various boron precursors have been employed including diborane (B_2H_6), boron trichloride (BCl_3) and triethyl boron (TEB ($B(CH_3)_3$)) [105, 106, 107]. While there is a variety of precursors that can be employed as boron source, choice for the nitrogen source is limited and ammonia (NH_3) is the precursor of choice for thermal CVD [108, 109, 110, 111] since N_2 has a low dissociation probability even at high temperatures. Another class of the precursors that acquires considerable interest is single source precursors like borazine ($B_3N_3H_6$) and ammonia-borane (H_3B-NH_3) [112, 113]. The precursors mentioned have various drawbacks for use like diborane is highly toxic and difficult to handle, BCl_3 reacts with NH_3 at room temperature to form solid ammonium chloride (NH_4Cl) that consumes the nitrogen precursor and clogs outlet tubing and pumps. TEB is pyrophoric and contains carbon that requires special care to be removed from the reactor and still will be incorporated into the film. The single source precursor borazine has low stability at room temperature with tendency for decomposition and ammoniabborane is solid that needs to be heated to a high temperature to achieve considerable vapour pressure. According to the facts mentioned above, in the current work, TEB and NH_3 were employed as boron and nitrogen precursors, respectively. Nevertheless, TEB is predicted, by the theoretical calculations, to react with NH_3 already at room temperature to form a stable adduct [114].

The TEB reaction mechanism during the growth is believed to happen in the way that it is pyrolysed in the gas phase to form BH_3 , similarly to what is predicted to happen with diborane. Thus, BH_3 and NH_3 are further decomposed in the reactor to

form sp^2 -BN while hydrogen carrier gas is suggested to remove ethyl from the reaction cell to avoid their incorporation into the film. To minimise the probability for these precursors to form adduct, as it was mentioned before, they are introduced into the reactor separately and are allowed to mix 10 cm before entering reaction cell.

The procedure to grow sp^2 -BN in the reactor described above is:

1. Fill the cell with argon to atmospheric pressure and open;
2. Load the substrates into the cell;
3. Pump down the system to a pressure of $<10^{-5}$ mbar;
4. Fill the system with a carrier gas to a process pressure;
5. Heat the susceptor to a temperature 400 - 600 °C below the growth temperature and hold at this temperature for 5 minutes to minimise temperature gradients in the susceptor;
6. Introduce ammonia (α - Al_2O_3 substrate) or SiH_4 (SiC substrate) in to the cell and continue heating the susceptor to a growth temperature;
7. Hold at the growth temperature to minimise temperature gradients in the susceptor;
8. Introduce boron precursor and SiH_4 if α - Al_2O_3 substrate is used or NH_3 if SiC substrate is used in to the cell to start the growth;
9. Monitor the system during the growth;
10. Stop the growth by removing the reaction gases (precursors) from the cell and turn of heating;
11. Cool down the susceptor in carrier gas atmosphere;
12. Purge the system with the Ar gas;
13. Repeat steps 2 and 3.

The procedure differs for different substrates since they require different pre-treatment where α - Al_2O_3 is nitridised to form an AlN buffer layer by feeding ammonia into the reactor but for SiC substrate pre-treatment SiH_4 is introduced to preserve Si terminated surface and obtain smooth surface[115].

The configuration of a gas system in the reactor allows choosing between Ar, H₂, N₂ and mixture of N₂ with H₂ or Ar as carrier gas for the growth of sp²-BN. Growth experiments with all the carrier gases have been done including use of H₂ mixture with N₂.

The temperature range that can be covered in the reactor with current setup is starting from 300 °C ending with 1800 °C that is limited by the two pyrometers for temperature measurements. The limiting factor for the highest accessible temperature is thermal insulation of the susceptor and the maximum power of the RF generator. The upper limit should, however, be avoided due to a risk of cracking or melting quartz tube. The highest growth temperature employed in this study is 1700 °C.

The pressure in the reaction cell is controlled by the throttle-valve that is controlling the throughput of the gas line between reaction cell and process pump. The pressure range that has been explored in the study is between 30 and 350 mbar, however results of these experiments are not presented and two pressure regimes are employed with 70 mbar and 100 mbar depending on a carrier gas flow.

Control of the growth rate, supersaturation and gas flow speed, is accomplished by mass flow controllers (MFC) that control flows of precursors and carrier gas into the reaction cell and throttle valve on the other side to control throughput of the pipes between the reaction cell and process pump, and this to control the speed of the gas mixture in the cell. Concentration of the precursors in the carrier gas can be varied in a wide range but in this work it was changed between 0.002% and 0.067% of TEB in H₂. Ammonia was adjusted to acquire required N/B ratio that was used in the range between 300 and 1300. While flows of carrier gas and ammonia are simply controlled by a MFC, flow of TEB in to the reactor (F_{prec} [sccm]) is determined by the vapour pressure of the TEB ($p_{eq,T}$ [mmHg]) at a temperature (T [K]), flow of bubbling gas (F_{carr} [sccm]) and pressure in the bubbler (p_{bubl} [mmHg]):

$$F_{prec} = \frac{P_{eq,T}}{P_{bubl} - P_{eq,T}} \times F_{carr},$$

$$\lg(p_{eq,T}) = B - \frac{A}{T}$$

where parameters A and B for TEB are 7.812 and 1814 respectively.

Graphite susceptor with a TaC protective coating was employed in deposition experiments, however initial growth experiments were conducted in a susceptor that had a SiC protective coating. It was observed that the coating was not suitable for the growth conditions applied for sp²-BN, since the coating was rapidly etched by the reaction gases (mainly H₂ and NH₃), and then the graphite was exposed to the reaction gases mixture and the susceptor got damaged that led to an uncontrollable variation of the temperature in the reaction cell. Thus it was necessary to change the susceptor protective coating to TaC.

7. Summary of the work

It was discovered that Si is needed to be present in the reactor gas phase and on the surface of the substrate for successful growth of crystalline sp^2 -BN (**Paper 3 and 4**). Thus, in all the growth experiments Si was added into the gas phase in the form of SiH_4 diluted in H_2 to a low concentration or it originated from SiC protective coating of the susceptor. SIMS investigations of the samples deposited in the presence of Si in the gas phase and without it, both showed presence of Si in the film, but with higher concentration for the sample deposited when SiH_4 was added during growth (**Paper 3**). Nonetheless, there was no conductivity observed for the samples that contain Si (not present in the papers included into the thesis). Necessity for the AlN buffer layer for the successful deposition of crystalline sp^2 -BN on α - Al_2O_3 substrate was investigated, where no growth of crystalline sp^2 -BN was observed when formation of AlN on α - Al_2O_3 was avoided (**Paper 1**). Opposite growth behaviour was observed when deposition was conducted on SiC substrate. It was established that crystalline sp^2 -BN can grow directly on the substrate and that in-situ deposited AlN buffer layer prevented growth of crystalline sp^2 -BN on SiC (**Paper 4**). In addition it was shown that AlN buffer layer should be of poor quality (thin and strained) for crystalline sp^2 -BN to form on AlN since it was not possible to deposit crystalline sp^2 -BN on pre-grown high quality AlN on SiC (**Paper 1 and 2**). The growth parameters influence on the quality of deposited films was investigated. Such growth parameters that were varied are temperature, precursors' concentration, precursors' ratio and type of carrier gas. This investigation was conducted for both α - Al_2O_3 (**Paper 2**) and SiC (**Paper 4**) substrates, where for the latter case different polytypes and surface terminations were tested. Result of these investigations revealed that pure H_2 carrier gas is required where optimal temperature is 1500 °C with nitrogen to boron ratio of around 640 with a low growth rate of 4 nm/min (**Paper 2, Paper 4 and Paper 6**).

Investigations of the crystalline structure of deposited films by use of XRD showed formation of twinned r-BN on both substrates (**Paper 1, 2 and 4**). Epitaxial

relation for the films was also determined. Twinning of the r-BN that was observed on SiC substrates is explained in terms of underlying substrate crystal stacking where a unit cell of, for example, 6H-SiC substrate has two opposite glide directions in a unit cell along $[1\bar{1}00]$ direction and this when the step height is number of halves of the unit cell height this two stacking sequences with opposite glide will lead to corresponding stacking sequence of r-BN deposited on top. Thus two domains with a rotation of 60° with respect to each other are observed (**Paper 6**).

Investigations of the nucleation and early stages of sp^2 -BN growth revealed that sp^2 -BN starts to grow with the hexagonal polytype on α - Al_2O_3 with AlN buffer layer with later transition to rhombohedral polytype growth while growth starts and proceeds to grow with r-BN polytype on SiC substrate (**Paper 5**). We propose that initial growth of certain polytype of sp^2 -BN is dependent on the crystalline structure, in particular on to the stacking sequence of the underlying substrate, while transition from h-BN to r-BN growth is suggested to be triggered by stress relaxation due to lattice mismatch (**Paper 5**). In addition it was observed that h-BN growth mode on AlN substrate is likely 2D since no island formation was observed whereas r-BN growth on SiC starts with the formation of triangular islands and the formation of triangular islands on α - Al_2O_3 with AlN buffer layer is assumed to be associated to transition to r-BN growth (**Paper 6**).

This work has a considerable impact on to the community working with the growth of sp^2 -BN on insulating or semiconducting substrate and describes the way for a successful growth of crystalline sp^2 -BN. Influence of Si on to the formation of crystalline sp^2 -BN in a CVD process was for the first time reported during this work. In addition, an AlN buffer layer was proved to be necessary for successful growth of sp^2 -BN on α - Al_2O_3 . Formation of crystalline structure and growth evolution on both α - Al_2O_3 and SiC substrates were for the first time described during this thesis work.

8. Future challenges

Even though a step towards development of epitaxial sp^2 -BN thin films for electronic and optoelectronic applications has been taken in this thesis, there is still a huge field to be investigated and understood in order to achieve high quality devices based on sp^2 -BN. The first problem to be solved for development of this material is usage of more clean boron precursor (less carbon) that possibly are trimethyl boron ($(CH_3)_3B$), ammonia-borane (H_3B-NH_3) and boron trichloride (BCl_3) and find more reactive nitrogen precursor (nitrogen plasma) that would allow reducing growth temperature leading to a possibility of sp^2 -BN integration with other semiconductor materials.

In order to employ sp^2 -BN as a semiconductor material, doping of the material should be investigated and well controlled. There are few studies focused on the doping of sp^2 -BN; however more detailed investigations are missing. This is necessary to realize p-n junction based on the sp^2 -BN that is simple electronic component.

As it is well established in the group 13-nitrides community, quantum wells should be made to increase external quantum efficiency of a LED. Thus, it is necessary to control band gap width of sp^2 -BN. Such studies have been proposed and reported in literature showing possibility to lower the band gap by alloying sp^2 -BN with graphite (sp^2 -C). This should be investigated along with the doping possibilities.

Another emerging field for sp^2 -BN is integration with graphene. Here, a lot of experiments have been done to deposit few layers or even mono-layer sp^2 -BN on metallic substrates as discussed above with a following transfer on to an insulating substrate followed by transfer of graphene on to the sp^2 -BN. A more elegant way would be in-situ growth of graphene on sp^2 -BN on insulating or semiconducting substrate. However, further investigation of both the CVD of sp^2 -BN to achieve smooth surface and CVD of graphene on sp^2 -BN is needed.

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10. Corrections to the papers

- Mikhail Chubarov, Henrik Pedersen, Hans Högberg, Zsolt Czigany, Anne Henry. Chemical vapour deposition of epitaxial rhombohedral BN thin films on SiC substrates. *CrystEngComm.*, **16**, 5430 (2014).

Page 3:

Appear: "... Cu cathode X-ray tube..."; Should be: "...Cu anode X-ray tube..."

- Mikhail Chubarov, Henrik Pedersen, Hans Högberg, Jens Jensen, Anne Henry. Growth of High Quality Epitaxial Rhombohedral Boron Nitride. *Cryst. Growth Des.* **12**, 3215 (2012)

Figure 1. In-plane lattice constant is indicated to be 2.501 Å. Correct value is 2.504 Å. Same error in the "Introduction" on second page in first column.

Papers

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