Thermal and Radical Enhanced Atomic Layer Deposition of Films Containing Boron, Nitrogen and Carbon

Ramazan Oğuzhan APAYDIN

**THERMAL AND RADICAL ENHANCED ATOMIC
LAYER DEPOSITION OF FILMS CONTAINING
BORON, NITROGEN AND CARBON**

Ramazan Oğuzhan Apaydın

THERMAL AND RADICAL ENHANCED ATOMIC LAYER DEPOSITION OF FILMS CONTAINING BORON, NITROGEN AND CARBON

DISSERTATION

to obtain
the degree of doctor at the University of Twente,
on the authority of the rector magnificus,
Prof.dr. T.T.M. Palstra,
on account of the decision of the graduation committee,
to be publicly defended
on Thursday the 2nd of April 2020 at 14.45 hours

by

Ramazan Oğuzhan Apaydın

born on the 29th of April 1988
in Samsun, Turkey

This dissertation has been approved by:

Supervisors:

Dr. Alexey Y. Kovalgin

Dr. ir. Michel P. de Jong

This work was financially supported by The Netherlands Organization for Scientific Research (NWO), Domain Applied and Engineering Sciences, Project “Ultra-thin layers and their stacks for next-generation electronics and energy storage devices”, nr. 13929 and carried out at MESA+ Institute for Nanotechnology, University of Twente. Toyota Europe and ASM International are acknowledged for their partial financial support of this project.

Cover: designed by Burcu Gümüşçü Sefüncü

Front and back cover image: *Fast Fourier Transform (FFT) image of a sample showing the interlayer distance of h-BN films (chapter 4).*

ISBN: 978-90-365-4980-6

DOI: 10.3990/1.9789036549806

URL: <https://doi.org/10.3990/1.9789036549806%20>

Printed by: Ipskamp Printing (Enschede, The Netherlands)

© 2020 by Ramazan Oğuzhan APAYDIN, The Netherlands. All rights reserved. No parts of this thesis may be reproduced, stored in a retrieval system or transmitted in any form or by any means without permission of the author. Alle rechten voorbehouden. Niets uit deze uitgave mag worden vermenigvuldigd, in enige vorm of op enige wijze, zonder voorafgaande schriftelijke toestemming van de auteur.

Graduation committee:

Chairman / Secretary:	Prof. dr. J.N. Kok	University of Twente
Supervisor:	Dr. A.Y. Kovalgin	University of Twente
Co- Supervisor:	Dr. ir. M.P. de Jong	University of Twente
Committee members:	Prof. dr. D.J. Gravesteijn	University of Twente
	Prof. dr. J.G.E. Gardeniers	University of Twente
	Prof. dr. G.C.A.M. Janssen	Delft University of Technology
	Prof. dr. ir. J.R. van Ommen	Delft University of Technology
	Prof. dr. A. Devi	Ruhr-University Bochum
	Dr. S. Kinge	Toyota Motor Europe

*to my parents,
brother, sister and beautiful niece,*

“Hiçbir şeye ihtiyacımız yok, yalnız bir şeye ihtiyacımız vardır; çalışkan olmak.”

Mustafa Kemal Atatürk

TABLE OF CONTENTS

1	Introduction	1
1.1	Motivation of the project	2
1.2	Introduction to atomic layer deposition	5
1.3	Thin film deposition facilities	7
1.4	Thesis outline	11
	References.....	12
2	Studying film growth: spectroscopic ellipsometry and adduct-assisted pathway.....	17
2.1	Introduction.....	18
2.2	SE modelling	18
2.2.1	Comparison of the thicknesses measured by SE, TEM and XRR.....	22
2.2.2	Compositional analysis by SE	22
2.3	Adduct-assisted pathway.....	23
2.4	Conclusions	25
	References.....	26
3	Studying B/BN composite material by XPS and SE.....	29
3.1	Introduction.....	30
3.2	Experimental details	30
3.3	Results and discussion.....	32
3.3.1	Spectroscopic ellipsometry analysis.....	32
3.3.1.1	Tunable refractive index (n) of B/BN composites	32
3.3.1.2	Development of SE model for a B/BN composite	34
3.3.1.2.1	Parameterization approaches.....	34
3.3.1.2.2	Optical function determination	35

3.3.2	Confirmation of the composite nature by XPS	39
3.3.2.1	XPS data of B/BN films	39
3.3.3	EFTEM analysis.....	41
3.4	Conclusions	42
	References.....	44
4	Comparative study of B/BN deposition in purely thermal and radical-enhanced modes	47
4.1	Introduction	48
4.2	Experimental details	48
4.3	Results and discussion.....	49
4.3.1	Purely thermal deposition	49
4.3.2	Hot-wire-assisted deposition	54
4.3.3	Plasma-assisted deposition.....	55
4.3.4	Comparative analysis of the film properties.....	56
4.3.4.1	XPS analysis.....	56
4.3.4.2	Stability in air	58
4.3.4.3	Crystallinity from HRTEM.....	59
4.3.4.4	Other analyses.....	61
4.4	Suggested deposition mechanisms.....	62
4.4.1	Surface-adduct pathway for purely thermal deposition.....	62
4.4.2	A comparison of pure-thermal and radical-enhanced modes.....	64
4.5	Conclusions	65
	References.....	67
5	Thermal deposition of BN from BBr₃ and NH₃	71
5.1	Introduction	72

5.2	Surface reactions in relation to BN growth	72
5.3	Proposed BN growth mechanisms	74
5.3.1	Thermal-BN deposition via surface adduct pathway.....	74
5.4	Modeling the thermal-BN growth	75
5.5	Experimental results	78
5.5.1	Experimental setup	78
5.5.2	Kinetics of thermal-BN deposition	78
5.5.2.1	The BN ALD window	78
5.5.2.2	Characterization of the BN layers	83
5.5.2.2.1	Refractive index (n) by SE	83
5.5.2.2.2	XPS analyses	84
5.5.2.2.3	XRD analyses.....	85
5.6	Conclusions	85
	References.....	87
6	The effects of using alternative approaches to growing BN from BBr₃ and NH₃.....	91
6.1	Introduction.....	92
6.2	Proposed BN growth mechanism in a radical-enhanced mode	92
6.3	Plasma-enhanced ALD of BN in a hot-wall reactor	93
6.3.1	Experimental setup	93
6.3.2	BN ALD window and the effect of non-optimized conditions	94
6.4	BN deposition in a cold-wall reactor	96
6.4.1	Experimental setup	97
6.4.2	Purely thermal mode	97
6.4.3	Hot-wire-assisted mode	98

6.4.4	Studying the byproduct formation.....	102
6.5	Conclusions	102
	Appendix 6.1: Ammonia-decay analysis	104
	Appendix 6.2. Ammonium bromide identification	106
	Appendix 6.3. In-situ study of ammonium bromide formation for optimizing boron nitride ALD from BBr ₃ and NH ₃	108
	Appendix 6.4. Ammonium bromide migration and removal issues	112
	References.....	114
7	Growing BCN and AlBCN films from TEB and TMA precursors.....	117
7.1	Introduction	118
7.2	Reactions in relation to BCN growth.....	119
7.2.1	Reactions between TEB and NH ₃	119
7.2.2	Reactions between TEB:NH ₃ and TMA:NH ₃ adducts	121
7.2.3	Thermal decomposition of TEB	122
7.3	Experimental details	123
7.3.1	Deposition methodology	123
7.3.2	Tuning the deposition conditions.....	123
7.4	Deposition of BCN films	126
7.4.1	Growth aspects from SE.....	126
7.4.2	Compositional analysis from XPS	129
7.4.2.1	Sputter depth profiles	129
7.4.2.2	Chemical bonding environments	130
7.5	AlBCN films obtained by super-cycles	133
7.5.1	Growth aspects from SE.....	134
7.5.2	Compositional analysis from XPS	136

7.5.2.1	Sputter depth profiles	136
7.5.2.2	Chemical bonding environments	137
7.6	Conclusions	141
Appendix 7.1: Stepwise growth of BCN films		143
Appendix 7.2: Thickness variation of BCN films mapped by ex-situ SE.....		144
Appendix 7.3: Thickness variation of AlBCN films mapped by ex-situ SE.....		145
Appendix 7.4: Sputter depth profile line intensities		146
References.....		147
8	Conclusions and recommendations	151
8.1	Conclusions	152
8.2	Recommendations	154
Summary		157
Samenvatting		159
List of Publications		161
Acknowledgements		163
Author's Biography		167

1 Introduction

1.1 Motivation of the project

The family of boron, nitrogen and carbon containing materials exhibits a variety of attractive optical, electronic and chemical properties and shows an example of excellent possibility to combine several functionalities in one compound ¹⁻⁶. Graphene, hexagonal boron nitride (h-BN) and *sp*²-hybridized Boron-Carbon-Nitrogen (BCN) composites exhibit a near-perfect match of their crystal lattices ⁷⁻⁹. Ultra-thin layers of these materials and their vertical stacks, with compositions varying from pure graphene to pure h-BN, can lead to discovering new effects in solid-state systems and are therefore very attractive for potential applications in next-generation technologies. Graphene, for example, features an exceptionally high charge carrier mobility ^{7,9} and optical transparency ¹⁰⁻¹², which are of prime importance for (opto)electronics. With its very large surface-to-volume ratio, graphene further holds considerable promise as a new anode material in energy-storage devices ¹³. On the other hand, h-BN has attracted much attention as a dielectric with relation to graphene-based devices. More generally, ultra-thin layered BCN-materials with varying composition are expected to enable a rich variety of electronic properties, notably a tunable bandgap, potentially resulting in new applications ^{14,15}.

h-BN is recognized as an ideal insulating template for graphene based 2D devices due to its excellent properties ¹⁶. Firstly, h-BN monolayers are isostructural to graphene, with a lattice mismatch of 1.7% ¹⁷. Multilayers of h-BN are structurally similar to graphite, exhibiting a layered honeycomb structure with strong covalent bonds between boron and nitrogen atoms within each layer, and weak van der Waals forces bonding together the neighboring layers ^{17,18}. Such structural properties enable excellent interaction of h-BN with graphene and graphite, and hence it has great potential for various nanoelectronics device applications ⁷. Furthermore, h-BN possesses high mechanical hardness and resilience ¹⁹, a wide bandgap of 5.9 eV ²⁰ and high thermal conductivity ²¹ encouraging its applications in transparent membranes ^{16,17}, gate dielectrics ^{22,23} and power devices ²⁴. For

example, enhanced mobilities and high current on-off ratios are obtained when graphene field effect transistors are integrated with h-BN ^{25,26}.

Although h-BN is an electrical insulator, inclusion of foreign elements (i.e. carbon) can, in principle, allow to tune its properties (i.e. decrease its bandgap), and is therefore an interesting avenue to explore. Such elements (i) can be located at grain boundaries, (ii) can substitute an atom ²⁷ or (iii) form separate phase(s) ²⁸. For example, the catalytic properties of BN can be improved with low levels of phosphorus (P) atoms present as dopants ²⁹. In addition, p-type conductivity in h-BN films has been achieved by doping with beryllium (Be) ³⁰, magnesium (Mg) ³¹ and zinc (Zn) ³². Further, excess boron (B) incorporation into boron nitride enables tuning the refractive index (n) ^{33,34} in a wide range; n increases with the B content due to the presence of B-B bonds. Moreover, higher electrical conductivity is reported when the boron content is increased ³⁵.

To reiterate, BCN-materials with varying composition (i.e., ratio of the constituting elements) are of particular interest to enable a rich variety of properties. For that reason, synthesis, characterization and possible applications of these materials are widely studied. Experimental ^{27,36-40} and theoretical ⁴¹⁻⁴⁵ studies showed that BCN-materials have attractive mechanical, electrical and optical properties. For example, Yuki et.al. ³⁷ reported that the optical bandgap of the BCN film decreased by ~35% and the electrical resistivity decreased by 3 orders of magnitudes (from 10^{12} to $10^9 \Omega \text{ cm}$) when the C content increased from 6% to 30%. Additionally, Ajayan et. al. ²⁸ reported an increased electrical conductivity with increasing percentage of carbon.

It should be noted that C and h-BN tend to form segregated C and BN domains in the BCN system, making the formation of single-phase BCN films challenging. Although B-, C- and N-containing materials are often referred to as “BCN” in the literature, the constituting phases are usually not well specified. It remains then a question mark whether such a “BCN” material is composed of a single phase or multiple phases. The latter can contain for example mixed inclusions of pure carbon and pure boron nitride. The same holds for B-rich BN,

which can be composed of a pure (elemental) boron (pure-B) and a pure boron nitride phase. Thus, further investigation of the materials, which are generally united under the term “BCN”, is certainly required.

The technologies available for fabrication nowadays have, however, clear drawbacks, for example high temperature (high-T) requirements, phase segregation in multicomponent films, reproducibility issues and low conformality, that limit the potential industrial applications of these materials and prevent achieving technological maturity. For that reason, alternative techniques for deposition to achieve the fabrication requirements are needed. To this purpose, atomic layer deposition (ALD) has emerged as an important technique for deposition of ultra-thin layers at relatively low temperatures for industrial applications due to its advantages over other methods.

First (1), high-T processes are more likely to lead to separated phases since this is thermodynamically favorable ^{28,43}. To synthesize a single-phase material (real BCN or B-rich BN in one phase) low-T methods are preferable. For the chosen precursors in this work, certainly for BBr₃ and TEB, ALD occurs at low temperatures ^{46,47}. Still low-T processes tend to reach chemical equilibrium, which may lead to phase separation. In this case, radical-assisted processes, e.g. hot-wire (hot tungsten filament) and plasma assistance, exhibit a higher chance of obtaining mixed phases, and thus for forming a single phase, as they occur not in equilibrium ⁴⁸. In addition, they allow lowering the process temperature to room temperature and limit the temperature effects even to a larger extend. Second (2), ALD allows to simplify the deposition chemistry, limiting the study to heterogeneous (surface) processes only. This finally helps to better understand the processes. Altogether, (1) and (2) rationally lead to (i) a pulsed manner of introducing precursors with purges in between, (ii) low-T, and (iii) possible use of HW or plasma. Therefore, thermal or radical enhanced ALD methods become convenient choices.

In this project, we focus on the deposition of boron–nitrogen and boron–carbon–nitrogen containing thin films by thermal and radical–enhanced methods. We explore both pulsed-deposition and ALD approaches, with the aim to comparatively study and

understand the growth mechanisms, observe the occurrence of either single or multiple phases, and study the material properties.

1.2 Introduction to atomic layer deposition

Atomic layer deposition is a technique, suitable for the production of thin films with a thickness control down to a fraction of a monolayer ^{49,50}. It is based on sequential introduction (pulse) of two or more reactive gases (also called precursors) into a reactor, resulting in self-limiting gas-solid reactions occurring at the surface of a suitable substrate ^{49,51}. Contrary to chemical vapor deposition (CVD), an inert gas purge between pulses of different precursors prevents chemical reactions in the gas phase ⁴⁹⁻⁵¹. Thus, an ALD cycle can be expressed as giving (i) precursor A, (ii) purge, (iii) precursor B, and (iv) purge. Ideally, in steps (i) and (iii), the precursors must exhibit self-limiting reactions on the surface. This means that a chemical reaction of a precursor in the gas phase with a surface that is already covered by the same precursor is not possible. Due to the self-limiting nature, ALD has the capability to coat complex shapes (i.e., high aspect ratio structures) with a conformal layer ⁵²⁻⁵⁵. Furthermore, the purging steps (steps (ii) and (iv)) should be long enough to ensure the removal of residual gases from the reactor. As a result of one cycle, a layer of certain thickness is deposited on the surface. This is referred to as the growth per cycle (GPC). ALD cycles are repeated until the desired thickness has been achieved. The reaction temperatures should be chosen such that condensation (i.e., physisorption of multilayers) of the reactants is prevented, whereas their chemisorption leads to the formation of not more than a monolayer. A schematic illustration of one ALD cycle for forming aluminum oxide (Al_2O_3) by sequential exposures to trimethylaluminum (TMA – $\text{Al}(\text{CH}_3)_3$) and water (H_2O) ⁵⁶ is given in Figure 1-1. After a complete cycle, the -OH terminated surface is reproduced; repeating the cycle builds up a film.

Figure 1-1. Schematic illustration of one ALD reaction cycle. (i) -OH terminated surface exposed to TMA results in CH₄ removal and leaves H₃C-terminations; (ii) purge: removal of CH₄ and excess TMA; (iii) the H₃C -surface is exposed to H₂O, eliminating CH₄ and re-creating -OH terminations; (iv) purge: removal of CH₄ and excess H₂O ⁵⁶.

ALD can be performed in thermal and radical-enhanced modes ⁵⁷. Thermal ALD processes are commonly used to deposit two-element materials such as oxides and nitrides. Thermal ALD of single-element films (metals or semiconductors), except for notable exceptions, is difficult ⁴⁹. A solution can be provided by radical-enhanced ALD (REALD) ⁵⁸. Radicals can enable reactions that are not possible in thermal mode. Furthermore, radicals can lower the deposition temperature down to room temperature, as occurs for example for Al₂O₃ REALD ⁵⁹. The radicals can be generated by dissociating one of the (two) precursors by, for example, a plasma source (the so-called plasma-enhanced ALD - PEALD). If ammonia (NH₃) gas is introduced through plasma, a variety of reactive NH_x (x=0–2) radicals as well as atomic hydrogen (at-H) species can be generated ⁶⁰. The presence of NH_x will greatly increase the rate of surface nitridation at low temperatures. The surface bombardment with energetic species (ions, electrons) can additionally provide energy to the surface and thus change film properties. For instance, several groups have observed improved crystallinity upon plasma assistance for aluminum nitride (AlN) ⁶¹, hafnium oxide (HfO₂) ⁶² and vanadium pentoxide (V₂O₅) ⁶³ films. However, detrimental effects may also occur, such as reduced thickness uniformity ^{64,65} and possible damage of the film. This makes PEALD less attractive for certain applications.

Another approach to generate radicals is by utilizing a hot-wire (HW) ^{66,67}. In this method, a hot tungsten (W) filament, heated up to ≈ 2700 K, can be used to dissociate molecules such as hydrogen (H_2) and ammonia into atomic hydrogen and NH_x ⁶⁶⁻⁷². Compared to plasmas, this method enables purely chemical film growth, since it excludes the presence of energetic charged species and (UV) photons, reducing poorly controlled chemical reactions, possible surface bombardment effects and photo-activation ^{66,67,73-75}.

1.3 Thin film deposition facilities

Thin film deposition experiments were performed using two different reactor systems, namely a home-built cluster and a Picuson plasma ALD/CVD (R-200) setup. The home-built cluster system (Figure 1-2) consists of two gas distribution networks and three reactors (all equipped with turbo-molecular pumps) connected to a loadlock. The latter minimizes surface/interface deterioration by constantly keeping the reactors under vacuum conditions (10^{-7} – 10^{-8} mbar base pressure). All the reactors allow installation of a spectroscopic ellipsometer (SE) for in-situ (real time) monitoring the film growth. The ellipsometer (Woollam M2000FI) operates in a wavelength range of 245–1688 nm. The reactors are equipped with high-speed ALD valves having a time resolution of 0.1 s. The home-built hot-wire (HW) tool can be installed to provide at-H and NH_x radicals by dissociation of H_2 or NH_3 . The HW can be mounted either in horizontal (not in line-of-sight with the substrate) or vertical (in line-of-sight with the substrate) position in both Reactor-1 and Reactor-3.

Figure 1-2. A drawing of the home-built cluster system consisting of 2 gas-distribution networks and 3 ALD/CVD reactors connected to a loadlock. A spectroscopic ellipsometer (Woollam M2000FI) can be mounted on all reactors to monitor the film growth in-situ.

A drawing of Reactor-1 (also referred to as the cold-wall reactor), which was employed for the experiments discussed in Chapter 6, is shown in Figure 1-3. In this setup, another chamber equipped with a Fourier Transform Infrared Spectrometer (FTIR) is positioned in the downstream direction (see Figure 1-2), which allows studying the reaction byproducts. Reactor-1 is rather big and has an effective volume of 70 liters – much larger compared to that of Reactors 2 and 3. Further, it does not contain a small inner chamber, unlike Reactor-2 and Reactor-3 (see Figure 1-4 for the latter). Reactor-1 was used for ALD of BN films from boron tribromide (BBr_3) and NH_3 , using nitrogen (N_2) or argon (Ar) as carrier gases. The NH_3 was introduced from top (through the so-called cross assembly), whereas the BBr_3 supplied via the gas ring located at 10 cm above the substrate.

Figure 1-3. A drawing of the cold-wall reactor (Reactor-1) with a volume of ~70 liters.

The homebuilt hot-wall Reactor-2 was used to deposit amorphous silicon (a-Si) layers from tri-silane (Si_3H_8) at 400 °C, to passivate B(C)N ALD films. This reactor has a small-volume (24 ml) inner reactor, placed inside a much bigger (several liters) cold-wall outer reactor. Importantly, the walls of the inner reactor were kept at elevated temperatures during deposition.

Reactor-3 (Figure 1-4) was used for the majority of experiments discussed in Chapters 3, 4 and 7. Similar to Reactor-2, the hot-wall small-volume inner reactor is placed inside a big-volume cold-wall outer reactor. Having small volumes is advantageous since, by reducing the precursor delivery- and purge times, it allows to efficiently maintain an ALD mode. The precursors can be supplied both from the top (through the cross-assembly) and the lateral gas inlets located at 2–3 cm distance above the substrate.

Figure 1-4. A cross-section of Reactor-3. The wafer is placed between the heated top and bottom part of the inner chamber with a volume of 32 ml. The hot-wire (tungsten filament), gas inlets and SE optical path are indicated.

The Picosun plasma reactor (Figure 1-5) was used for studying depositions in both thermal and plasma-enhanced ALD (PEALD) modes, as further discussed in Chapters 3, 4, 5 and 6. The reactor is equipped with a plasma source, to generate a maximum power of 2.5 kW, and an in-situ Woollam M2000XI SE.

Figure 1-5. Picosun plasma ALD/CVD reactor equipped with a plasma source and spectroscopic ellipsometer.

1.4 Thesis outline

Chapter 2 discusses the application of spectroscopic ellipsometry for determining thickness, optical functions and composition of the films. It further discusses the chemical reaction mechanism. Chapter 3 presents a study of the composite nature of boron rich boron nitride films. It is shown, by using x-ray photoelectron spectroscopy (XPS) and SE, that the films consist of two separate phases, namely pure boron and pure boron nitride. The optical SE model developed in this chapter is further applied in Chapter 4. Chapter 4 discusses the growth mechanism of BN films deposited from diborane (B_2H_6) and NH_3 in a pulsed regime, to mimic an ALD process. Further, purely-thermal and radical-enhanced deposition modes are compared by gradually changing the degree of NH_3 dissociation, from low by hot-wire to high by plasma-assistance. It is demonstrated that, in thermal mode, the growth and composition of the layers are strongly dependent on the total gas pressure. This allows to hypothesize a growth model via a so-called surface-adduct mechanism (pre-introduced in Chapter 2, Section 2.3). Chapter 5 reports on the applicability of the surface-adduct mechanism to ALD of BN from BBr_3 and NH_3 . Chapter 6 compares purely-thermal and radical-assisted methods. It further reports on the effects of reactor design on the film growth aspects, comparing the results obtained with the hot-wall and cold-wall reactors. Chapter 7 investigates thermal deposition of B-C-N films from triethylborane (TEB) and NH_3 with various amounts of carbon. Additionally, so-called ALD super-cycles, leading to the incorporation of AlN into BN or B-C-N matrix are studied. Chapter 8 concludes the thesis and gives recommendations for future research.

References

- ¹ R. Haubner, M. Wilhelm, R. Weissenbacher, and B. Lux, in *High Perform. Non-Oxide Ceram. II. Struct. Bond.*, edited by M. Jansen (2002), pp. 1–45.
- ² D.W. Palmer, in *Compr. Semicond. Sci. Technol.* (Elsevier, 2011), pp. 390–447.
- ³ T. Oku, N. Koi, and K. Suganuma, *J. Phys. Chem. Solids* **69**, 1228 (2008).
- ⁴ S. Wang, Q. Chen, and J. Wang, *Appl. Phys. Lett.* **99**, 063114 (2011).
- ⁵ D. Jin-Xiang, Z. Xiao-Kang, Y. Qian, W. Xu-Yang, C. Guang-Hua, and H. De-Yan, *Chinese Phys. B* **18**, 4013 (2009).
- ⁶ W. Liu, T. Yanase, T. Nagahama, and T. Shimada, *J. Alloys Compd.* **792**, 1206 (2019).
- ⁷ J. Wang, F. Ma, W. Liang, and M. Sun, *Mater. Today Phys.* **2**, 6 (2017).
- ⁸ N.Y. Kim, H.Y. Jeong, J.H. Kim, G. Kim, H.S. Shin, and Z. Lee, *ACS Nano* **11**, 7084 (2017).
- ⁹ J. Wang, F. Ma, and M. Sun, *RSC Adv.* **7**, 16801 (2017).
- ¹⁰ H. Falomir, M. Loewe, E. Muñoz, and A. Raya, *Phys. Rev. B* **98**, 195430 (2018).
- ¹¹ M. Zamani and M. Abbasnejad, *Physica C*, **554**, 19 (2018).
- ¹² R.R. Nair, P. Blake, A.N. Grigorenko, K.S. Novoselov, T.J. Booth, T. Stauber, N.M.R. Peres, and A.K. Geim, *Science*, **320** (5881), 1308 (2008).
- ¹³ J. Zhu, R. Duan, S. Zhang, N. Jiang, Y. Zhang, and J. Zhu, *Springerplus* **3**, 585 (2014).
- ¹⁴ Q. Peng and S. De, *Phys. E Low-Dimensional Syst. Nanostructures* **44**, 1662 (2012).
- ¹⁵ A. Ramasubramaniam, D. Naveh, and E. Towe, *Nano Lett.* **11**, 1070 (2011).
- ¹⁶ V. Yadav and V. Kulshrestha, *Nanoscale* **11**, 12755 (2019).
- ¹⁷ S.K. Jang, J. Youn, Y.J. Song, and S. Lee, *Sci. Rep.* **6**, 1 (2016).
- ¹⁸ Y. Ding, J. Shi, M. Zhang, X. Jiang, H. Zhong, P. Huang, M. Wu, and X. Cao, *RSC Adv.* **6**, 29190 (2016).
- ¹⁹ C. Li, Y. Bando, C. Zhi, Y. Huang, and D. Golberg, *Nanotechnology* **20**, (2009).
- ²⁰ K. Watanabe, T. Taniguchi, and H. Kanda, *Nat. Mater.* **3**, 404 (2004).
- ²¹ I. Jo, M.T. Pettes, J. Kim, K. Watanabe, T. Taniguchi, Z. Yao, and L. Shi, *Nano Lett.* **13**, 550 (2013).
- ²² N. Izyumskaya, D.O. Demchenko, S. Das, Ü. Özgür, V. Avrutin, and H. Morkoç, *Adv. Electron. Mater.* **3**, 1 (2017).
- ²³ K. Zhang, Y. Feng, F. Wang, Z. Yang, and J. Wang, *J. Mater. Chem. C* **5**, 11992 (2017).

- ²⁴ G.C. Constantinescu and N.D.M. Hine, *Nano Lett.* **16**, 2586 (2016).
- ²⁵ C.R. Dean, A.F. Young, I. Meric, C. Lee, L. Wang, S. Sorgenfrei, K. Watanabe, T. Taniguchi, P. Kim, K.L. Shepard, and J. Hone, *Nat. Nanotechnol.* **5**, 722 (2010).
- ²⁶ S.K. Jang, J. Jeon, S.M. Jeon, Y.J. Song, and S. Lee, *Solid. State. Electron.* **109**, 8 (2015).
- ²⁷ C.W. Ong, X.A. Zhao, K.F. Chan, Y.M. Ng, P.W. Chan, C.L. Choy, and R.W.M. Kwok, *Thin Solid Films* **307**, 152 (1997).
- ²⁸ L. Ci, L. Song, C. Jin, D. Jariwala, D. Wu, Y. Li, A. Srivastava, Z.F. Wang, K. Storr, L. Balicas, F. Liu, and P.M. Ajayan, *Nat. Mater.* **9**, 430 (2010).
- ²⁹ J. Zhao, B. Lin, Y. Zhu, Y. Zhou, and H. Liu, *Catal. Sci. Technol.* **8**, 5900 (2018).
- ³⁰ B. He, W.J. Zhang, Z.Q. Yao, Y.M. Chong, Y. Yang, Q. Ye, X.J. Pan, J.A. Zapien, I. Bello, S.T. Lee, I. Gerhards, H. Zutz, and H. Hofsäss, *Appl. Phys. Lett.* **95**, 2 (2009).
- ³¹ R. Dahal, J. Li, S. Majety, B.N. Pantha, X.K. Cao, J.Y. Lin, and H.X. Jiang, *Appl. Phys. Lett.* **98**, 88 (2011).
- ³² K. Nose, H. Oba, and T. Yoshida, *Appl. Phys. Lett.* **89**, (2006).
- ³³ S.P. Murarka, C.C. Chang, D.N.K. Wang, and T.E. Smith, *J. Electrochem. Soc.* **126**, 1951 (1979).
- ³⁴ T.H. Yuzuriha and D.W. Hess, *Thin Solid Films* **140**, 199 (1986).
- ³⁵ C.W. Ong, K.F. Chan, and C.L. Choy, *Thin Solid Films* **388**, 217 (2001).
- ³⁶ A. Prakash and K.B. Sundaram, *Appl. Surf. Sci.* **396**, 484 (2017).
- ³⁷ T. Yuki, S. Umeda, and T. Sugino, *Diam. Relat. Mater.* **13**, 1130 (2004).
- ³⁸ M.K. Lei, Q. Li, Z.F. Zhou, I. Bello, C.S. Lee, and S.T. Lee, *Thin Solid Films* **389**, 194 (2001).
- ³⁹ J. Wang, C. Chen, C. Yang, Y. Fan, D. Liu, and W. Lei, *Curr. Graphene Sci.* **2**, 3 (2017).
- ⁴⁰ S. Beniwal, J. Hooper, D.P. Miller, P.S. Costa, G. Chen, S.Y. Liu, P.A. Dowben, E.C.H. Sykes, E. Zurek, and A. Enders, *ACS Nano* **11**, 2486 (2017).
- ⁴¹ J. Zhu, S. Bhandary, B. Sanyal, and H. Ottosson, *J. Phys. Chem. C* **115**, 10264 (2011).
- ⁴² E. Hernández, C. Goze, P. Bernier, and A. Rubio, *Phys. Rev. Lett.* **80**, 4502 (1998).
- ⁴³ K. Yuge, *Phys. Rev. B - Condens. Matter Mater. Phys.* **79**, 1 (2009).
- ⁴⁴ J. Da Rocha Martins and H. Chacham, *ACS Nano* **5**, 385 (2011).
- ⁴⁵ L. Song, Z. Liu, A.L.M. Reddy, N.T. Narayanan, J. Taha-Tijerina, J. Peng, G. Gao, J. Lou, R. Vajtai, and P.M. Ajayan, *Adv. Mater.* **24**, 4878 (2012).

- ⁴⁶ A. Haider, C. Ozgit-Akgun, E. Goldenberg, A.K. Okyay, and N. Biyikli, *J. Am. Ceram. Soc.* **97**, 4052 (2014).
- ⁴⁷ B. Mårlid, M. Ottosson, U. Pettersson, K. Larsson, and J. Carlsson, *Thin Solid Films* **402**, 167 (2002).
- ⁴⁸ H.B. Profijt, S.E. Potts, M.C.M. van de Sanden, and W.M.M. Kessels, *J. Vac. Sci. Technol. A Vacuum, Surfaces, Film.* **29**, 050801 (2011).
- ⁴⁹ M.G. Steven, *Chem. Rev.* **110**, 111 (2010).
- ⁵⁰ T. Muneshwar, M. Miao, E.R. Borujeny, and K. Cadien, in *Handbook of Thin Film Deposition* (2018), pp. 359-377.
- ⁵¹ R.L. Puurunen, *J. Appl. Phys.* **97**, 121301 (2005).
- ⁵² T. Weiss and W. Ebert, *Opt. Photonik* **12**, 42 (2017).
- ⁵³ J.W. Elam, G. Xiong, C.Y. Han, H.H. Wang, J.P. Birrell, U. Welp, J.N. Hryn, M.J. Pellin, T.F. Baumann, J.F. Poco, and J.H. Satcher, *J. Nanomater.* **2006**, 1 (2006).
- ⁵⁴ J.W. Elam, D. Routkevitch, P.P. Mardilovich, and S.M. George, *Chem. Mater.* **15**, 3507 (2003).
- ⁵⁵ R. Zazpe, M. Knaut, H. Sopha, L. Hromadko, M. Albert, J. Prikryl, V. Gärtnerová, J.W. Bartha, and J.M. Macak, *Langmuir* **32**, 10551 (2016).
- ⁵⁶ G.N. Parsons, S.M. George, and M. Knez, *MRS Bull.* **36**, 865 (2011).
- ⁵⁷ C. Detavernier, J. Dendooven, D. Deduytsche, and J. Musschoot, in *ECS Trans.* (ECS, 2008), pp. 239-246.
- ⁵⁸ H. Kim, *J. Vac. Sci. Technol. B Microelectron. Nanom. Struct.* **21**, 2231 (2003).
- ⁵⁹ S.B.S. Heil, P. Kudlacek, E. Langereis, R. Engeln, M.C.M. Van De Sanden, and W.M.M. Kessels, *Appl. Phys. Lett.* **89**, 1 (2006).
- ⁶⁰ A. Fridman, *Plasma Chemistry* (Cambridge University Press, Cambridge, 2008).
- ⁶¹ H. Van Bui, F.B. Wiggers, A. Gupta, M.D. Nguyen, A.A.I. Aarnink, M.P. de Jong, and A.Y. Kovalgin, *J. Vac. Sci. Technol. A Vacuum, Surfaces, Film.* **33**, 01A111 (2015).
- ⁶² Y. Lee, S. Kim, J. Koo, I. Kim, J. Choi, H. Jeon, and Y. Won, *J. Electrochem. Soc.* **153**, G353 (2006).
- ⁶³ J. Musschoot, D. Deduytsche, H. Poelman, J. Haemers, R.L. Van Meirhaeghe, S. Van den Berghe, and C. Detavernier, *J. Electrochem. Soc.* **156**, P122 (2009).
- ⁶⁴ Z. Zhu, P. Sippola, O.M.E. Ylivaara, C. Modanese, M. Di Sabatino, K. Mizohata, S. Merdes, H. Lipsanen, and H. Savin, *Nanoscale Res. Lett.* **14**, 55 (2019).
- ⁶⁵ H. Kim, C. Cabral, C. Lavoie, and S.M. Rossnagel, *J. Vac. Sci. Technol. B Microelectron. Nanom. Struct.* **20**, 1321 (2002).
- ⁶⁶ H. Umemoto, K. Ohara, D. Morita, T. Morimoto, M. Yamawaki, A. Masuda, and H. Matsumura, *Jpn. J. Appl. Phys.* **42**, 5315 (2003).

- ⁶⁷ Y.J. Shi, B.D. Eustergerling, and X.M. Li, *Thin Solid Films* **516**, 506 (2008).
- ⁶⁸ B. Stannowski, J.K. Rath, and R.E.I. Schropp, *Thin Solid Films* **395**, 339 (2001).
- ⁶⁹ Y. Shi, *Acc. Chem. Res.* **48**, 163 (2015).
- ⁷⁰ I. Langmuir, *J. Am. Chem. Soc.* **34**, 860 (1912).
- ⁷¹ I. Langmuir and G.M.J. Mackay, *J. Am. Chem. Soc.* **36**, 1708 (1914).
- ⁷² I. Langmuir, *J. Am. Chem. Soc.* **37**, 417 (1915).
- ⁷³ M. Yang, A.A.I. Aarnink, A.Y. Kovalgin, R.A.M. Wolters, and J. Schmitz, *Phys. Status Solidi* **212**, 1607 (2015).
- ⁷⁴ V. V. Afanas'ev, J.M.M. de Nijs, P. Balk, and A. Stesmans, *J. Appl. Phys.* **78**, 6481 (1995).
- ⁷⁵ H. Shimizu, K. Sakoda, T. Momose, M. Koshi, and Y. Shimogaki, *J. Vac. Sci. Technol. A Vacuum, Surfaces, Film.* **30**, 01A144 (2012).

2 Studying film growth: spectroscopic ellipsometry and adduct-assisted pathway

Abstract

This chapter discusses the issues important for studying thin films by spectroscopic ellipsometry (SE) and in relation to the specific film-formation mechanism explored in this thesis. The SE optical models, applied for studying optical functions, measuring film thickness and estimating film composition, are explained. The thickness values obtained by SE are compared with those from high-resolution transmission electron microscopy (HRTEM) and x-ray reflectometry (XRR). The composition is verified with XPS. The results show a good agreement indicating applicability of the developed SE model. In-situ SE is used to study the growth in real time (to be shown in Chapters 3–7) and determine film composition (to be discussed in Chapters 2–4). Further, the surface reaction mechanism, known from the literature and referred to as the surface-adduct pathway, is explained. This mechanism is further hypothesized to occur in the processes discussed in Chapters 4–7.

2.1 Introduction

This chapter reports on the theory and application of spectroscopic ellipsometry (SE) for studying optical functions, measuring thickness and estimating composition of thin films. The relevant optical models will be explained in Section 2.2. Section 2.3 discusses the surface reaction pathway (further referred to as adduct pathway or adduct mechanism) which is proposed to occur for BN films. This mechanism is investigated in Chapters 4–7.

2.2 SE modelling

SE is an optical characterization technique which is used to determine a variety of properties (e.g., refractive index n , extinction coefficient k , thickness) of thin films with high accuracy and in a non-destructive manner¹⁻³. SE is widely used for real time (in-situ) studies of film growth. It has been shown that SE is a reliable technique to obtain physical, optical and electrical properties, providing insights into growth mechanism of various materials.

Spectroscopic ellipsometry measures the change in the polarization of light reflected from a sample, as a function of wavelength λ . The thickness and optical functions (n and k) are obtained by fitting the following model (equation 2.1) to the experimental data with the Levenberg-Marquardt algorithm^{1,2}.

$$\tan(\Psi)e^{i\Delta} = \frac{r_p}{r_s} = r. \quad (\text{eq. 2.1})$$

In this equation, r is defined as the ratio of the amplitude reflection coefficients for p -polarized light (r_p) to s -polarized light (r_s). Psi (Ψ) and delta (Δ) represent the magnitude of the reflectivity ratio and the phase difference between r_p and r_s , respectively. Ψ and Δ are the parameters experimentally (directly) measured by SE.

The analysis of the measured psi and delta values for each λ or photon energy (E) allows to extract sample properties such as thickness and optical functions. For that, an optical model is required. The entire modeling includes: (i)

identifying the number and order of contributing sub-layers, (ii) modeling (or measuring) dielectric functions (ϵ) of the contributing layers as a function of λ or E , and (iii) fitting the measured Ψ - and Δ -data for each λ or E ¹. The validity of the analysis is mathematically estimated by the mean square error (MSE), χ^2 , which represents the agreement between the measured and modeled (fitted) data ². Since (some of the) optical properties are usually unknown, they become the fitting parameters. Having too many fitting parameters increases the uncertainty; carrying out a correct modelling procedure is thus very crucial for truthful interpretation of the results.

In this study, we used a stacked-layer model (see Figure 2-1) consisting of several sub-layers. Each sub-layer was assigned to have optical functions of the corresponding material. Since silicon (Si) exhibits well-known temperature (T) dependent optical functions $n(\lambda, T)$ and $k(\lambda, T)$ ^{1,4}, this was used for in-situ surface-temperature measurements. For Si and silicon dioxide (SiO_2), these functions were taken from the literature ^{1,5} and fixed in the model. The SiO_2 thickness was pre-determined by ex-situ SE and subsequently fixed in the model. A capping layer of amorphous Si (a-Si) was sometimes used to protect the films upon the exposure to oxidizing ambient (air).

Figure 2-1. *Stacked-layer SE model.*

Optical functions of the layer of interest (in our case B-, N- and C-containing layers) were fitted using Kramers–Kronig consistent (KK-consistent)

B-spline parameterization (node spacing 0.3 eV) without assuming a particular spectral shape⁶ for each location (ex-situ wafer mapping) and each time frame (in-situ measurements). Following the B-spline parameterization, each film was analyzed using one of the optical models given below.

The Tauc-Lorentz (TL) and Lorentz (L) oscillators were employed to model the optical functions of boron (pure-B) films. The complex dielectric function (ε) used in these oscillators can be parameterized by equation 2.2^{1,7}.

$$\varepsilon = \varepsilon_{1m} + i\varepsilon_{2m} \quad (\text{eq. 2.2})$$

In this equation, ε_{1m} and ε_{2m} are the real and imaginary parts of the dielectric function - ε , respectively, and m is the oscillator number. When ε_{2m} is known, ε_{1m} can be obtained by Kramers-Kronig integration of ε_{2m} as shown in equation 2.3:

$$\varepsilon_{1m} = \frac{2}{\pi} P \int_{Eg_m}^{\infty} \frac{\xi \varepsilon_{2m}(\xi)}{\xi^2 - E^2} d\xi, \quad (\text{eq. 2.3})$$

with the principle value integral (P) given in ref.¹ and Eg denotes the energy gap. In a Tauc-Lorentz oscillator, ε_{2m} is defined by equations 2.4 and 2.5:

$$\varepsilon_{2m} = \left[\frac{Amp_m Eo_m Br_m (E - Eg_m)^2}{(E^2 - Eo_m^2)^2 + Br_m^2 E^2} \right] \frac{1}{E} \rightarrow E > Eg \quad (\text{eq. 2.4})$$

$$\varepsilon_{2m} = 0 \rightarrow E \leq Eg_m, \quad (\text{eq. 2.5})$$

where Amp_m is the amplitude and Eo_m is the central energy of the m^{th} oscillator, and Br_m is the broadening parameter.

The ε_{2m} parametrization for a Lorentz oscillator is given in equation 2.6. The components of the equation have already been described above.

$$\varepsilon_{2m} = \frac{Amp_m Br_m Eo_m}{(Eo_m^2 - E^2)^2 + E^2 Br_m^2} \quad (\text{eq. 2.6})$$

Each oscillator function describes an electronic transition or, in the case of TL, a series of transitions between two bands. Dielectric functions formed by multiple transitions can be constructed by summation of the relevant oscillator functions.

To successfully model pure-B films and B/BN composites, it was necessary to include a Lorentz oscillator with a thickness dependent amplitude (see Chapter 3 for details), to describe a feature near the band edge (at ~3.3 eV). Including this thickness dependence significantly improved the fit accuracy. To note, this feature did not match with any known electronic transitions of BN according to the theoretical and experimental works surveyed ⁸⁻¹².

The refractive index, n , was fitted using the Sellmeier model (equation 2.7), limited to the transparent range ^{1,2}:

$$n^2(\lambda) = A + B\lambda^2/(\lambda^2 - C) . \quad (\text{eq. 2.7})$$

In this equation, A , B and C are Sellmeier coefficients which are obtained by fitting this model to experimental data ^{1,13}. Consistent thickness values were obtained from both KK-consistent B-spline parameterization (in the entire wavelength range 245–1688 nm) and the Sellmeier (transparent region only) model.

Finally, the surface roughness of the layer can be taken into account by using the Bruggeman effective medium approximation (EMA) ^{1,14,15}. The EMA used for this analysis considers the (surface) rough layer to consist of 50 vol. % of (ambient) voids and 50 vol. % of the corresponding layer material.

The correlation between multiple fit parameters was minimized by variable angle SE (VASE) measurements (ex-situ) and multi-sample analysis (MSA). The former provides more measurement events performed under different angles on the same location (spot) on the wafer. The MSA compares the same material at different film thicknesses, increasing the consistency in determining optical functions. Further details on VASE and MSA can be found in ref. ^{5,16-22}.

Sensitivity tests were performed to confirm that the fits represented unique and global solutions rather than local or shallow minima, and to estimate errors in fitting the parameters ²³. The sensitivity analysis delivers an MSE value for a range of values of one fit parameter.

2.2.1 Comparison of the thicknesses measured by SE, TEM and XRR

In order to verify the applicability of the SE optical model to determine the film thickness, we measured thicknesses of several stoichiometric-BN samples deposited at various conditions, by high-resolution transmission electron microscopy (HRTEM) and X-ray reflectometry (XRR), as given in Tables 2-1 and 2-2.

Table 2-1. A comparison of BN film thicknesses as determined by SE and HRTEM.

Sample Method	1	2	3
SE	15 nm	8 nm	18 nm
HRTEM	12 nm	8 nm	14 nm

Table 2-2. A comparison of BN film thicknesses as determined by SE and XRR.

Sample Method	1	2	3	4	5
SE	30 nm	15 nm	13 nm	15 nm	13 nm
XRR	28 nm	14 nm	13 nm	15 nm	13 nm

The comparison indicates all the thicknesses to be in agreement. This verifies the applicability of the developed optical model and provides a solid platform for further characterization of the deposited thin films.

2.2.2 Compositional analysis by SE

The EMA model was originally developed to predict the effect of inclusions of a given material into another material by using the materials dielectric functions^{1,2,24,25}. The model can adequately describe optical functions of a layer consisting of two uniformly mixed components (similar to the roughness determination). In case of a two-phase material, the EMA gives the following complex dielectric function ϵ_{EMA} of the composite^{1,15}:

$$\varepsilon_{EMA} = \frac{\varepsilon_a \varepsilon_b + \kappa \varepsilon_{EMA} (f_a \varepsilon_a + f_b \varepsilon_b)}{\kappa \varepsilon_{EMA} (f_a \varepsilon_b + f_b \varepsilon_a)} \quad (\text{eq. 2.8})$$

In this equation, f_a and f_b are the volume fractions of the “a” and “b” component, respectively, and ε_a and ε_b are their corresponding dielectric functions. Further, κ is defined as $\kappa = (1 - q)/q$ using the screening factor q ranging between 0 and 1^{1,15}. The screening factor is given by $q=1/3$ for the EMA model used in this work.

To use the EMA model, individual optical functions of the contributing “a” and “b” components have to be known. For that, we used the Sellmeier model optimized for stoichiometric BN since this material possesses transparency in the entire range of our ellipsometer. Further, we used a combination of Tauc-Lorentz and Lorentz (with a thickness dependent amplitude – see Chapter 3) oscillator models developed for pure-B. Substituting the optical functions of stoichiometric BN and pure-B into equation 2.8 revealed pure boron volume fractions in the B/BN composites. This methodology showed good agreement with XPS measurements, as will be discussed in Chapter 3. The EMA model was employed to determine the composition of samples discussed in Chapter 4 as well.

2.3 Adduct-assisted pathway

It is well known that so-called Lewis-acids and Lewis-bases can react with each other, resulting in the formation of an adduct²⁶. Examples of Lewis acids are group III metal-organic compounds (e.g., trimethylaluminum – TMA) and the corresponding halides (e.g., AlCl_3 , BBr_3 ^{27,28}), whereas group V hydrides (e.g., NH_3) belong to Lewis bases. Reaction 2.1 gives an example of such adduct formation in gas phase from TMA and NH_3 ^{29,30}:

where $\text{H}_3\text{N}:\text{Al}(\text{CH}_3)_3$ is the adduct.

The adducts can decompose at certain temperatures and form gaseous compounds. Formation of a gas-phase $\text{H}_3\text{N}:\text{Al}(\text{CH}_3)_3$ (also referred to as

TMA:NH₃) adduct was shown by Sauls et. al.²⁹ and Interrante et. al.³¹. For AlN growth, occurrence of a surface adduct was confirmed in ref.^{30,32}. A similar surface adduct was further hypothesized to play an important role in gallium nitride (GaN) ALD at low temperatures^{22,33–35}.

For AlN ALD from TMA and NH₃, a two-step process has been suggested³⁰. Namely, it includes (see Figure 2-2) (i) formation of the surface adduct by a reaction between the chemisorbed TMA and gas-phase-NH₃, and (ii) subsequent reaction of the adduct-NH₃ group with a neighboring -CH₃ group of the chemisorbed TMA. This mechanism finally results in -NH₂- bridges between neighboring aluminum atoms, forming units of AlN. After each NH₃ exposure, the growth surface becomes NH₂-terminated and thereby chemically activated for the subsequent TMA exposure. A schematic representation of the adduct pathway for AlN is given below.

Figure 2-2. Surface-adduct assisted formation of AlN³⁰.

Hypothesizing the occurrence of a similar two-step mechanism for growing GaN from trimethylgallium (TMG) and ammonia, Banerjee et.al. successfully realized polycrystalline GaN films by purely thermal ALD at 400 °C^{22,33,34}. Similarly to AlN, beyond a specific temperature, the TMG:NH₃ surface adduct was assumed to convert into Ga-NH₂-Ga linkages with the elimination of methane (see Figure 2-3), forming a NH₂-terminated GaN surface in a self-limiting fashion. The adduct-formation reaction will proceed until all available chemisorbed-TMG sites are occupied. It has been reported that the rate of occupation could be enhanced by increasing the partial pressure of NH₃ (P_{NH_3}). The P_{NH_3} either shifts the surface reactions towards the adduct formation (assuming the adduct formation to be a

reversible reaction in equilibrium) or just provides more NH_3 for occupying the available surface sites (regardless whether the reaction is reversible or not).

Figure 2-3. The proposed mechanism of thermal-GaN ALD ³⁴.

The described surface-adduct pathway may be applicable to other precursor systems as well. This thesis investigates the growth mechanism of BN films from diborane (B_2H_6) and NH_3 , boron tribromide (BBr_3) and NH_3 , as well as triethylborane (TEB) and NH_3 precursors. These precursor systems will be discussed one by one in Chapters from 4 to 7. A similar mechanism involving surface-adduct formation can be suggested to explain the experimental observations.

2.4 Conclusions

First part of this chapter shortly presented the approach used in this thesis to obtain the thicknesses, optical functions and composition of thin films by spectroscopic ellipsometry. The thicknesses from SE were in good agreement with those obtained by HRTEM and XRR. The SE analysis was further extended to estimating the fractions of different phases present in the layers, i.e., enabling the analysis of composite materials. Altogether, this indicated the applicability of the SE approach chosen.

Second part of this chapter outlined the surface-adduct film-growth mechanism, earlier approved for AlN ALD and recently hypothesized for GaN ALD. The mechanism will be taken as a basis to explain the BN deposition results presented in Chapters 4-7 for various precursor systems and deposition methodologies.

References

- ¹ H. Fujiwara, *Spectroscopic Ellipsometry: Principles and Applications* (John Wiley & Sons, Ltd, Chichester, UK, 2007).
- ² H.G. Tompkins and E.A. Irene, *Handbook of Ellipsometry* (William Andrew, Norwich, NY, 2005).
- ³ E. Langereis, S.B.S. Heil, H.C.M. Knoop, W. Keuning, M.C.M. van de Sanden, and W.M.M. Kessels, *J. Phys. D. Appl. Phys.* **42**, 073001 (2009).
- ⁴ P. Lautenschlager, M. Garriga, L. Vina, and M. Cardona, *Phys. Rev. B* **36**, 4821 (1987).
- ⁵ C.M. Herzinger, B. Johs, W.A. McGahan, J.A. Woollam, and W. Paulson, *J. Appl. Phys.* **83**, 3323 (1998).
- ⁶ B. Johs and J.S. Hale, *Phys. Status Solidi* **205**, 715 (2008).
- ⁷ J.A. Woollam Co, (2011).
- ⁸ J.A. Zapien, R.W. Collins, and R. Messier, *Thin Solid Films* **364**, 16 (2000).
- ⁹ J.A. Zapien, R. Messier, and R.W. Collins, *Diam. Relat. Mater.* **10**, 1304 (2001).
- ¹⁰ J.A. Zapien, R.W. Collins, and R. Messier, *J. Vac. Sci. Technol. A Vacuum, Surfaces, Film.* **20**, 1395 (2002).
- ¹¹ S. Lousinian, N. Kalfagiannis, and S. Logothetidis, *Solid State Sci.* **11**, 1801 (2009).
- ¹² S.L. Ren, A.M. Rao, P.C. Eklund, and G.L. Doll, *Appl. Phys. Lett.* **62**, 1760 (1993).
- ¹³ J. Mistrik, S. Kasap, H.E. Ruda, C. Koughia, and J. Singh, in *Springer Handb. Electron. Photonic Mater.* (Springer International Publishing, Cham, 2017), pp. 1-1.
- ¹⁴ D.E. Aspnes, J.B. Theeten, and F. Hottier, *Phys. Rev. B* **20**, 3292 (1979).
- ¹⁵ H. Fujiwara, J. Koh, P.I. Rovira, and R.W. Collins, *Phys. Rev. B* **61**, 10832 (2000).
- ¹⁶ J.N. Hilfiker, N. Singh, T. Tiwald, D. Convey, S.M. Smith, J.H. Baker, and H.G. Tompkins, *Thin Solid Films* **516**, 7979 (2008).
- ¹⁷ W.A. McGahan, B. Johs, and J.A. Woollam, *Thin Solid Films* **234**, 443 (1993).
- ¹⁸ K. Järrendahl and H. Arwin, *Thin Solid Films* **313-314**, 114 (1998).
- ¹⁹ C.M. Herzinger, P.G. Snyder, F.G. Celii, Y. -C. Kao, D. Chow, B. Johs, and J.A. Woollam, *J. Appl. Phys.* **79**, 2663 (1996).
- ²⁰ C.M. Herzinger, H. Yao, P.G. Snyder, F.G. Celii, Y. -C. Kao, B. Johs, and J.A. Woollam, *J. Appl. Phys.* **77**, 4677 (1995).
- ²¹ H.G. Tompkins, T. Zhu, and E. Chen, *J. Vac. Sci. Technol. A Vacuum, Surfaces, Film.* **16**, 1297 (1998).

- ²² S. Banerjee, A.J. Onnink, S. Dutta, A.A.I. Aarnink, D.J. Gravesteijn, and A.Y. Kovalgin, *J. Phys. Chem. C* **122**, 29567 (2018).
- ²³ D.-M. Rosu, E. Ortel, V.-D. Hodoroaba, R. Kraehnert, and A. Hertwig, *Appl. Surf. Sci.* **421**, 487 (2017).
- ²⁴ G. Bruno, E. Irene, K. Hingerl, J. Humlicek, M. Losurdo, D.E. Aspnes, P. Zeppenfeld, H. Wormeester, C. Cobet, E. Speiser, F. Bechstedt, C. Rockstuhl, F.L. Christoph Menzel, T. Novikova, A. De Martino, S.A. Little, R.W. Collins, S. Marsillac, M. Cardona, and M.L. Sadowski, *Defining and Analysing the Optical Properties of Materials at the Nanoscale: A Collection of Thoughts, Opinions, Ideas and Data That Have Matured over Years on Exploiting Ellipsometry for a Range of Characteristic Needs*, NanoCharM, (2010).
- ²⁵ D.A.G. Bruggeman, *Ann. Phys.* **416**, 636 (1935).
- ²⁶ K. Seshan, *Handbook of Thin-Film Deposition Processes and Techniques*, 2nd ed. (Noyes Publications, Norwich, NY, 2002).
- ²⁷ C.D. Hunt, in *Chem. Elem.* (Elsevier, 1997), pp. 139–215.
- ²⁸ K. Possemiers, P. Van Der Voort, and E.F. Vansant, *J. Chem. Soc. Faraday Trans.* **92**, 679 (1996).
- ²⁹ F.C. Sauls, L. V. Interrante, and Z. Jiang, *Inorg. Chem.* **29**, 2989 (1990).
- ³⁰ M.E. Bartram, T.A. Michalske, J.W. Rogers, and R.T. Paine, *Chem. Mater.* **5**, 1424 (1993).
- ³¹ L. V. Interrante, L.E. Carpenter, C. Whitmarsh, W. Lee, M. Garbaskas, and G.A. Slack, *MRS Proc.* **73**, 359 (1986).
- ³² T.M. Mayer, J.W. Rogers, and T.A. Michalske, *Chem. Mater.* **3**, 641 (1991).
- ³³ S. Banerjee and A.Y. Kovalgin, *ECS Trans.* **86**, 21 (2018).
- ³⁴ S. Banerjee, *From Radical-Enhanced to Pure Thermal ALD of Aluminium and Gallium Nitrides*, University of Twente, 2019.
- ³⁵ D. Sengupta, S. Mazumder, W. Kuykendall, and S.A. Lowry, *J. Cryst. Growth* **279**, 369 (2005).

3 Studying B/BN composite material by XPS and SE

Abstract

This work investigates boron-rich boron nitride (BN) thin films deposited using sequential pulses of diborane (B_2H_6) and ammonia (NH_3) with argon (Ar) purge in between, in the substrate temperature range of 275-375 °C. We observe two different phases in these films, namely pure boron (pure-B) and boron nitride (BN). Refractive indices (n) of the B/BN composites are found to be consistently higher than n of stoichiometric BN, and lower than n of a pure-B reference. Namely, n obtained at 632 nm gradually increases from 1.7 to 2.9 by tuning the composition from stoichiometric BN to pure-B. Further, the boron rich samples reveal an absorption behavior between 1 and 5 eV, which is assigned to the pure-B phase. The developed SE optical model adequately estimates the relative amounts of pure-B and BN phases as well as reveals the optical functions of pure-B, stoichiometric BN, and the B/BN composites. The relative amounts of the phases are in agreement with X-ray photoelectron spectroscopy (XPS) measurements, thereby verifying the SE model for determining composition of the B/BN composite films. As compared to a sharp B 1s peak of pure-B, the XPS analysis shows broadening of the B 1s peak towards higher binding energies (i.e., towards those of BN) for B/BN, resulting in a clear asymmetry due to the appearance of two separate peaks. It is shown that single-peak fitting of XPS data fails to represent the experimentally obtained data. On the other hand, the N 1s peak allows good fitting with one stoichiometric-BN peak only, indicating a well-defined BN phase. Spatial distribution of the phases is investigated by planar view energy filtered transmission electron microscopy (EFTEM). The corresponding cross-correlation maps of elemental B and N show laterally homogeneous distribution of the elements within the measurement error.

3.1 Introduction

The possibility of including other elements (e.g., carbon) into boron nitride (BN), to tailor its properties, motivates further exploration of boron nitride containing films. For example, low-amount additives of phosphorus can improve the catalytic properties of BN¹ while beryllium (Be), magnesium (Mg) or zinc (Zn) doping leads to p-type conductivity²⁻⁴. Moreover, making BCN by adding carbon (C) to BN noticeably influences the mechanical, electronic and optical properties⁵⁻¹¹.

Further, boron (B) incorporation into boron nitride was investigated by several groups. Theoretical work¹² conducted to explore the local structure (short- or long-range order), electronic structure and mechanical properties, predicted a phase segregation in amorphous B/BN material with boron fractions higher than BN. The same work proposed interesting applications of B/BN in the field of nano-glass ceramics. Experimental works¹³⁻¹⁶ reported (i) tunable optical and altered electronic properties and (ii) the presence of both B-B and B-N bonding environments. These works however did not explicitly identify the material as phase-segregated (i.e., a composite).

This chapter investigates whether a composite nature of B/BN can be experimentally confirmed and quantitatively addressed by modeling. We confirm the multi-phase nature of the B/BN films by spectroscopic ellipsometry (SE) and x-ray photoelectron spectroscopy (XPS). We further investigate the distribution of phases using energy filtered transmission electron microscopy (EFTEM) analysis. The optical SE model developed in this chapter for B/BN composites will further be applied in Chapter 4 to clarify composition of the films deposited from B₂H₆ and NH₃ precursors.

3.2 Experimental details

The B/BN films were deposited in Reactor-3 of the home-built ALD/CVD cluster system from sequentially introduced diborane (B₂H₆, 5% in Ar) and

ammonia (NH₃) pulses. A detailed description of the reactor can be found in Chapter 1 and ref. ^{17,18}. The variously-composed films were obtained either in purely thermal deposition mode or by assistance with a hot-wire (HW).

A stoichiometric-BN reference sample was deposited on silicon dioxide (SiO₂) in a Picosun R-200 ALD reactor (see Chapter 1) from the same precursors and in the same manner, but by adding a plasma assistance. The reference layers of pure-B were deposited on silicon (Si) by chemical vapor deposition (CVD) from B₂H₆ (5% in Ar) at 220-300 °C.

Prior to deposition, Si (100) wafers underwent a three-step wafer cleaning procedure. This included (i) removal of native oxide by a 1-min dip into 1% HF, (ii) rinsing in deionized (DI) water, and (iii) ozone-steam cleaning followed by another HF dip and rinsing. Further, a 100 nm thick silicon dioxide (SiO₂) layer was grown by thermal oxidation at 1050 °C in dry oxygen.

The B/BN films were obtained in the pressure range of 10⁻³ – 5x10⁻² mbar, at substrate temperatures between 270 and 360 °C. The precursors were introduced via alternating pulses with Ar-purge in between, to avoid gas phase reactions. The typical pulse- and purge-durations were: 0.5-2.5 s of B₂H₆, 4-6 s of post-B₂H₆ purge, 2.5-3 s of NH₃ and 4-6 s of post-NH₃ purge.

The SE measurements were carried out using a Woollam M2000UI spectroscopic ellipsometer, operating in the wavelength range of 246-1689 nm (0.72-5.05 eV), in combination with CompleteEASE 5.19 modeling software. The XPS spectra were acquired with a Quantera SCM (scanning XPS microprobe from Physical Electronics) instrument using monochromatic Al K α radiation at 1486.6 eV. The C 1s peak due to ambient hydrocarbon contamination was calibrated at 284.8 eV ¹⁹. Binding energies of the photoelectron lines of the samples were charge-referenced to this C 1s line. For compositional analysis, XPS sputter depth profiling was performed using Ar ions. A Philips CM300ST-FEG transmission electron microscope (TEM) was used to perform the EFTEM measurements.

3.3 Results and discussion

3.3.1 Spectroscopic ellipsometry analysis

3.3.1.1 Tunable refractive index (n) of B/BN composites

The refractive indices of the B/BN samples with various amounts of pure-B (in the range of 30-65 vol.%, as determined by XPS) were found to be consistently higher compared to the stoichiometric BN and lower compared to the pure-B references. The stoichiometric BN exhibited $n=1.7$ at 632 nm and $n=1.68$ at 1500 nm, which reasonably agreed with the reported values²⁰⁻²². To account for the effect of pure-B incorporation *in the presumably composite material*, the n was modelled by including EMA in the SE model (see Figure 3-1.a). This implied that the samples were considered to be composed of uniformly mixed pure-B and stoichiometric-BN phases with a certain fraction (f_B) of the pure-B phase ($0 \leq f_B \leq 1$).

Performing KK-consistent B-spline parameterization reveals n , whereas the pure-B fraction can be calculated from XPS:

$$f_B = N_B - N_N \quad (\text{eq. 3.1})$$

In this equation, N_B is the fraction of B atoms (atomic percentage of B divided by 100%) and N_N is the share of N atoms. To note, this equation only holds for $N_B > N_N$. Assuming that all N atoms to bond with B atoms to form a stoichiometric-BN phase with a B:N ratio of 1:1, equation 3.1 can be re-written for a mixture of B and BN and the atomic fraction can be converted into pure-B volume fraction $f_{V,B}$:

$$f_{V,B} = \frac{(N_B - N_N) \frac{a_B}{\rho_B}}{(N_B - N_N) \frac{a_B}{\rho_B} + N_N \frac{a_B + a_N}{\rho_{BN}}} \quad (\text{eq. 3.2})$$

In this equation, ρ_B and ρ_{BN} are the mass densities of the boron and boron nitride phases, respectively, and a_B and a_N are the atomic masses of B and N. Since ρ_B and ρ_{BN} have very similar values ($\rho_B=2.35$ g/cm³²³ and $\rho_{BN}=2.28$ g/cm³²⁴), it follows that:

$$f_{V,B} = \frac{(N_B - N_N)a_B}{(N_B - N_N)a_B + N_N(a_B + a_N)} = \frac{N_B - N_N}{N_B + N_N \frac{a_N}{a_B}}. \quad (\text{eq. 3.3})$$

With $a_N/a_B \approx 1.3$, within the error margin the fractions f_B and $f_{V,B}$ can be assumed to be equal:

$$\frac{N_B - N_N}{N_B + N_N \frac{a_N}{a_B}} \approx \frac{N_B - N_N}{N_B + N_N} = N_B - N_N. \quad (\text{eq. 3.4})$$

Therefore, f_B is further mentioned without specifically attributing it to either atomic or volume fraction.

On one hand, fractions f_B can be practically calculated from the XPS results by equation 3.4 and then used as input data to the EMA model; the latter reveals n . On the other hand, n can be directly calculated from B-spline fitting without assuming any particular spectral shape of $n(\lambda)$. A comparison of the as-calculated n -values is given below. Figure 3-1.a shows the EMA predicted refractive index assuming certain f_B , as simulated by SE. In Figure 3-1.b, the n -values obtained directly from B-spline fitting are compared with the EMA prediction; a good agreement within $\sim 10\%$ can be seen.

Figure 3-1. (a) The evolution of the refractive index $n(\lambda)$ with f_B , as calculated by the EMA for a composite of pure-B and stoichiometric-BN (b) Comparison of experimental (symbols; the corresponding f_B -values are calculated from XPS) and calculated (lines; the corresponding f_B -values are taken from (a)) refractive indices.

Clearly, changing the f_B significantly affects the refractive index. The layers with no pure-B ($f_B=0$) exhibit a value of n that agrees with literature for BN^{20,21}.

Similar observations have been reported by other research groups for boron-rich boron nitride, as well as for carbon containing boron nitride and gallium nitride²⁵⁻²⁹. Varying pure-B share enables tuning the refractive index between 1.7-2.9 at 632 nm and 1.7-2.7 at 1500 nm. The experimentally obtained B-spline n -values are fairly consistent (within ~10%) with the n calculated by EMA. This may be a first indication of the co-existence of uniformly mixed pure-B and stoichiometric-BN phases, i.e., the formation of a composite. To further verify this hypothesis, the SE model was further developed in detail.

3.3.1.2 Development of SE model for a B/BN composite

Accurate SE modelling requires knowing optical functions of pure-B and stoichiometric-BN components of the composite. The parameterization used for fine-tuning the optical functions is described below.

3.3.1.2.1 Parameterization approaches

The KK-consistent B-spline functions fitted to the spectra of the films revealed an absorption behavior that did not match with any electronic transitions of boron nitride in the theoretical and experimental works that have been surveyed³⁰⁻³³. A further comparison with the SE data of the pure-B films revealed the similar absorption behavior, suggesting the formation of a pure-B phase and thus a B/BN mixture. A comparison of the optical functions is given in Figure 3-2. One should keep in mind that a pure-B film exhibits thickness dependent optical functions; this will be discussed below.

The determination of the thickness dependent optical functions of pure-B was thus a first step. The Tauc-Lorentz oscillator model was employed to represent the optical functions. For layers thinner than 5 nm, the ~3.3 eV absorption peak (see Figure 3-4) was described by a Lorentz oscillator. Next, the Sellmeier model was employed to describe n of stoichiometric BN, for which $k = 0$ in the measurement range of 245 – 1689 nm. Finally, the EMA was applied to adequately describe optical functions of a layer consisting of the two uniformly mixed components. Details of all models have been given in Chapter 2.

Figure 3-2. Imaginary part (ϵ_2) of the complex dielectric function (ϵ) of (i) CVD-grown boron reference (thickness 6-113 nm), (ii) ~50 vol. % of pure-B into B/BN composite (thickness 12-43 nm), and (iii) plasma-grown (see the experimental) stoichiometric-BN reference (thickness 10-27 nm). The indicated pure-B share is determined from XPS.

3.3.1.2.2 Optical function determination*

For stoichiometric BN, a B-spline fit (MSA) to a combined dataset of in-situ (25 frames) and ex-situ (25 points) SE measurements found an absorption coefficient less than 7000 cm^{-1} ($k < 0.025$) over the entire λ range ($246 < \lambda < 1689$ nm). Since the sensitivity limit of SE to k is in this order of magnitude³⁴, the layer was approximated as transparent. This allowed to model $n(\lambda)$ with the Sellmeier equation, $n^2(\lambda) = A + B\lambda^2/(\lambda^2 - C)$. A fit on the dataset described above yields values 2.17, 0.72 and $0.04 \mu\text{m}^2$ for A, B and C, respectively, for the peak centered at 199 nm, i.e., at 6.24 eV. Figure 3-3 shows the as-obtained dielectric function of BN (ϵ_{BN}).

For pure-B, a B-spline fit to a combined dataset of in-situ (18 frames) and ex-situ (18 points) SE from 8 depositions of pure-B (see Section 3.2 for experimental conditions) revealed an absorption spectrum comparable to the literature³⁵⁻⁴³, that could be modeled by a Tauc-Lorentz (TL) oscillator. Including a Lorentz (L) oscillator with a thickness-dependent amplitude significantly improved the fits

* Contributed by A.J. Onnink, University of Twente. This section concerns a joint publication of R.O. Apaydin and A.J. Onnink, see the list of publications at the end of this thesis.

due to a better description of the feature near the band edge. The feature is only significant in ultrathin (< 5 nm) layers. Namely, the $r\chi^2$ (reduced chi square) decreased from 78.8 to 9.6. (To bear in mind, $r\chi^2$ represents the agreement between the measured data and the data simulated by the optical model.) Figure 3-4 shows the resulting $\epsilon(\lambda)$ for pure-B. The Lorentzian feature at 3.3 eV may correspond to the effective optical response of B nano-islands ⁴⁴.

Figure 3-3. Real (ϵ_1^{BN}) and imaginary (ϵ_2^{BN}) part of the dielectric function of a layer (10 to 27 nm thick) of stoichiometric BN deposited on 100 nm SiO_2 by plasma-assistance. A single dielectric function could describe this range of thicknesses, indicating that the thickness dependence of ϵ^{BN} could be neglected above 10 nm [†].

[†] This graph is contributed by A.J. Onnink (University of Twente) and included into the joint publication of R.O. Apaydin and A.J. Onnink, see the list of publications at the end of this thesis.

Figure 3-4. Real (ϵ_1^B) and imaginary (ϵ_2^B) part of the dielectric function of pure-B deposited on Si by CVD. For the 6-113 nm dataset, the fitted Lorentz amplitude is zero within the error margin. The TL-parameters are: Amp = 100, Br = 11.646 eV, E_0 = 8.282 eV, and E_g = 1.086 eV[‡].

Figure 3-5 illustrates that the $\epsilon_2(\lambda)$ -shape from B-spline fits resembles that of $\epsilon_2(\lambda)$ for pure-B, suggesting that the EMA may apply. To test, f_B was determined by SE for 23 samples and compared to that determined by XPS under the assumption of having stoichiometric BN phases. Figure 3-6 shows the results for one wafer (5 points of comparison). The values of f_B from SE agree with f_B from XPS within the error margin (< 10%); the latter is determined from the SE parameter sensitivity analysis. Thus, SE allows quantitative estimation of f_B in these B/BN films, although less precisely than XPS. The agreement with XPS verifies the validity of the developed SE model in this particular case, and suggests a composite material which contains a mixture of pure-B and stoichiometric-BN phases. The SE model is particularly sensitive to f_B because of the prominent increase in the film's absorption coefficient, between 1 and 5 eV, attributed to the B enrichment.

[‡] This graph is contributed by A.J. Onnink (University of Twente) and included into the joint publication of R.O. Apaydin and A.J. Onnink, see the list of publications at the end of this thesis.

Figure 3-5. Real (ϵ_1) and imaginary (ϵ_2) parts of the dielectric function of a B/BN film on Si, compared to ϵ_1^B and ϵ_2^B of the pure-B reference shown in Figure 3-4. The B/BN data were obtained by MSA of a sample with thickness of 12-46 nm and $f_B = 0.50$ as determined by XPS §.

Figure 3-6. Wafer mapping of the SE-determined pure-B share (given by the colors, in vol.%) in a B/BN composite. The bold numbers on the map correspond to the B-shares from XPS.

§ This graph is contributed by A.J. Onnink (University of Twente) and included into the joint publication of R.O. Apaydin and A.J. Onnink, see the list of publications at the end of this thesis.

3.3.2 Confirmation of the composite nature by XPS

The overall film composition can be estimated from the total area of elemental XPS peaks (B 1s and N 1s). Peak fitting of the B 1s region may further allow a categorization of the population of B atoms by chemical environment. This can aid in distinguishing 2-phase amorphous B/BN composite films in which the chemical environment of B atoms is widely distributed. Section 3.3.2.1 below discusses the peak fitting results of B/BN films, clearly indicating 2 bonding environments of B atoms.

3.3.2.1 XPS data of B/BN films

The composition was deduced from B 1s and N 1s spectra acquired during sputter-depth profiling. It was observed that the B 1s spectra broadened towards higher binding energies, compared to the pure-B reference, causing asymmetry (Figure 3-7.a). However, the N 1s spectra match quite well with that of the stoichiometric BN reference (Figure 3-7.b), showing no broadening.

Figure 3-7. Comparison of (a) B 1s and (b) N 1s spectra of samples containing different fractions of pure-B, as indicated in the figure legend. To be noted: the shown samples contain less than 4 at. % of oxygen in the bulk, therefore, possible contribution of oxygen to the broadening can be excluded. The indicated f_B values are determined from XPS.

On the one hand, the lack of broadening of the N 1s spectra of the B/BN samples as well as the similar-to-BN FWHM indicate a well-defined BN phase. On the other hand, the observed asymmetry in the B 1s spectra may point to the

existence of two B 1s peaks, namely of pure-B and of stoichiometric BN. Confirming this would support the co-existence of the two phases.

The B 1s spectra were further investigated by deconvolution of the experimental peak using a double-peak model (Figure 3-8). All spectra were fitted by Gaussian peaks after subtracting an iteratively determined Shirley background ⁴⁵. We neglected the Lorentzian lifetime broadening of the B 1s (71 meV) and N 1s peaks (130 meV) ⁴⁶. The fitting analysis was performed by setting the B 1s peak positions at 188.4 eV (pure-B component) and 190.6 eV (BN component), as determined from the reference samples and the literature ^{6,24,47,48}. The shot noise in the spectrum was calculated as the square root of the background counts and included into the error bars ⁴⁹. Single-peak fitting was additionally performed for a comparison.

Figure 3-8. Deconvolution of the B 1s XPS peak by single-peak (1-Gaussian) and double-peak (2-Gaussian) fitting, after subtracting of a Shirley background. From XPS, the sample contains ~55 vol.% of pure-B.

From Figure 3-8, it is evident that the 1-Gaussian fitting fails to describe the experimental B 1s data, giving more than 3 times higher $r\chi^2$ compared to that of the 2-Gaussian fitting. In addition, for the single-peak fitting, the fitted and experimental peak maxima do not match. This confirms that at least 2 components are required to adequately describe the experimental B 1s spectra, confirming once again a composite nature of the films.

3.3.3 EFTEM analysis

Planar-view EFTEM measurements (see Figure 3-9) were performed on a representative B/BN sample with $f_B=0.5$ (from SE). To obtain the elemental maps of B and N, the area of interest was limited to a certain range of pixels (marked by red rectangles in the figure) in order to exclude the contribution of perforation in the TEM grid used. After calculating the pixel sizes, intensities of the pixels corresponding to B were plotted versus N-pixel intensities in a cross correlation graph (Figures 3-9.c and 3-9.d).

It can be seen that both B and N are homogeneously distributed within the measurement error. One cannot observe any lateral clustering of pure-B and BN phases. Although both XPS and SE clearly indicate about 50 *vol.%* of pure-B, EFTEM does not reveal any lateral inhomogeneity. This conclusion is rather expected from the methodology used for growing the films. To bear in mind, the films were obtained from sequential pulses of B_2H_6 and NH_3 , with Ar-purges in between. Such a process would naturally lead to a vertical inhomogeneity of the elemental distribution rather than a lateral inhomogeneity, due to incomplete nitridation of a the pure-B phase formed by B_2H_6 pulses during corresponding NH_3 pulses.

Figure 3-9. Images (a) and (b) show elemental maps of B and N obtained from two different areas of a sample consisting of 50 vol.% of pure-B and 50 vol.% of stoichiometric-BN phase, as determined by in-situ SE. Images (c) and (d) give the B-vs-N cross correlation maps obtained from the red-boxed areas of (a) and (b), respectively. No clear lateral inhomogeneity (clustering) of pure-B and BN phases can be seen.

3.4 Conclusions

This work investigated the multi-phase (composite) nature of B/BN thin films. It has been shown that the refractive index (n) of the films was strongly dependent on the pure boron fraction: a gradual increase of n from 1.7 (stoichiometric BN) to 2.9 (pure-B) was achieved by tuning the pure-B share. The film composition and optical properties were successfully modelled by spectroscopic ellipsometry. The developed SE model could quantitatively describe the experimental n -values as well as the co-existence of pure-B and stoichiometric-BN phases in the films. The SE data revealed absorption behavior between 1 and 5 eV, matching that of a pure-B phase.

The composite nature of the films was further supported by XPS. The B 1s peak revealed broadening towards higher binding energies and a clear asymmetry

compared to the pure-B or stoichiometric-BN reference. No N 1s-peak broadening was observed; the peak showed good matching with that of the stoichiometric-BN reference. This further confirmed the presence of a well-defined BN phase. The cross-correlation maps of elemental B and N, obtained from planar-view EFTEM, indicated laterally homogeneous distribution of these elements, suggesting their vertical inhomogeneity.

References

- ¹ J. Zhao, B. Lin, Y. Zhu, Y. Zhou, and H. Liu, *Catal. Sci. Technol.* **8**, 5900 (2018).
- ² B. He, W.J. Zhang, Z.Q. Yao, Y.M. Chong, Y. Yang, Q. Ye, X.J. Pan, J.A. Zapien, I. Bello, S.T. Lee, I. Gerhards, H. Zutz, and H. Hofsäss, *Appl. Phys. Lett.* **95**, 2 (2009).
- ³ R. Dahal, J. Li, S. Majety, B.N. Pantha, X.K. Cao, J.Y. Lin, and H.X. Jiang, *Appl. Phys. Lett.* **98**, 88 (2011).
- ⁴ K. Nose, H. Oba, and T. Yoshida, *Appl. Phys. Lett.* **89**, (2006).
- ⁵ C.W. Ong, X.A. Zhao, K.F. Chan, Y.M. Ng, P.W. Chan, C.L. Choy, and R.W.M. Kwok, *Thin Solid Films* **307**, 152 (1997).
- ⁶ L. Ci, L. Song, C. Jin, D. Jariwala, D. Wu, Y. Li, A. Srivastava, Z.F. Wang, K. Storr, L. Balicas, F. Liu, and P.M. Ajayan, *Nat. Mater.* **9**, 430 (2010).
- ⁷ A. Prakash and K.B. Sundaram, *Appl. Surf. Sci.* **396**, 484 (2017).
- ⁸ T. Yuki, S. Umeda, and T. Sugino, *Diam. Relat. Mater.* **13**, 1130 (2004).
- ⁹ M.K. Lei, Q. Li, Z.F. Zhou, I. Bello, C.S. Lee, and S.T. Lee, *Thin Solid Films* **389**, 194 (2001).
- ¹⁰ J. Wang, C. Chen, C. Yang, Y. Fan, D. Liu, and W. Lei, *Curr. Graphene Sci.* **2**, 3 (2017).
- ¹¹ S. Beniwal, J. Hooper, D.P. Miller, P.S. Costa, G. Chen, S.Y. Liu, P.A. Dowben, E.C.H. Sykes, E. Zurek, and A. Enders, *ACS Nano* **11**, 2486 (2017).
- ¹² A. Çetin and M. Durandurdu, *J. Am. Ceram. Soc.* **101**, 1929 (2018).
- ¹³ J.J. Pouch, S.A. Alterovitz, K. Miyoshi, and J.O. Warner, *MRS Proc.* **93**, 323 (1987).
- ¹⁴ C.W. Ong, K.F. Chan, and C.L. Choy, *Thin Solid Films* **388**, 217 (2001).
- ¹⁵ M.D. Wiggins, C.R. Aita, and F.S. Hickernell, *J. Vac. Sci. Technol. A Vacuum, Surfaces, Film.* **2**, 322 (1984).
- ¹⁶ J.G. Kho, K.T. Moon, G. Nouet, P. Ruterana, and D.P. Kim, *Thin Solid Films* **389**, 78 (2001).
- ¹⁷ A.Y. Kovalgin, M. Yang, S. Banerjee, R.O. Apaydin, A.A.I. Aarnink, S. Kinge, and R.A.M. Wolters, *Adv. Mater. Interfaces* **4**, 1700058 (2017).
- ¹⁸ M. Yang, Hot-Wire Assisted Atomic Layer Deposition of Tungsten Films, University of Twente, 2018.
- ¹⁹ T.L. Barr and S. Seal, *J. Vac. Sci. Technol. A Vacuum, Surfaces, Film.* **13**, 1239 (2002).
- ²⁰ M.J. Rand and J.F. Roberts, *J. Electrochem. Soc.* **115**, 423 (1968).
- ²¹ S. Weissmantel, G. Reisse, B. Keiper, and S. Schulze, *Diam. Relat. Mater.* **8**, 377 (1999).

- ²² H. Dumont, B. Bayle, and B. Bonnetot, *Phys. Status Solidi* **2473**, 2470 (2003).
- ²³ C.P. Talley, L.E. Line, and Q.D. Overman, in *Boron Synth. Struct. Prop.* (Springer US, Boston, MA, 1960), pp. 94–104.
- ²⁴ N.R. Glavin, C. Muratore, M.L. Jespersen, J. Hu, P.T. Hagerty, A.M. Hilton, A.T. Blake, C.A. Grabowski, M.F. Durstock, M.E. McConney, D.M. Hilgefort, T.S. Fisher, and A.A. Voevodin, *Adv. Funct. Mater.* **26**, 2640 (2016).
- ²⁵ S. Banerjee, R.O. Apaydin, and A.Y. Kovalgin, in *ECS 234 Meet.* (ECS 234 meeting, Oral presentation, Cancun, 2018).
- ²⁶ V.O. Todi and K.B. Sundaram, *Electrochem. Solid-State Lett.* **14**, G49 (2011).
- ²⁷ V.S. Sulyaeva, Y.M. Rumyantsev, V.G. Kesler, and M.L. Kosinova, *Thin Solid Films* **581**, 59 (2015).
- ²⁸ S.P. Murarka, *J. Electrochem. Soc.* **126**, 1951 (1979).
- ²⁹ T.H. Yuzuriha and D.W. Hess, *Thin Solid Films* **140**, 199 (1986).
- ³⁰ J.A. Zapien, R.W. Collins, and R. Messier, *Thin Solid Films* **364**, 16 (2000).
- ³¹ J.A. Zapien, R.W. Collins, and R. Messier, *J. Vac. Sci. Technol. A Vacuum, Surfaces, Film.* **20**, 1395 (2002).
- ³² S.L. Ren, A.M. Rao, P.C. Eklund, and G.L. Doll, *Appl. Phys. Lett.* **62**, 1760 (1993).
- ³³ S. Lousinian, N. Kalfagiannis, and S. Logothetidis, *Solid State Sci.* **11**, 1801 (2009).
- ³⁴ B. von Blanckenhagen, D. Tonova, and J. Ullmann, *Appl. Opt.* **41**, 3137 (2002).
- ³⁵ C. Feldman and K. Moorjani, *Johns Hopkins APL Tech. Dig.* **7**, 2 (1968).
- ³⁶ N. Morita and A. Yamamoto, *Jpn. J. Appl. Phys.* **14**, 825 (1975).
- ³⁷ F.H. Cocks, P.L. Jones, and L.J. Dimmey, *Appl. Phys. Lett.* **36**, 970 (1980).
- ³⁸ L.J. Dimmey, H. Park, P.L. Jones, and F.H. Cocks, *J. Electron. Mater.* **10**, 111 (1981).
- ³⁹ K. Nakamura, *J. Electrochem. Soc.* **131**, 2691 (1984).
- ⁴⁰ K. Shirai and S. Gonda, *J. Phys. Chem. Solids* **53**, 1081 (1992).
- ⁴¹ U. Kuhlmann, H. Werheit, T. Lundström, and W. Robers, *J. Phys. Chem. Solids* **55**, 579 (1994).
- ⁴² M. Terauchi, Y. Kawamata, M. Tanaka, M. Takeda, and K. Kimura, *J. Solid State Chem.* **133**, 156 (1997).
- ⁴³ H. Akazawa, *J. Vac. Sci. Technol. A Vacuum, Surfaces, Film.* **28**, 411 (2010).
- ⁴⁴ D. Bedeaux and J. Vlieger, *Optical Properties of Surfaces*, 2nd ed. (Imperial College Press, London, 2004).
- ⁴⁵ D.A. Shirley, *Phys. Rev. B* **5**, 4709 (1972).

⁴⁶ C. Nicolas and C. Miron, J. Electron Spectros. Relat. Phenomena **185**, 267 (2012).

⁴⁷ L. Chen, T. Goto, T. Hirai, and T. Amano, J. Mater. Sci. Lett. **9**, 997 (1990).

⁴⁸ K.K. Kim, A. Hsu, X. Jia, S.M. Kim, Y. Shi, M. Hofmann, D. Nezich, J.F. Rodriguez-Nieva, M. Dresselhaus, T. Palacios, and J. Kong, Nano Lett. **12**, 161 (2012).

⁴⁹ J.F. Moulder, W.F. Stickle, P.E. Sobol, and K.D. Bomben, *Handbook of X-Ray Photoelectron Spectroscopy* (Perkin-Elmer Corporation, Physical Electronics Division, Minnesota, 1992).

4 Comparative study of B/BN deposition in purely thermal and radical-enhanced modes

Abstract

This chapter studies the deposition of boron/boron nitride (B/BN) composite films at 275-375 °C of the substrate temperature by giving alternating pulses of diborane (B_2H_6) and ammonia (NH_3) with argon (Ar)-purges in between, to avoid gas-phase reactions of the precursors. This allows to mimic an atomic layer deposition (ALD) process, ensuring merely surface reactions and presumably simplifying the growth mechanism. This work further compares purely thermal and radical-enhanced deposition modes, by gradually changing the degree (and mechanism) of NH_3 dissociation, from low by hot-wire (HW) to high by plasma-assistance. It is demonstrated that, in purely thermal mode, the growth of the layers and their composition are strongly dependent on total gas pressure. By changing the pressure, the pure boron (pure-B) content (not to be confused with the total boron content) in the B/BN composites could be varied in the range of ~6-70 vol.%.

The pressure dependence is consistent with a growth model via the so-called surface-adduct mechanism. The plasma-assisted deposition results in polycrystalline BN with near stoichiometric B/N ratio at 310 °C. These films exhibit crystal planes stacked perpendicular to the substrate surface with an interplane distance of 3.57 Å corresponding to hexagonal boron nitride (h-BN).

The films are stable in air up to at least six months after their deposition.

4.1 Introduction

Several methods have been used to deposit boron nitride, including molecular beam epitaxy (MBE) ^{1,2}, ion beam assisted deposition (IBAD) ^{3,4}, magnetron sputtering ⁵, RF sputtering ⁶, pulsed laser deposition ⁷ and chemical vapor deposition (CVD) ⁸⁻¹². Among these, CVD is the most intensively studied method, commonly utilizing diborane (B_2H_6) and ammonia (NH_3) gas mixtures as precursors. However, the high growth temperatures (close to 1000 °C) required to form crystalline films, limit many (potential) applications of BN ^{13,14}. In addition, different thermal expansion coefficients of the substrate and of the deposited film negatively affect the processing at high temperatures. Boron nitride films deposited at temperatures below 800 °C are usually amorphous ^{14,15}.

To reduce the growth temperature, several radical-enhanced deposition methods have been employed. Radicals can be generated by dissociating NH_3 with, for example, a plasma source (the so-called plasma-enhanced CVD or PECVD), thereby producing a variety of nitrogen-containing (NH_x , $x=0-2$) radicals. Another approach to generate radicals is by utilizing a hot-wire (HW). Further details on the radical-assisted methods can be found in Chapter 1.

This chapter compares purely thermal and radical-enhanced deposition methods, by gradually changing the degree (and mechanism) of NH_3 dissociation, from low by HW- to high by plasma-assistance. It demonstrates that, in purely thermal mode, the growth of the layers and their composition are strongly dependent on total gas pressure. By changing the pressure, the pure boron content (B bonded to B instead of to N) in the B/BN composites can be varied in the range of ~6-70 vol.%. The pressure dependence will be discussed in line with a growth model via the so-called surface-adduct pathway (see Chapter 2).

4.2 Experimental details

The deposition experiments were performed in both home-built cluster and Picosun plasma ALD/CVD reactor. The details were already given in Chapter 1.

The experiments were conducted in the total pressure range of 10^{-3} -12 mbar. The substrate temperature was kept between 275-375 °C. Diborane (B_2H_6) and ammonia (NH_3) gases were used as boron and nitrogen sources, respectively.

Prior to deposition, silicon (Si) (100) and SiO_2 substrates were processed following the procedure explained in Chapter 3. The deposited films were characterized by x-ray photoelectron spectroscopy (XPS) and in-situ (real time) and ex-situ spectroscopic ellipsometer (SE) (see previous chapter for equipment details). In-situ spectroscopic ellipsometer (SE) was used to monitor the actual surface temperature¹⁶. Films deposited with plasma were further characterized by transmission electron microscopy (TEM), energy filtered TEM (EFTEM), grazing incidence angle x-ray diffraction (GIXRD) and x-ray reflectivity (XRR) techniques. Details for TEM equipment can be found in Chapter 3. GIXRD and XRR analyses were carried out with a X'pert Powder XRD system from Malvern Panalytical.

Spectroscopic ellipsometry analysis were performed using EMA, Sellmeier, Tauc Lorentz and Lorentz models, as explained in Chapters 2 and 3. The pure-B shares (in volume %, *vol.*%) given in this chapter were obtained solely from SE.

4.3 Results and discussion

4.3.1 Purely thermal deposition

Thermal decomposition of B_2H_6 occurs continuously, therefore, self-limiting reactions in the studied temperature (T) range are not expected. This was confirmed experimentally and shown in Figure 4-1.a, clearly demonstrating the ongoing deposition of pure boron on SiO_2 from B_2H_6 . An incubation time is observed (Figure 4-1.b); temperature clearly promotes the nucleation of B on SiO_2 decreasing the incubation time. No incubation was observed on silicon wafers at all temperatures studied.

Figure 4-1. The temperature dependence of growth per minute (GPM) (a) and incubation time (b) of pure boron films on SiO₂, measured by SE. The incubation time is defined as the growth time required to obtain a constant GPM. Conditions: CVD at 1 mbar of total pressure, 200 sccm of B₂H₆ (5% in Ar) and 500 sccm of Ar flow **.

The demonstrated non-self-limiting nature of boron deposition implies two co-existing processes in the BN formation mechanism:

- ✓ process (1) – non self-limiting thermal decomposition of B₂H₆, leading to the formation of a pure-B phase, presumably BH_x (x=0-3) terminated, and
- ✓ process (2) - reaction of this pure-B with NH₃, thereby incorporating nitrogen in the layers (i.e., nitridation of the pure-B).

Process (2) is self-limiting in the sense that the nitrogen content cannot exceed a certain share.

In the subsequent experiments, the effects of substrate temperature, total pressure (ranging from 5×10⁻³ mbar to 12 mbar) and diborane dose on the growth rate per cycle (GPC), as well as on the amount of pure-B, were investigated. It was observed that the nitrogen content slightly increases with lowering the substrate temperature from 375 °C to 290 °C, whereas the GPC decreases from 0.045 nm/cycle to 0.021 nm/cycle. These results suggest that the temperature rather affects the B₂H₆ chemisorption (process 1) and its subsequent decomposition than

** Courtesy of Xingyu Liu, University of Twente

the nitridation reaction (process 2). A strong enhancement of the GPC with increasing the B_2H_6 pulse time, as shown in Figure 4-2.a, implies that the GPC is limited by the B_2H_6 dose. The B_2H_6 pulse time also crucially determines the pure-B share in the layers (Figure 4-2.b).

Figure 4-2. Dependence of GPC (a) and pure-B share in vol.% (b) on B_2H_6 pulse duration, both measured by SE. Conditions: 4-6 s of Ar for post- B_2H_6 purge / 2.5-3 s of NH_3 pulse / 4-6 s of Ar for post- NH_3 purge, at a substrate temperature of 280 ± 10 °C and a total pressure of 2×10^{-3} mbar.

Further, increasing the total pressure (P_{tot}) leads to a higher nitrogen content (share) and a correspondingly lower amount of pure-B (Figure 4-3.a). This will be further discussed in Section 4.1, in view of the proposed adduct-assisted reaction pathway. However, a gradual decrease of the GPC was observed with increasing the P_{tot} (Figure 4-3.b). This rather unusual result can be explained by a decreased delivery of B_2H_6 to the wafer surface at a higher pressure (i.e., lower diffusion rate of B_2H_6) or a suppressed (dissociative) chemisorption of B_2H_6 (the rate limiting step) on the as-nitridized surface in comparison to a surface terminated by B_2H_6 decomposition products.

Figure 4-3. SE measurements of the pure-B share in vol.% (a) and GPC (b) as a function of the total gas pressure. Conditions: 2 s of B_2H_6 pulse / 6 s of Ar for post- B_2H_6 purge / 3 s of NH_3 pulse / 6 s of Ar for post- NH_3 purge, at a substrate temperature of 280 ± 10 °C.

Since the P_{tot} has a large impact on both GPC and pure-B share, we further expand the pressure range up to 12 mbar (see Figure 4-4). These experiments were carried out using the Picosun reactor, in purely thermal mode.

Figure 4-4. SE measurements of GPC (a) and pure-B share in vol.% (b) as a function of the total gas pressure. Conditions: 0.1-2.5 s of B_2H_6 pulse / 4-6 s of Ar post- B_2H_6 purge / 2.5-11.5 s of NH_3 pulse / 4-10 s of Ar for post- NH_3 purge, at a substrate temperature of 290 ± 20 °C. Symbols: squares for $P_{tot} < 1$ mbar, diamonds for $P_{tot} \geq 1$ mbar with 0.2 s B_2H_6 -pulse duration, triangles for $P_{tot} \geq 1$ mbar with 0.1 s B_2H_6 -pulse duration. Showing the cumulative datasets from different reactors, substrates and pulse times allows to generalize the pressure effect.

Although all obtained at different B_2H_6 -pulse, Ar-purge and NH_3 -pulse durations (see Figure 4-4 caption), the measurements in Figure 4-4.a exhibit the same trend of the GPC versus P_{tot} . Namely, the GPC slightly decreases with increasing the pressure for $P_{tot} < 0.1$ mbar and starts to increase rapidly for P_{tot}

exceeding 1 mbar. The pure boron share gradually decreases with increasing the P_{tot} , being as high as ~70 vol.% in the low-pressure range and as low as ~6 vol.% in the high-pressure range (Figure 4-4.b). This figure exhibits a consistent and clear effect of P_{tot} . Showing the cumulative datasets from different reactors, substrates and pulse times allows to generalize the pressure effect.

Obviously, changing P_{tot} would affect partial pressure of both diborane ($P_{\text{B}_2\text{H}_6}$) and ammonia (P_{NH_3}). It should however be noted that the difference between $P_{\text{B}_2\text{H}_6}$ and P_{NH_3} was at least one order of magnitude. Namely, for $P_{\text{tot}} > 1$ mbar, the $P_{\text{B}_2\text{H}_6}$ was kept in the range of 10^{-3} - 10^{-2} mbar, whereas the P_{NH_3} was changing between 10^{-2} and 10^{-1} mbar. Considering the large difference in the partial pressures, in combination with the significant decay of the pure-B share with increasing P_{tot} , a dominant role of the P_{NH_3} in the growth process might be suggested.

As proposed above, the film growth may occur via processes (1) and (2). Assuming the dependence of their rates on P_{tot} , it is evident that the strong increase of the GPC at $P_{\text{tot}} \geq 1$ mbar can hardly occur if process (1) dominates. If the latter was the case, this would not match with the gradually decreasing amount of the pure-B phase. We therefore conclude that the sharp rise of GPC is caused by process (2); the latter controls the growth at $P_{\text{tot}} \geq 1$ mbar. Process (2) may in turn enhance process (1) by changing the surface nitridation state. The proposed effect of NH_3 on the chemisorption of B_2H_6 is still to be explored. For example, it is reported that presence of H_2 may increase the activation energy required for diborane decomposition¹⁷.

Summarizing, the experiments performed in purely thermal mode indicate the importance of B_2H_6 in the growth rate and the film composition at $P_{\text{tot}} < 0.1$ mbar, whereas the impact of nitridation by NH_3 dominates at $P_{\text{tot}} \geq 1$ mbar. Clearly, higher P_{tot} increases the GPC and lowers the pure-B share. Decreasing the pure-B share below 6 vol.% is however problematic in purely thermal mode and at low temperatures. Sections 4.3.2 and 4.3.3 address the effectiveness of two radical-enhanced approaches towards growing stoichiometric BN from B_2H_6 and NH_3 .

4.3.2 Hot-wire-assisted deposition

The impact of a HW on the dissociation of NH_3 has been investigated by several groups, confirming the formation of mainly NH_2 radicals^{18,19}. This also means providing a corresponding flux of atomic hydrogen (at-H) to the substrate. Importantly, the at-H flux is expected to be even larger compared to that of NH_2 , due to a higher recombination probability of the latter. The generation, recombination and delivery of the radicals to the growth surface were previously studied in our experiments on tellurium etching (for at-H) and silicon nitridation (for NH_2)²⁰.

The HW-assisted deposition led to a dramatic decrease in the GPC with increasing the HW temperature (T_{HW}). Namely, being ~ 0.01 nm/cycle for the HW-off mode (i.e., HW at room temperature), the GPC decreased to ~ 0.001 nm/cycle at $T_{\text{HW}} = 2100$ K (see Figure 4-5). (To note, an efficient dissociation of NH_3 was already observed for $T_{\text{HW}} > 1600$ K²⁰). In spite of the lower GPC, more nitrogen was incorporated into the layers with increasing the T_{HW} . For the specific conditions (see Figure 4-3 caption), the pure-B share decreased from ~ 50 vol.% at $T_{\text{HW}} = 300$ K to ~ 37 vol.% at $T_{\text{HW}} = 1800$ K. This was determined by SE and confirmed by XPS. Furthermore, a clear shift of the XPS B 1s peak position from that of pure-B towards that of stoichiometric-BN was observed with increasing the T_{HW} (to be discussed in Section 4.3.4.1).

Figure 4-5. Dependence of GPC on T_{HW} . Conditions: 2 s of B_2H_6 pulse/ 6 s of Ar for post- B_2H_6 purge / 3 s of NH_3 pulse/ 6 s of Ar for post- NH_3 purge, at a substrate temperature of 275 °C and a total pressure of 2×10^{-3} mbar.

Although utilizing the HW has a clear effect on both GPC and stoichiometry, the concentration of as-generated N-containing radicals seems to be not high enough to effectively nitridize the growing film. The competing interaction of at-H with the surface was hypothesized to decrease the GPC. This will be discussed in Section 4.4.2. We further proceed with a plasma radical source, as it is expected to provide a higher degree of NH_3 dissociation.

4.3.3 Plasma-assisted deposition

The depositions were performed with the Picosun reactor on an SiO_2 layer (100 nm) at 310 °C. To bear in mind, the previously-described experiments were performed at comparable substrate temperatures of 290 ± 20 °C. The total gas pressure was kept at 1 mbar for all plasma experiments, corresponding to the pure-B share of ~6 vol.% of the purely thermal mode (recall Figure 4-4.b). The other process conditions were kept identical to the thermal counterpart. Remarkably, the GPC with plasma (0.017 nm/cycle) was hardly changed compared to that of the thermal mode (0.020 nm/cycle), meaning that the plasma merely enhanced the nitridation process. The latter was confirmed by both SE and XPS. The XPS revealed near stoichiometric BN films at the surface (see Figure 4-6); the difference

between the B and N shares increased with sputter depth, possibly due to preferential sputtering ²¹.

Figure 4-6. XPS sputter depth profile of a plasma deposited BN film. Conditions: 0.2 s of B_2H_6 pulse / 5 s of Ar for post B_2H_6 purge / 11.5 s of NH_3 pulse/ 10 s of Ar for post- NH_3 purge, at a substrate temperature of 310 °C and a total pressure of 1 mbar.

4.3.4 Comparative analysis of the film properties

4.3.4.1 XPS analysis

A comparison of the B 1s and N 1s spectra showed a significant influence of the growth methods. The amount of pure-B, estimated by SE and verified by XPS, decreased from ~50 to ~37 vol.% for the thermally- and HW-deposited films, respectively. The plasma enhancement resulted in 46 at.% of N, 50 at.% of B, and 4 at.% of oxygen.

The B 1s spectra were taken after sputtering the top 0.5-1 nm of the film surface, to prevent the contribution of various surface contaminants. A comparison of the B 1s spectra of pure-B as well as thermally-, HW- and plasma-deposited B/BN films is given in Figure 4-7.

Figure 4-7. (a) XPS B 1s spectra of pure-B (i), thermally- and HW- deposited B/BN (ii)-(iii), and plasma-deposited BN films (iv). (b) XPS N 1s spectra of films (ii)-(iv) from (a). For deposition conditions see the captions of Figures 4-4, 4-5 and 4-6.

Going from thermal through HW- to plasma-assisted deposition, one can clearly see that the B 1s peak broadens towards higher binding energies, and that the binding energy of the main peak gradually shifts from 188.4 eV (i.e., B-B bonding²²) to 190.6 eV (i.e., B-N bonding^{10,11,23}). This confirms that effective nitridation is enabled by the external energy sources. In addition to the B 1s spectra, we analyzed the N 1s-peak binding energies (Figure 4-7.b). For all the samples, the N 1s peak positions corresponded to stoichiometric-BN; no shift towards higher or lower binding energies was observed.

To investigate the gradual shift of the B 1s peak with increasing a degree of nitridation (Figure 4-7), B 1s peak deconvolution was performed (Figure 4-8). It was concluded that the broad features seen for the thermally- and HW-deposited films could adequately be described by two Gaussian peaks at binding energies of pure-B and stoichiometric-BN. On the other hand, the B 1s peak of the plasma-deposited film was fitted by a single Gaussian peak at the B-N binding energy. These results are consistent with the formation of mixed pure-B and stoichiometric-BN phases in the thermally- and HW-deposited films, whereas plasma assistance leads to growing near-stoichiometric BN. More discussion on the existence of these two phases mixed in the as-made films can be found in Chapter 3.

Figure 4-8. *B 1s peak deconvolution for (a) pure-B, (b) thermally- and (c) HW- deposited B/BN, and (d) plasma-deposited BN. Contributions of several chemical bonding environments (B-O^{24,25}, B-B²² and B-N^{10,11,23}) are included in the fits. For deposition conditions see the captions of Figures 4-4, 4-5 and 4-6.*

4.3.4.2 Stability in air

Environmental stability of BN is of prime importance for practical applications and occurs for films with a sufficient degree of crystallinity. It is known that (partially) amorphous and low-crystal-order BN films can quickly degrade in air due to their interaction with oxidizing species¹⁴, whereas h-BN layers are chemically inert in many environments²⁶. Degradation in air is therefore a measure of the film crystallinity.

The degradation can be investigated by ex-situ SE. The measurements were performed on as-deposited (i.e., measured within 20 minutes) samples and after their exposure to air for more than 6 months. To draw conclusions regarding the degradation of the films, a comparison of the delta-values (see Chapter 2) was carried out, since delta is rather sensitive to changes in thickness and optical functions¹⁶. It can be concluded from Figure 4-9 that the thermally- and HW-deposited samples significantly changed their optical responses after this long exposure, presumably due to their oxidation, whereas the plasma-deposited

samples showed no change. The latter might be a first indication of a crystalline structure^{13,14}.

Figure 4-9. Delta-values of (a) thermally-, (b) HW- and (c) plasma -deposited layers, for as-deposited samples and after their exposure to air for 6 months. Graphs (d-f) show the difference between the corresponding delta-values in (a-c), respectively. The sharp difference observed in (f) is a measurement artefact.

4.3.4.3 Crystallinity from HRTEM

A crystalline structure of the plasma-deposited films is confirmed by HRTEM. Figure 4-10.a shows a lamellar-type structure with crystal planes perpendicular to the substrate surface. Line profile analysis (the inset) performed on the FFT1 area reveals interplane distances (d -spacing) ranging between 3.4 and 3.8 Å. These values fall in the range previously reported for hexagonal boron nitride (3.3-3.7 Å)^{8,9,12,15,27-29}.

A detailed analysis of the interplane distance was further conducted by using radial profile analysis with ImageJ 1.52i³⁰ and Radial Profile Extended³¹ software. Fast Fourier Transform (FFT) analysis of the 3 boxed areas in Figure 4-10.a revealed an average interplane distance of 3.57 Å, with a second periodicity at 2.16 Å, as depicted in Figure 4-10.b. The former matches with the (002) *d*-spacing of h-BN (3.3-3.7 Å), while the latter corresponds to the (100) *d*-spacing of h-BN (2.17 Å). This is close to the values in sphalerite β-BN (2.09 Å)³² and wurtzite γ-BN (2.20 Å and 2.10 Å)³³. These two structures however do not have any *d*-spacing above 2.2 Å, and so cannot cause the broad peak centered at 3.57 Å. In the 3.3-3.7 Å range reported for BN, the larger spacing shifts have been attributed to curved³⁴ and turbostratic³⁵ BN. The *d*-spacing may increase due to the presence of NH_x (x=1-2) groups in BN, similar to the effect of hydroxyl or carboxyl groups reported for graphite^{36,37}.

Figure 4-10. (a) HRTEM image of a plasma-deposited BN layer (after 4 months being stored in air) on thermally grown SiO₂. The 3 boxes indicate the areas for Fast Fourier Transform (FFT) analysis. Inset: line profile inside area FFT1, showing the interlayer distance ranging between 3.4 and 3.8 Å (with a pixel size of 0.2 Å). (b) Radial profiles of the FFT power spectra of the 3 boxed areas in (a) ††.

†† Contributed by A.J. Onnink (University of Twente) and included into the joint publication of R.O. Apaydin and A.J. Onnink, see the list of publications at the end of this thesis.

4.3.4.4 Other analyses

The plasma-deposited samples showed no detectable amount of pure-B, as additionally confirmed by EFTEM. The elemental maps indicated only nitrogen and boron with some trace amounts of oxygen (see Figure 4-11).

Figure 4-11. EFTEM element-maps of the plasma-deposited BN sample of Figure 4-10: (a) boron, (b) nitrogen, (c) oxygen and (d) silicon.

GIXRD analysis of the plasma-deposited film of Figure 4-10 confirmed the occurrence of an h-BN phase in that film. The diffraction-peak positions in Figure 4-12 coincide well with the values reported for h-BN³⁸. Fitting the mass density by XRR revealed 1.82 g/cm³ - close to 1.89 g/cm³ reported for h-BN films³⁹.

Figure 4-12. GIXRD pattern of the plasma-deposited BN sample of Figure 4-10. Miller indices are given in the image. The peaks coincide well with the corresponding positions (indicated by vertical red bars) reported for h-BN ³⁸.

4.4 Suggested deposition mechanisms

The demonstrated dependence of both GPC and pure-B share on P_{tot} (recall Figure 4-4) allows to hypothesize the so-called surface-adduct pathway (see Section 2.3) for the formation of BN layers from B_2H_6 and NH_3 at high pressures.

4.4.1 Surface-adduct pathway for purely thermal deposition

B_2H_6 and BH_3 gases are Lewis acids ^{40,41} whereas NH_3 is a Lewis base ⁴². Such acids and bases can readily react and form corresponding adducts. The basics of the adduct formation were already given in Chapter 2.

We start with an overview of previous reports, among others by Carpenter et.al. ⁴³, Gómez- Aleixandre et.al. ⁴⁴, Rand et.al. ⁴⁵ and Gerry et.al. ⁴⁶. The essential reactions between diborane and ammonia are summarized elsewhere ⁴⁷. It should be noted that the formation of a gas phase $\text{H}_6\text{B}_2\text{:NH}_3$ adduct from B_2H_6 and NH_3 has been suggested to be the most energetically favorable reaction, based on the calculations performed by Nguyen et.al. ⁴⁸. Further, through a subsequent release

of H_2 and BH_3 , first $H_2B=NH_2$ and then $HB=NH$ species can be produced. As the reaction temperature increases, the adduct complex progressively loses hydrogen and, at temperatures above 500 °C, boron nitride can finally be obtained ^{43–46,49–51}. Gómez-Aleixandre et.al. ⁴⁴ showed that, as a result of the limited (partial) dissociation of ammonia at temperatures lower than 850 °C, the interaction between diborane and ammonia, leading to BN, is strongly temperature dependent.

The gas-phase decomposition of B_2H_6 was studied by many researchers ^{52–58,59}. On a surface, B_2H_6 is known to cause non-self-limiting formation of solid boron ^{17,59–61}. The studies of Fehlner ^{62–65}, Mappes ⁶⁶, and Sarubbi et.al. ⁶⁷ suggested BH_3 species to dominate in the gas phase. Mohammedi et.al. ¹⁷ proposed a growth model based on chemisorption of BH_3 and the subsequent elimination of H_2 . A similar mechanism for the interaction of B_2H_6 with silicon oxide surfaces has been proposed by Gillis-D'Hamers ^{68,69}. The authors showed that, upon the chemisorption, diborane forms BH- or BH_2 -terminated surface sites. To simplify the reaction schematic in our case, we only draw BH-terminations in Figure 4-13.

Thus, the initial step in thermal deposition of BN from B_2H_6 and NH_3 is likely the decomposition of B_2H_6 (in gas phase or on the surface), forming BH-terminations accompanied by a release of H_2 . In the next step, we hypothesize the NH_3 adsorption and the occurrence of a surface adduct, analogous to the known ⁷⁰ gas-phase $H_3B:NH_3$ adduct. This and the following steps are proposed to occur similarly to the formation of AlN and GaN films (see Chapter 2). Further, a reaction of the adduct- NH_3 with hydrogen of a neighboring -BH termination occurs, releasing H_2 (Figure 4-13.a). This forms - NH_2 - bridges between neighboring B atoms (i.e., B- NH_2 -B linkages), analogous to Al- NH_2 -Al linkages in AlN ALD ⁷¹. Such B- NH_2 -B linkages laterally expand over the entire growth surface in a self-limiting fashion. Exposure to B_2H_6 during the subsequent precursor pulse restores the required BH-terminations (not a self-limiting process), again with releasing H_2 . It should be noted that direct thermal nitridation of a pure-B phase is thermodynamically inhibited at temperatures below 900 °C ⁷². However, via the

proposed adduct-assisted pathway, nitrogen can still be effectively incorporated at much lower temperatures.

Figure 4-13. Proposed schematic of BN formation from B_2H_6 and NH_3 . (a) In thermal mode: via the formation of a surface adduct and then its conversion into B-NH₂-B linkages. (b) In radical-enhanced mode (HW or plasma): via additional removal of surface species by atomic hydrogen (at-H) and involvement of NH_x ($x=1-2$) radicals, as well as via direct nitridation by atomic nitrogen (for plasma only).

4.4.2 A comparison of pure-thermal and radical-enhanced modes

Applying radical-enhanced methods (HW or plasma) is expected to alter the growth mechanism. The dissociation of NH_3 into NH_x ($x=0-2$) radicals^{18,73–75} and at-H may facilitate alternative chemical routes and thus suppress the adduct-assisted pathway. First, the generated at-H can remove hydrogen of the BH terminations (so-called hydrogen abstraction^{76,77}), thereby decreasing the number of H-B surface sites required to maintain the adduct-assisted mechanism (Figure 4-13.b). On the other hand, the presence of reactive NH_x radicals in sufficient quantities can still support the formation of B-NH₂-B and/or B-NH-B linkages. Atomic nitrogen can further directly nitridize elemental boron. For optimized process conditions, radical-enhanced methods increase the nitrogen-share (see Sections 4.3.2 and 4.3.3), still having diborane chemisorption as the rate limiting step. On the other hand, non-optimized conditions may lead to a lower GPC (see

Figure 4-5) and an increased B-share. The latter is due to a decreased efficiency of nitrogen incorporation via the surface-adduct mechanism, as schematically shown in Figure 4-13.b. A deficiency of NH_x radicals at the growth surface, for example due to a low-power radical source or because of their recombination on the way to the substrate ¹⁸, results in boron rich samples. Our experiments show that the highest degree of nitrogen incorporation is provided by plasma-assisted growth; this gives near-stoichiometric, crystalline and air-stable BN films at a substrate temperature of 310 °C.

4.5 Conclusions

This chapter studied the formation of B/BN composites using purely thermal, hot-wire- and plasma-assisted deposition methods by sequentially pulsing B_2H_6 and NH_3 precursors. It has been demonstrated that, in purely thermal mode, increasing the total gas pressure considerably enhances the GPC, incorporating a bigger share of nitrogen in the layers and thereby reducing the pure-B content from ~70 vol.% to 6-7 vol.%. However, a further decrease of the pure-B share, to obtain a stoichiometric BN in thermal mode, is challenging. To improve both stoichiometry and crystallinity, HW- and plasma-assisted methods have been explored. Utilizing the HW had a clear effect on both GPC and film composition, although the concentration of NH_2 radicals was not sufficiently high to strongly decrease the pure-B share. Switching to plasma provided near-stoichiometric, crystalline and air-stable BN films at just 310 °C.

Concerning the growth mechanism in purely thermal mode, we hypothesized a surface-adduct-assisted reaction pathway, analogous to the earlier suggested surface-adduct mechanisms for growing AlN and GaN by thermal ALD at low temperatures. Namely, BH-terminated surface sites react with NH_3 , forming surface adducts. The adduct- NH_3 consequently reacts with hydrogen of a neighboring BH-termination, forming B- NH_2 -B linkages and releasing H_2 . A subsequent B_2H_6 pulse restores the original BH-terminations, once more eliminating H_2 . The adduct-assisted pathway is proposed to enable effective

incorporation of nitrogen into BN films at low temperatures. Applying HW or plasma may provide additional reaction pathways and alter the growth mechanism.

References

- ¹ S. Nakhaie, J.M. Wofford, T. Schumann, U. Jahn, M. Ramsteiner, M. Hanke, J.M.J. Lopes, and H. Riechert, *Appl. Phys. Lett.* **106**, 213108 (2015).
- ² T.Q.P. Vuong, G. Cassaboiss, P. Valvin, E. Rousseau, A. Summerfield, C.J. Mellor, Y. Cho, T.S. Cheng, J.D. Albar, L. Eaves, C.T. Foxon, P.H. Beton, S. V. Novikov, and B. Gil, *2D Mater.* **4**, 021023 (2017).
- ³ J. Ying, X.W. Zhang, Y.M. Fan, H.R. Tan, and Z.G. Yin, *Diam. Relat. Mater.* **19**, 1371 (2010).
- ⁴ C. Ronning, A.D. Banks, B.L. McCarson, R. Schlessner, Z. Sitar, R.F. Davis, B.L. Ward, and R.J. Nemanich, *J. Appl. Phys.* **84**, 5046 (1998).
- ⁵ Y. Panayiotatos, S. Logothetidis, A. Laskarakis, A. Zervopoulou, and M. Gioti, *Diam. Relat. Mater.* **11**, 1281 (2002).
- ⁶ S. Kotake, T. Hasegawa, K. Kamiya, Y. Suzuki, T. Masui, Y. Kangawa, K. Nakamura, and T. Ito, *Appl. Surf. Sci.* **216**, 72 (2003).
- ⁷ M. Xie, J. Wang, and Y.K. Yap, *J. Phys. Chem. C* **114**, 16236 (2010).
- ⁸ S.K. Jang, J. Youn, Y.J. Song, and S. Lee, *Sci. Rep.* **6**, 30449 (2016).
- ⁹ Y. Shi, C. Hamsen, X. Jia, K.K. Kim, A. Reina, M. Hofmann, A.L. Hsu, K. Zhang, H. Li, Z.-Y. Juang, M.S. Dresselhaus, L.-J. Li, and J. Kong, *Nano Lett.* **10**, 4134 (2010).
- ¹⁰ K.K. Kim, A. Hsu, X. Jia, S.M. Kim, Y. Shi, M. Hofmann, D. Nezich, J.F. Rodriguez-Nieva, M. Dresselhaus, T. Palacios, and J. Kong, *Nano Lett.* **12**, 161 (2012).
- ¹¹ N.R. Glavin, C. Muratore, M.L. Jespersen, J. Hu, P.T. Hagerty, A.M. Hilton, A.T. Blake, C.A. Grabowski, M.F. Durstock, M.E. McConney, D.M. Hilgert, T.S. Fisher, and A.A. Voevodin, *Adv. Funct. Mater.* **26**, 2640 (2016).
- ¹² K.H. Lee, H.-J. Shin, J. Lee, I. Lee, G.-H. Kim, J.-Y. Choi, and S.-W. Kim, *Nano Lett.* **12**, 714 (2012).
- ¹³ J.L. Andújar, E. Bertran, and M.C. Polo, *J. Vac. Sci. Technol. A Vacuum, Surfaces, Film.* **16**, 578 (1998).
- ¹⁴ C. Gómez-Aleixandre, A. Essafti, M. Fernández, J.L.G. Fierro, and J.M. Albella, *J. Phys. Chem.* **100**, 2148 (1996).
- ¹⁵ A. Ismach, H. Chou, D.A. Ferrer, Y. Wu, S. McDonnell, H.C. Floresca, A. Covacevich, C. Pope, R. Piner, M.J. Kim, R.M. Wallace, L. Colombo, and R.S. Ruoff, *ACS Nano* **6**, 6378 (2012).
- ¹⁶ H. Fujiwara, *Spectroscopic Ellipsometry: Principles and Applications* (John Wiley & Sons Ltd, 2007).
- ¹⁷ V. Mohammadi, W.B. de Boer, and L.K. Nanver, *Appl. Phys. Lett.* **101**, 111906 (2012).

- ¹⁸ H. Umemoto, K. Ohara, D. Morita, T. Morimoto, M. Yamawaki, A. Masuda, and H. Matsumura, *Jpn. J. Appl. Phys.* **42**, 5315 (2003).
- ¹⁹ G. Yuan, H. Shimizu, T. Momose, and Y. Shimogaki, *J. Vac. Sci. Technol. A Vacuum, Surfaces, Film.* **32**, 01A104 (2014).
- ²⁰ A.Y. Kovalgin, M. Yang, S. Banerjee, R.O. Apaydin, A.A.I. Aarnink, S. Kinge, and R.A.M. Wolters, *Adv. Mater. Interfaces* **4**, 1700058 (2017).
- ²¹ T. Ichiki and T. Yoshida, *Appl. Phys. Lett.* **64**, 851 (1994).
- ²² L. Chen, T. Goto, T. Hirai, and T. Amano, *J. Mater. Sci. Lett.* **9**, 997 (1990).
- ²³ L. Ci, L. Song, C. Jin, D. Jariwala, D. Wu, Y. Li, A. Srivastava, Z.F. Wang, K. Storr, L. Balicas, F. Liu, and P.M. Ajayan, *Nat. Mater.* **9**, 430 (2010).
- ²⁴ M. Belyansky, M. Trenary, and C. Ellison, *Surf. Sci. Spectra* **3**, 147 (1994).
- ²⁵ C. Kimura, H. Sota, H. Aoki, and T. Sugino, *Diam. Relat. Mater.* **18**, 478 (2009).
- ²⁶ G.R. Bhimanapati, N.R. Glavin, and J.A. Robinson, in *Semicond. Semimetals*, edited by C.J. Francesca Iacopi, John J. Boeckl (Elsevier Ltd, 2016), pp. 101–147.
- ²⁷ O. Cometto, B. Sun, S.H. Tsang, X. Huang, Y.K. Koh, and E.H.T. Teo, *Nanoscale* **7**, 18984 (2015).
- ²⁸ J. Wang, F. Ma, and M. Sun, *RSC Adv.* **7**, 16801 (2017).
- ²⁹ S.M. Kim, A. Hsu, M.H. Park, S.H. Chae, S.J. Yun, J.S. Lee, D.-H. Cho, W. Fang, C. Lee, T. Palacios, M. Dresselhaus, K.K. Kim, Y.H. Lee, and J. Kong, *Nat. Commun.* **6**, 8662 (2015).
- ³⁰ C.A. Schneider, W.S. Rasband, and K.W. Eliceiri, *Nat. Methods* **9**, 671 (2012).
- ³¹ P. Carl, Radial profile extended, plugin to ImageJ, (2017).
- ³² R.W.G. Wyckoff, *Crystal Structures Vol. 1*, 2nd ed. (Interscience Publishers, New York, 1963).
- ³³ Y.-N. Xu and W.Y. Ching, *Phys. Rev. B* **48**, 4335 (1993).
- ³⁴ P. Ahmad, M.U. Khandaker, N. Muhammad, F. Rehman, G. Khan, M.A. Rehman, S.M. Ahmed, M. Gulzar, A. Numan, and A.S. Khan, *Ceram. Int.* **43**, 7358 (2017).
- ³⁵ S. Chen, P. Li, S. Xu, X. Pan, Q. Fu, and X. Bao, *J. Mater. Chem. A* **6**, 1832 (2018).
- ³⁶ M. Cabello, X. Bai, T. Chyrka, G.F. Ortiz, P. Lavela, R. Alcántara, and J.L. Tirado, *J. Electrochem. Soc.* **164**, A3804 (2017).
- ³⁷ L. Zhechkov, *Simulations of the Hydrogen Storage Capacities of Carbon Materials*, TU Dresden, 2007.
- ³⁸ S. Yuan, S. Linas, C. Journet, P. Steyer, V. Garnier, G. Bonnefont, A. Brioude, and B. Toury, *Sci. Rep.* **6**, 20388 (2016).
- ³⁹ S. V. Nguyen, *J. Electrochem. Soc.* **141**, 1633 (1994).

- ⁴⁰ Y. Katsuma, L. Wu, Z. Lin, S. Akiyama, and M. Yamashita, *Angew. Chemie* **131**, 323 (2019).
- ⁴¹ R.H. Petrucci, F.G. Herring, J.D. Madura, and C. Bissonnette, *General Chemistry Principles and Modern Applications*, 11th ed. (Pearson Canada Inc., 2017).
- ⁴² S. Sakai, *J. Phys. Chem.* **99**, 9080 (1995).
- ⁴³ J.D. Carpenter and B.S. Ault, *J. Phys. Chem.* **96**, 7913 (1992).
- ⁴⁴ C. Gomez-Aleixandre, D. Diaz, F. Orgaz, and J.M. Albella, *J. Phys. Chem.* **97**, 11043 (1993).
- ⁴⁵ M.J. Rand and J.F. Roberts, *J. Electrochem. Soc.* **115**, 423 (1968).
- ⁴⁶ M.C.L. Gerry, W. Lewis-Bevan, A.J. Merer, and N.P.C. Westwood, *J. Mol. Spectrosc.* **110**, 153 (1985).
- ⁴⁷ D. Franz, M. Hollenstein, and C. Hollenstein, *Thin Solid Films* **379**, 37 (2000).
- ⁴⁸ V.S. Nguyen, M.H. Matus, M.T. Nguyen, and D.A. Dixon, *J. Phys. Chem. A* **112**, 9946 (2008).
- ⁴⁹ S. Frueh, R. Kellett, C. Mallery, T. Molter, W.S. Willis, C. King'ondeu, and S.L. Suib, *Inorg. Chem.* **50**, 783 (2011).
- ⁵⁰ M.G. Hu, R.A. Geanangel, and W.W. Wendlandt, *Thermochim. Acta* **23**, 249 (1978).
- ⁵¹ V.I. Simagina, N.V. Vernikovskaya, O.V. Komova, N.L. Kayl, O.V. Netskina, and G.V. Odegova, *Chem. Eng. J.* **329**, 156 (2017).
- ⁵² L.H. Long, *J. Inorg. Nucl. Chem.* **32**, 1097 (1970).
- ⁵³ N.N. Greenwood and R. Greatrex, *Pure Appl. Chem.* **59**, 857 (1987).
- ⁵⁴ N.N. Greenwood, *Chem. Soc. Rev.* **21**, 49 (1992).
- ⁵⁵ A.B. Baylis, G.A. Pressley, E.J. Sinke, and F.E. Stafford, *J. Am. Chem. Soc.* **86**, 5358 (1964).
- ⁵⁶ L. V. McCarty and P.A. Di Giorgio, *J. Am. Chem. Soc.* **73**, 3138 (1951).
- ⁵⁷ S.A. Fridmann and T.P. Fehlner, *Inorg. Chem.* **11**, 936 (1972).
- ⁵⁸ T.P. Fehlner and S.A. Fridmann, *J. Am. Chem. Soc.* **93**, 2824 (1971).
- ⁵⁹ H. Habuka, S. Akiyama, T. Otsuka, and W.F. Qu, *J. Cryst. Growth* **209**, 807 (2000).
- ⁶⁰ V. Mohammadi, N. Golshani, K.R.C. Mok, W.B. de Boer, J. Derakhshandeh, and L.K. Nanver, *Microelectron. Eng.* **125**, 45 (2014).
- ⁶¹ M.L. Yu, D.J. Vitkavage, and B.S. Meyerson, *J. Appl. Phys.* **59**, 4032 (1986).
- ⁶² T.P. Fehlner and W.S. Koski, *J. Am. Chem. Soc.* **86**, 2733 (1964).
- ⁶³ T.P. Fehlner, *J. Am. Chem. Soc.* **87**, 4200 (1965).
- ⁶⁴ T.P. Fehlner and G.W. Mappes, *J. Phys. Chem.* **73**, 873 (1969).

- ⁶⁵ T.P. Fehlner and S.A. Fridmann, *Inorg. Chem.* **9**, 2288 (1970).
- ⁶⁶ A.B. Baylis, G.A. Pressley, and F.E. Stafford, *J. Am. Chem. Soc.* **88**, 2428 (1966).
- ⁶⁷ F. Sarubbi, T.L.M. Scholtes, and L.K. Nanver, *J. Electron. Mater.* **39**, 162 (2010).
- ⁶⁸ I. Gillis-D'Hamers, K.C. Vrancken, P. Van Der Voort, E.F. Vansant, and G. De Roy, *J. Chem. Soc. Faraday Trans.* **88**, 1459 (1992).
- ⁶⁹ I. Gillis-D'Hamers, P. Van Der Voort, K.C. Vrancken, G. De Roy, and E.F. Vansant, *J. Chem. Soc. Faraday Trans.* **88**, 65 (1992).
- ⁷⁰ J.D. Carpenter and B.S. Ault, *J. Phys. Chem.* **95**, 3507 (1991).
- ⁷¹ M.E. Bartram, T.A. Michalske, J.W. Rogers, and R.T. Paine, *Chem. Mater.* **5**, 1424 (1993).
- ⁷² F. Ye, L. Zhang, Y. Liu, S. Li, M. Su, X. Yin, and L. Cheng, *Prog. Nat. Sci. Mater. Int.* **22**, 433 (2012).
- ⁷³ Y.J. Shi, B.D. Eustergerling, and X.M. Li, *Thin Solid Films* **516**, 506 (2008).
- ⁷⁴ R. D'Agostino, F. Cramarossa, S. De Benedictis, and G. Ferraro, *Plasma Chem. Plasma Process.* **1**, 19 (1981).
- ⁷⁵ G.P. Miller and J.K. Baird, *J. Phys. Chem.* **97**, 10984 (1993).
- ⁷⁶ S. Agarwal, A. Takano, M.C.M. van de Sanden, D. Maroudas, and E.S. Aydil, *J. Chem. Phys.* **117**, 10805 (2002).
- ⁷⁷ H.A. Kazmi and D.J. Le Roy, *Can. J. Chem.* **42**, 1145 (1964).

5 Thermal deposition of BN from BBr₃ and NH₃

Abstract

In this chapter thermal deposition of boron nitride thin films by sequential introduction of boron tribromide (BBr₃) and ammonia (NH₃) precursors with an Ar purge in between is investigated.

We further continue exploring the role of the surface adducts (see also Chapter 4) and thus hypothesize the existence of an analogous BBr₃:NH₃ surface adduct which facilitates the growth of BN layers. The reaction kinetics is simulated using a Mathcad code. The results are in agreement with the assumption that the adduct surface coverage may depend on the ammonia partial pressure (P_{NH_3}) in the reactor, assuming the reaction to occur in equilibrium. In accordance with the expectations, the growth per cycle (GPC) exhibit a reasonable dependence on P_{NH_3} : the GPC increases at least by factor 2 in the P_{NH_3} range studied. The SE analysis reveals the refractive index (n) similar to that reported for α -BN and h -BN. The XPS results indicate stoichiometric BN films with O contamination less than 5 at.%; the films are however found to be environmentally instable. The GIXRD results reveal nanocrystalline structure of the films.

5.1 Introduction

This chapter discusses the growth of boron nitride (BN) layers by a sequential introduction of boron tribromide (BBr_3) and ammonia (NH_3) precursors, with Ar-purges in between, in thermal ALD mode. We show that BN growth can take place with reasonably high (~ 0.08 nm/cycle) growth per cycle (GPC) values. The suggested mechanism relies on the speculated existence of a $\text{BBr}_3\text{:NH}_3$ surface adduct and its conversion into BN. The formation of the surface adduct is enhanced by the partial pressure of NH_3 (P_{NH_3}), directly affecting the GPC.

Section 5.2 reviews the previously reported surface reactions in relation to BN growth. Section 5.3 proposes the BN growth model, based on a similar model reported in the literature, as explained in Sections 2.3 and 5.2. Section 5.4 deals with the expected reaction kinetics of BN growth. Section 5.5 reports the experimental results, in line with the proposed deposition mechanism. Section 5.6 concludes this chapter.

5.2 Surface reactions in relation to BN growth

Various gas-phase and surface reactions (including the adduct formation) in relation to ALD of aluminum nitride (AlN) and gallium nitride (GaN) films have been discussed in Chapter 2. Here, we extend that knowledge towards a possible formation of halide-based adducts with boron included. Boron trihalides (BX_3 , $\text{X} = \text{Br, Cl, F}$) are known to be typical Lewis acids. These halides show a strong affinity for sharing a pair of electrons with Lewis bases, such as NH_3 , to satisfy the octet rule ¹. In this way, stable donor-acceptor complexes having a B-N bond can be formed. Such boron halide complexes have been investigated in both experimental ²⁻¹¹ and theoretical works ¹²⁻¹⁹. The studies showed that, once introduced into the system, boron halides react with Lewis bases to form adducts. This may suggest a similar growth mechanism as reported for AlN and GaN ALD.

Gas phase adducts of boron halides were experimentally observed by many researchers, see for example Refs. ^{2-4,6}. In addition, theoretical studies have been performed in order to obtain understanding of the gas phase reactions. Reinhardt et.al. ^{12,13} suggested the formation of a gas phase adduct (reaction 5.1), that decomposes to aminodichloroborane (reaction 5.2) by the elimination of hydrogen chloride (HCl). One should keep in mind that HCl can react with available NH₃ molecules and form NH₄Cl ^{8,9,20}.

Possemiers et.al. ^{8,9,21} further studied the reactions between BCl₃ and NH₃ on silica surfaces. In their studies, they introduced BCl₃ and NH₃ gases onto silica surfaces in a sequential manner, preventing gas phase reactions. They reported that NH₃ exposure on the BCl₃ pre-treated surface results in an increased NH₃ sorption capacity of the surface. Upon sorption, surface boron species react with NH₃, forming chemisorbed =BNH₂ groups and NH₄Cl (sublimes above 100 °C). Above 200 °C, secondary amines (=B-NH-B=) are being formed via a consecutive reaction mechanism, completely covering the surface at 300 °C. Subsequent introduction of precursors results in a cross-linked borazine-like B-N polymeric structure, which finally forms BN with NH₄Cl released as the reaction by-product. The main reactions of the BCl₃-treated surface with ammonia are summarized below:

Formation of the compounds reported by Possemiers et al. was also studied by George et al. ¹⁰. They investigated the formation of BN on zirconium dioxide (ZrO₂) particles by sequential exposures to BCl₃ and NH₃. Upon the delivery of

NH₃ molecules onto the BCl₃-treated surface, absorption bands attributed to -BNH₂ and -B₂NH surface species were observed by Fourier transform infrared spectroscopy (FTIR), indicating the -NH₂- bridge formation analogous to that reported for AlN growth ²².

As can be deduced from the above-mentioned studies, BN deposition reactions proceed in a similar manner compared to the reactions reported for AlN ALD ²² (recall Figure 2-2).

5.3 Proposed BN growth mechanisms

5.3.1 Thermal-BN deposition via surface adduct pathway

Based on the known mechanisms of AlN ALD ²², Banerjee et.al. ²³ recently hypothesized a similar mechanism for GaN ALD. In this work, we further extend the mechanism to BN growth from BBr₃ and NH₃. Namely, the BN growth is proposed to occur in two stages (see Figure 5-1): (i) formation of a BBr₃:NH₃ ‘surface adduct’ complex (reversible or irreversible), and (ii) conversion of this complex into B-NH₂-B linkage (irreversible), resulting in a unit of BN. From this model, the GPC is expected to depend on NH₃ partial pressure (P_{NH_3}) and NH₃ pulse time (t_{NH_3}). The latter is usually the case, but the former is not typical for ALD. If the surface adduct formation is reversible, a higher P_{NH_3} increases the surface density of the adduct by shifting the equilibrium in the direction of adduct formation. This further leads to enhancing the B-NH₂-B linkage formation, thereby increasing the GPC. The formation of BN units will proceed until bridging all neighboring sites via -NH₂- linkages is complete, provided that a sufficient amount of NH₃ is present in the reactor.

Figure 5-1. Proposed mechanism of BN growth by two-step reaction. First, formation of surface adducts; second conversion of the adducts into B-NH₂-B linkages. Although the chemisorption of BBr₃ can result in a variety of BBr_x (x=1-3) surface species, here, for simplicity, we limit that to B-Br terminated surface only. The exact nature of the BBr₃ chemisorption is beyond the scope of this work.

5.4 Modeling the thermal-BN growth

The first step in the proposed mechanism, i.e., the BBr₃:NH₃ surface-adduct formation, is assumed to be reversible. This is analogous to the reversible formation of the BCl₃:NH₃ gas-phase adduct known from the literature²⁴. Briefly, Kapralova et. al.²⁴ reported pressure dependent reaction rates for the BCl₃-NH₃ system (at 72 °C) and attributed a decrease of the reaction rate of HCl elimination, in a certain pressure range, to the reversible adduct formation. Reinhardt et.al.^{12,13} theoretically investigated the BCl₃-NH₃ reactions and showed that the adduct formation is an exothermic reaction yielding approximately 25 kcal/mol energy. Since first HCl release requires just a bit higher energy of ~32 kcal/mol, the adduct may start decomposing by releasing HCl and thus yielding Cl₂BNH₂. Kingsmill et.al.²⁵ reported that the BBr₃:NH₃ adduct occurs already at room temperature; however, the removal of first HBr molecule requires a temperature of 240 °C.

The assumed reversibility of the BBr₃:NH₃ surface-adduct formation implies that, once physisorbed as adduct, before establishing a stable B-NH₂-B linkage, NH₃ can desorb back into the gas phase. The linkage irreversibly forms from reaction of an adduct-NH₃ with -Br of an adjacent B-Br_x site. For TMA:NH₃ and BCl₃:NH₃ surface adducts, such reactions have been reported^{8,9,22}. Although chemisorption of BBr₃ can result in a variety of BBr_x (x=1-3) surface species, here,

for simplicity, we limit the discussion to B-Br (i.e., x=1) terminated surfaces only. The exact mechanism of the BBr₃ chemisorption is beyond the scope of this work.

The reversible adsorption of NH₃ on the chemisorbed B-Br sites can be described by the Langmuir adsorption-desorption kinetics²⁶. Equation 5.1 shows the adduct surface coverage θ expressed via the concentration of NH₃ (C_{NH3}). In this equation, NH₃ adsorption and desorption rate constants are given by k_a and k_d , respectively. From equation 5.1, the surface coverage is a function of t_{NH3} and C_{NH3} . The latter corresponds to the partial pressure (P_{NH3}) via $C_{NH3}=P_{NH3}/k_B T$, where k_B is the Boltzmann constant and T is the temperature.

$$\theta(t_{NH3}) = \left(\frac{k_a C_{NH3}}{k_a C_{NH3} + k_d} \right) [1 - e^{-(k_a C_{NH3} + k_d)t_{NH3}}] \quad (\text{eq. 5.1})$$

θ is further plotted versus t_{NH3} and P_{NH3} in Figure 5-2.a, after choosing reasonable (i.e., physically solid) values for k_a ($10^{-11} \text{ cm}^3 \text{ s}^{-1}$) and k_d (10^6 s^{-1})[‡] 26-29. It can be seen that the adduct surface coverage is P_{NH3} dependent and increases with the total pressure. According to Langmuir kinetics, θ approaches to 1 at infinitely high pressure. θ saturates within a few microseconds at low P_{NH3} ; this time shortens at higher pressures. The time required to reach the equilibrium coverage can be affected by changing the k_a and k_d values over several orders of magnitudes. For example, $k_a=10^{-18} \text{ cm}^3 \text{ s}^{-1}$ and $k_d=10^{-2} \text{ s}^{-1}$ cause an equilibrium within tens of seconds. Such rates are however hardly physical, since one is too low and the other is too high.

Since the adduct formation is assumed to be reversible, physisorbed NH₃ molecules can either desorb back to the gas phase or form irreversible -NH₂- bridges by reacting with neighboring -BBr sites thereby eliminating HBr. These considerations were applied in the Mathcad code and the -NH₂- coverage was calculated as a function of t_{NH3} and P_{NH3} . Since the adduct-to-NH₂- conversion rate

‡ For example, k_a values for reactions between boron trifluoride (BF₃) and NH₃, and boron trichloride (BCl₃) and NH₃ range between 10^{-10} and $10^{-14} \text{ cm}^3/\text{s}$. Due to the lack of information, we were not able to find any k_d values reported for reactions of boron halide with NH₃ and therefore used the values reported for GaN deposition, ranging between 10^6 - 10^8 s^{-1} 26-29.

constant is unknown, it was varied between 10^{-14} and $10^{-16} \text{ cm}^2 \text{ s}^{-1}$, yielding time scales similar to those experimentally obtained for GPC (see Figure 5-3.b). As Figure 5-2.b and 5-2.c show, up to several minutes of t_{NH_3} is required to convert all surface adduct sites into $-\text{NH}_2-$ linkages. A complete $-\text{NH}_2-$ coverage indicates the formation of a BN monolayer.

Figure 5-2. Simulated surface coverage with (a) adduct for $k_a = 10^{-11} \text{ cm}^3 \text{ s}^{-1}$ and $k_d = 10^6 \text{ s}^{-1}$, (b) $-\text{NH}_2-$ for $k_{\text{BN}} = 10^{-15} \text{ cm}^2 \text{ s}^{-1}$, (c) $-\text{NH}_2-$ for k_{BN} of 10^{-14} , 10^{-15} and $10^{-16} \text{ cm}^2 \text{ s}^{-1}$.

Indicated pressures correspond to P_{NH_3} . k_{BN} represents the rate of $-\text{NH}_2-$ bridge formation.

From Figure 5-2, the BN deposition is clearly affected by P_{NH_3} . A low P_{NH_3} would result in a low adduct surface coverage and very long t_{NH_3} would be required to complete the surface coverage with $-\text{NH}_2-$ linkages. On the other hand, a high P_{NH_3} would result in a larger adduct surface coverage, requiring a short t_{NH_3} to establish the linkages. The next sections will experimentally confirm these findings.

5.5 Experimental results

5.5.1 Experimental setup

Boron nitride films were deposited on 100 nm thick thermally grown SiO₂ layers by sequentially pulsing BBr₃ and NH₃. An inert (argon - Ar) gas purge was applied between the pulses in order to achieve atomic layer deposition (ALD) conditions. The depositions were performed in a Picosun Plasma R-200 reactor. The total reactor gas-pressure was kept in the range of 1-12 mbar, while the substrate temperatures (T_s) were varied between 240 and 370 °C. The typical pulse and purge times were set to 0.1 s for BBr₃, 30 s for post-BBr₃ Ar-purge, 5-40 s for NH₃, and 20-60 s for post-NH₃ Ar-purge. The details of the ALD window determination are addressed in Section 5.5.2.1.

The film growth was monitored in-situ by a Woollam M-2000XI spectroscopic ellipsometer (SE) served with a J.A. Woollam CompleteEASE software, to determine film thickness and optical constants. The approach and the SE models have been explained in Chapter 2. The XPS sputter depth profiles were obtained with a Thermo theta probe spectrometer of a Quantera SXM microprobe system, using monochromatic Al-K α (1486.6 eV) radiation. The XRR and XRD data were acquired using a Panalytical Empyrean system and analyzed by a Qualx2.0 software ³⁰.

5.5.2 Kinetics of thermal-BN deposition

5.5.2.1 The BN ALD window

The thermal-ALD (t-ALD) experiments were carried out at different t_{NH_3} ($5 \leq t_{\text{NH}_3} \leq 40$ s) and P_{NH_3} ($0.1 \leq P_{\text{NH}_3} \leq 1.5$ mbar) values. To minimize gas phase reactions and promote surface reactions only, long (30-60 s) Ar-purges were necessary (see caption of Figure 5-3) to efficiently remove BBr₃ and especially NH₃. Figure 5-3 clearly shows that the GPC varies with both the P_{NH_3} (Figure 5-3.a) and t_{NH_3} (Figure 5-3.b). One can clearly notice an enhancement by at least a factor of two (i.e., from 0.04 to 0.08 nm/cycle) of the GPC with increasing the P_{NH_3} . A

towards-saturation GPC trend can still be observed while changing the t_{NH_3} , for each P_{NH_3} value (Figure 5-3.b), pointing to an “effective” ALD window. The observed pressure-dependence of the towards-saturation region is rather atypical for ALD. One can see in Figure 5-3.b that the GPC does not quite saturate even at very long pulse durations (20 s, 40 s), indicating still ongoing surface reactions. This could involve the ongoing formation of the surface adduct and its conversion into -NH₂- linkages. Such reaction(s) is(are) presumably rather slow in view of the time range indicated. The actual saturation of the GPC, typical for ALD in general and the particular precursors used, is expected at a longer t_{NH_3} , after completing the B-NH₂-B surface coverage. The sharp increase in the GPC (see the values within the green circle in Figure 5-3.a), which corresponds to the purge time of 20-30 s, only occurs for $P_{\text{NH}_3} > 1$ mbar. This may indicate an insufficient removal of the NH₃ by the 20-30 s long post-NH₃ purges, due to its adsorption on the reactor walls at such high P_{NH_3} . The insufficient purge presumably caused gas phase reactions, significantly enhancing the growth.

Figure 5-3. Variation of GPC as a function of (a) P_{NH_3} and post-NH₃ purge time and (b) t_{NH_3} , as-measured by in-situ SE. Conditions for (a): 0.1 s of BBr₃ pulse / 30 s of Ar for post-BBr₃ purge / 10 s of NH₃ pulse / 20-60 s of Ar for post-NH₃ purge. The indicated $0.1 < P_{\text{NH}_3} < 1.5$ mbar corresponds to $1 \leq P_{\text{tot}} \leq 12$ mbar. Conditions for (b): 0.1 s of BBr₃ pulse / 30 s of Ar for post-BBr₃ purge / 5-40 s of NH₃ pulse / 60 s of Ar for post-NH₃ purge. The given P_{NH_3} values correspond to a total pressure in the range of 1-12 mbar. All depositions were performed at $T_s = 240 \pm 10$ °C on 100 nm thermally grown SiO₂. The dashed lines in (b) are given to guide the eye.

Regarding the influence of substrate temperature, it has been observed that the GPC decreased from 0.05 to 0.033 nm/cycle and from 0.075 to 0.052 nm/cycle at P_{NH_3} of 0.12 mbar and 1.43 mbar, respectively, with increasing substrate

temperature from 240 to 365 °C (Figure 5-4). Although the GPC of a perfect ALD process should be nearly temperature independent within the ALD window, there are exceptions to this rule. For example, in a recent study on GaN ALD²⁹, a gradual increase of the GPC with increasing T_s has been observed. Indications of an ALD process in such cases would be the following: (i) still self-limiting (although temperature dependent) surface reactions and (ii) the right material stoichiometry (i.e., the effective removal of byproducts). The decrease in GPC might indicate a decreased surface-adduct coverage at a higher T_s , in terms of the model proposed in Section 5.3, due to the desorption of NH_3 . The later would mean that the adduct formation is favorable at lower temperatures. A change of the growth mechanism with temperature is less likely, since both graphs in Figure 5-4 reveal similar activation energies for P_{NH_3} of 0.12 and 1.43 mbar (P_{tot} of 1 and 12 mbar respectively).

Figure 5-4. Arrhenius plot of GPC against reciprocal temperature for samples deposited at P_{NH_3} of (a) 0.12 and (b) 1.43 mbar (P_{tot} of 1 and 12 mbar, respectively). The dashed lines are the linear fits. The as-obtained activation energies (ϵ_a) are given inside the graphs. Conditions: 0.1 s of BBr_3 pulse / 30 s of Ar for post- BBr_3 purge / 10 s of NH_3 pulse / 60 s of Ar for post- NH_3 purge.

The BN deposition was further studied by analyzing the shape evolution of individual growth cycles. The GPC curve obtained by in-situ SE consisted of well-defined steps (Figure 5-5.a). Before proceeding further, it is important to emphasize the following. The extremely small variations in thickness within an ALD cycle, are due to the changes in signal, as interpreted by the SE optical model.

Apart from the actual thickness variations, changing the surface optical properties upon the corresponding chemical reactions may also be sufficient to cause this effect. Only the starting and ending points of each cycle correspond to the real thickness values, since they compose the entire growth curve and result in the final film thickness. The latter can be independently verified by other ex-situ measurement techniques (as discussed in Chapter 2 – Section 2.2.1).

The first step of a cycle, interpreted by SE as a thickness increase, corresponds to the introduction of BBr_3 and presumably indicates its successful chemisorption. Figure 5-5.b compares the shapes of individual ALD cycles obtained by in-situ SE for different P_{NH_3} . The corresponding step height^{§§} evolutions are quantified in Figure 5-5.c and 5-5.d. The gradual (with P_{NH_3}) increase of the step height after each BBr_3 pulse (Figure 5-5.c) and the smaller decrease after each NH_3 pulse (Figure 5-5.d) may indicate a higher concentration of $\text{-NH}_2\text{-}$ linkages as a result of applying a higher P_{NH_3} . These linkages serve as BBr_3 chemisorption sites for the subsequent cycle, increasing the surface coverage of the chemisorbed -B-Br (recall Figure 5-1), and resulting in a larger step. On the contrary, a lower P_{NH_3} leads to lower $\text{-NH}_2\text{-}$ coverage, therefore leaving unreacted B-Br sites on the surface from the previous BBr_3 pulse and resulting in a weaker step. The fact that a higher P_{NH_3} leads to a larger step after introducing BBr_3 supports the necessity of having NH_x groups to enhance the BBr_3 chemisorption. In other words, increasing the $\text{-NH}_2\text{-}$ coverage leads to a large BBr_3 uptake. Similarly, increasing the -B-Br coverage leads to a large NH_3 uptake, in line with the effect observed earlier and mentioned in the literature. See the earlier literature review given in this chapter.

The same effect comes into play when t_{NH_3} is altered (Figure 5-5.e). A higher t_{NH_3} causes more nitridation of the -B-Br -chemisorbed surface, leading to enhanced surface coverage with $\text{-NH}_2\text{-}$ linkages. This in turn, may result in a higher surface

^{§§} Step height and thickness decrease reported in the text and in Figure 5-5 represent the increase in thickness (as interpreted by SE) following a BBr_3 pulse and the decrease in thickness upon an NH_3 pulse, respectively.

coverage in the subsequent BBr_3 pulse, leading to a larger step and therefore a higher GPC (recall Figure 5-3.b).

Figure 5-5. Thickness evolution (as interpreted by in-situ SE) within individual ALD cycles. **(a)** Representative step-wise growth in every ALD cycle; **(b)** Influence of P_{NH_3} (at $P_{\text{NH}_3} = 0.12\text{--}1.43$ mbar, $P_{\text{tot}} = 1\text{--}12$ mbar), **(c,d)** Quantification of the step increase / decrease during one ALD cycle versus P_{NH_3} and for different post- NH_3 purge durations (see the legend), and **(e)** the effect of t_{NH_3} at $P_{\text{NH}_3} = 0.12$ mbar ($P_{\text{tot}} = 1$ mbar).

5.5.2.2 Characterization of the BN layers

The BN films were deposited at a substrate temperature of 240, 320 and 365 °C and P_{NH_3} ranging from 0.12 to 1.43 mbar ($P_{\text{tot}} = 1\text{--}12$ mbar). The pulse durations used for all samples discussed in this section were: 0.1 s of BBr_3 , 30 s of Ar for post- BBr_3 purge, 10 s of NH_3 and 60 s of Ar for post- NH_3 purge. A GaN layer on top of the BN is in-situ deposited to diminish the aging effect.

5.5.2.2.1 Refractive index (n) by SE

The refractive indices obtained at 632 nm and 1500 nm wavelengths (Figures 5-6.a and 5-6.b, respectively) reasonably agree with the values reported for stoichiometric boron nitride films having amorphous (a-BN), nanocrystalline or hexagonal (h-BN) structure ^{31,32}. To bear in mind, extinction coefficients were below the sensitivity limits of the measurements system, therefore considered as zero. Further, n of an a-BN has been reported between 1.65 and 1.9 ^{31,33,34}; n of a h-BN, falls in the range between 1.55 and 2.17 ^{35–38}. From the figures, the n at 632 nm prominently decreases with increasing T_s for $P_{\text{NH}_3} = 0.12$ mbar, whereas for $P_{\text{NH}_3} = 1.43$ mbar it increases. The trends of n at 1500 nm are less evident. The behavior of n at 632 nm can be explained by the Urbach rule ^{39–41} since this wavelength is in the spectral region of the Urbach tail for the interband transitions of BN ³⁷. It could also be related to impurities and defect states. For example, Hoffman et.al. ⁴² reported absorptions in the photon energy range of 1–5 eV and attributed this to impurities and defect states. However, the observed behavior of n requires additional investigation which is out of the scope of this work.

Figure 5-6. Variation of the refractive index of as-deposited BN (15 ± 3 nm) as a function of T_s and P_{NH_3} at (a) 632 nm and (b) 1500 nm.

5.5.2.2.2 XPS analyses

Sputter-depth profiling was performed using 0.5-1 kV Ar⁺ ions to obtain bonding environments from the bulk. The surface carbon peak position was referenced to the C 1s line of adventitious hydrocarbons at 284.8 eV⁴³. B 1s and N 1s spectra were analyzed to obtain the bonding environments in the bulk. All the spectra were deconvoluted by Gaussian peaks after assuming an iterated Shirley background. We neglected the lifetime broadening of the B 1s and N 1s peaks⁴⁴. It was observed that the B 1s and N 1s spectra fitted very well with those of a boron nitride reference⁴⁵, providing a strong indication of the occurrence of (near) stoichiometric BN films.

It was observed that the as-deposited layers contained less than 5 at.% of oxygen in the bulk (see Figure 5-7.a). However, after aging in air for several months, the layers revealed an oxygen amount of ~10 at.% (see Figure 5-7.b), indicating their atmospheric instability and thus amorphous or nanocrystalline nature^{46,47}.

Figure 5-7. Sputter depth profiles of a GaN / BN / SiO₂ / Si stack (a) as-deposited and (b) after aging in air for several months. The near stoichiometric BN layer inhibits an increase of the oxygen amount from ~5 at.% (as-deposited) to >10 at.% (after aging). Conditions: $T_s = 240\text{ }^{\circ}\text{C}$, $P_{\text{NH}_3} = 0.12\text{ mbar}$, $P_{\text{tot}} = 1\text{ mbar}$, 0.1 s of BBr₃ pulse / 30 s of Ar for post-BBr₃ purge/ 10 s of NH₃ pulse/ 60 s of Ar for post-NH₃ purge. The GaN layer on top of the BN is in-situ deposited to diminish the aging effect; apparently, oxygen is still able to diffuse through.

5.5.2.2.3 XRD analyses

The grazing incidence angle XRD (GIXRD) spectra of the samples deposited at $T_s = 360\text{ }^{\circ}\text{C}$ and P_{NH_3} of 0.12 and 1.43 mbar (P_{tot} of 1 and 12 mbar, respectively) showed 2 broad BN-derived peaks located at 21° and 54° of 2θ values with very low intensities, indicating a poor crystallinity. Peaks due to the GaN capping layer can also be observed. It can be concluded that changing the pressure did not affect the crystalline structure significantly.

Figure 5-8. GIXRD patterns of the thermal-BN samples ($\sim 15\text{ nm}$ thick). The corresponding Miller indices are indicated above the peaks for BN (#) and GaN (*). The peak positions coincide with those reported for *h*-BN^{48,49}. The GaN peak positions are taken from ref.²³.

5.6 Conclusions

This chapter studied ALD of BN in view of the hypothesized role of $\text{BBr}_3\text{:NH}_3$ surface adduct in the film formation process. The proposed ALD model involved (i) formation of a $\text{BBr}_3\text{:NH}_3$ surface adduct complex (presumably reversible), and (ii) conversion of this complex into B-NH₂-B linkage (irreversible), resulting in a unit of BN. The proposed ALD mechanism could also be viewed as the replica of the adduct pathway reported for AlN^{22,50} and proposed for GaN^{23,29} ALD.

The kinetics of the surface adduct formation and its conversion into -NH₂-linkages were calculated using a Mathcad code. The results showed that the adduct surface coverage depends primarily on ammonia partial pressure. The experimental observations of the strong dependence of GPC on both partial pressure and NH₃-pulse duration were in qualitative agreement with the simulations. The pressure dependence, atypical for ALD, was indeed the novelty of this work.

The ex-situ layer characterization revealed (i) refractive index (n) similar to that reported for a-BN and h-BN, (ii) stoichiometric BN films with O contamination less than 5 at.%, (iii) environmental instability of the films and (iv) their nanocrystalline / amorphous structure.

References

- ¹ H. Hirao, K. Omoto, and H. Fujimoto, *J. Phys. Chem. A* **103**, 5807 (1999).
- ² A.C. Legon and H.E. Warner, *J. Chem. Soc. Chem. Commun.* **1397**, 1397 (1991).
- ³ K. Iijima and S. Shibata, *Bull. Chem. Soc. Jpn.* **53**, 1908 (1980).
- ⁴ K. Iijima and S. Shibata, *Bull. Chem. Soc. Jpn.* **56**, 1891 (1983).
- ⁵ R.E. McCoy and S.H. Bauer, *J. Am. Chem. Soc.* **78**, 2061 (1956).
- ⁶ P. Cassoux, R.L. Kuczkowski, and A. Serafini, *Inorg. Chem.* **16**, 3005 (1977).
- ⁷ E.W. Hughes, *J. Am. Chem. Soc.* **78**, 502 (1956).
- ⁸ K. Possemiers, P. Van Der Voort, and E.F. Vansant, *J. Chem. Soc. Faraday Trans.* **92**, 679 (1996).
- ⁹ K. Possemiers, N.R.E.N. Impens, and E.F. Vansant, *J. Chem. Soc. - Faraday Trans.* **93**, 2309 (1997).
- ¹⁰ J.D. Ferguson, A.W. Weimer, and S.M. George, *Thin Solid Films* **413**, 16 (2002).
- ¹¹ S. Prouhet, G. Vignoles, F. Langlais, A. Guette, and R. Naslain, *ChemInform* **25**, (2010).
- ¹² S. Reinhardt, M. Gastreich, and C.M. Marian, *Phys. Chem. Chem. Phys.* **2**, 955 (2000).
- ¹³ S. Reinhardt, C.M. Marian, and I. Frank, *Angew. Chemie Int. Ed.* **40**, 3683 (2001).
- ¹⁴ P.R.R. Barreto, A.E. Kull, and M.A. Cappelli, *MRS Proc.* **750**, Y5.13 (2002).
- ¹⁵ A. Haaland, *Angew. Chemie Int. Ed. English* **28**, 992 (1989).
- ¹⁶ V. Jonas, G. Frenking, and M.T. Reetz, *J. Am. Chem. Soc.* **116**, 8741 (1994).
- ¹⁷ V. Jonas and G. Frenking, *J. Chem. Soc., Chem. Commun.* 1489 (1994).
- ¹⁸ M.D. Allendorf and C.F. Melius, *J. Phys. Chem. A* **101**, 2670 (1997).
- ¹⁹ H. Anane, A. Boutalib, I. Nebot-Gil, and F. Tomás, *J. Phys. Chem. A* **102**, 7070 (1998).
- ²⁰ F.M. Tao, *J. Chem. Phys.* **110**, 11121 (1999).
- ²¹ K. Possemiers, K.C. Vrancken, P. Van Der Voort, and E.F. Vansant, *J. Chem. Soc. Faraday Trans.* **91**, 2173 (1995).
- ²² M.E. Bartram, T.A. Michalske, J.W. Rogers, and R.T. Paine, *Chem. Mater.* **5**, 1424 (1993).
- ²³ S. Banerjee and A.Y. Kovalgin, *ECS Trans.* **86**, 21 (2018).
- ²⁴ G.A. Kapralova, T. V. Suchkova, and A.M. Chaikin, *Mendeleev Commun.* **3**, 118 (2004).

- ²⁵ C.A. Kingsmill, N.H. Werstiuk, and N.P.C. Westwood, *J. Am. Chem. Soc.* **109**, 2870 (1987).
- ²⁶ R.I. Masel, *Principles of Adsorption and Reaction on Solid Surfaces* (John Wiley & Sons, 1996).
- ²⁷ X. Ou, R. Wallace, and A.F. Janzen, *Can. J. Chem.* **71**, 51 (1993).
- ²⁸ C. Theodoropoulos, T.J. Mountziaris, H.K. Moffat, and J. Han, *J. Cryst. Growth* **217**, 65 (2000).
- ²⁹ S. Banerjee, A.A.I. Aarnink, D.J. Gravesteijn, and A.Y. Kovalgin, *J. Phys. Chem. C* **123**, 23214 (2019).
- ³⁰ A. Altomare, N. Corriero, C. Cuocci, A. Falcicchio, A. Moliterni, and R. Rizzi, *J. Appl. Crystallogr.* **48**, 598 (2015).
- ³¹ M.J. Rand and J.F. Roberts, *J. Electrochem. Soc.* **115**, 423 (1968).
- ³² S. Weissmantel, G. Reisse, B. Keiper, and S. Schulze, *Diam. Relat. Mater.* **8**, 377 (1999).
- ³³ J.J. Pouch, S.A. Alterovitz, K. Miyoshi, and J.O. Warner, *MRS Proc.* **93**, 323 (1987).
- ³⁴ A. Abdellaoui, A. Bath, B. Bouchikhi, and O. Baehr, *Mater. Sci. Eng. B* **47**, 257 (1997).
- ³⁵ T. Takahashi, H. Itoh, and M. Kuroda, *J. Cryst. Growth* **53**, 418 (1981).
- ³⁶ T. Ishii and T. Sato, *J. Cryst. Growth* **61**, 689 (1983).
- ³⁷ D. Jin-Xiang, Z. Xiao-Kang, Y. Qian, W. Xu-Yang, C. Guang-Hua, and H. De-Yan, *Chinese Phys. B* **18**, 4013 (2009).
- ³⁸ D.C. Cameron, M.Z. Karim, and M.S.J. Hashmi, *Thin Solid Films* **236**, 96 (1993).
- ³⁹ F. Urbach, *Phys. Rev.* **92**, 1324 (1953).
- ⁴⁰ I. Studenyak, M. Kranj, and M. Kurik, *Int. J. Opt. Appl.* **4**, 76 (2014).
- ⁴¹ M. V. Kurik, *Phys. Status Solidi* **8**, 9 (1971).
- ⁴² D.M. Hoffman, G.L. Doll, and P.C. Eklund, *Phys. Rev. B* **30**, 6051 (1984).
- ⁴³ T.L. Barr and S. Seal, *J. Vac. Sci. Technol. A Vacuum, Surfaces, Film.* **13**, 1239 (1995).
- ⁴⁴ C. Nicolas and C. Miron, *J. Electron Spectros. Relat. Phenomena* **185**, 267 (2012).
- ⁴⁵ J.F. Moulder, W.F. Stickle, P.E. Sobol, and K.D. Bomben, *Handbook of X-Ray Photoelectron Spectroscopy* (Perkin-Elmer Corporation, Physical Electronics Division, Minnesota, 1992).
- ⁴⁶ C. Gómez-Aleixandre, A. Essaifi, M. Fernández, J.L.G. Fierro, and J.M. Albella, *J. Phys. Chem.* **100**, 2148 (1996).

⁴⁷ T.A. Anutgan, M. Anutgan, I. Atilgan, and B. Katircioglu, *Thin Solid Films* **518**, 419 (2009).

⁴⁸ Q. Li, W. Luo, L. Su, J. Chen, K.-C. Chou, and X. Hou, *RSC Adv.* **6**, 92748 (2016).

⁴⁹ S. Yuan, S. Linas, C. Journet, P. Steyer, V. Garnier, G. Bonnefont, A. Brioude, and B. Toury, *Sci. Rep.* **6**, 20388 (2016).

⁵⁰ T.M. Mayer, T.A. Michalske, and J.W. Rogers, *Chem. Mater.* **3**, 641 (1991).

6 The effects of using alternative approaches to growing

BN from BBr₃ and NH₃

Abstract

In this chapter the effects of using alternative approaches, namely plasma assistance and switching to a cold wall reactor, on the deposition of boron nitride thin films are investigated. The films are obtained by a sequential introduction of boron tribromide (BBr₃) and ammonia (NH₃) precursors with an Ar purge in between. Using plasma assisted growth, to switch from pure thermal to radical enhanced deposition mode, leads to lower GPC values compared to the thermal process. Furthermore, the appearance of a pure-B phase is observed by SE, presumably indicating a different growth mechanism than for thermal deposition. Indeed, the GPC does not follow the Arrhenius behavior typical for a purely thermal process. Next, switching to a cold wall reactor reveals results similar to those obtained with a hot-wall reactor (see Chapter 5). We observe (i) pressure dependence of GPC, (ii) lower GPC in the case of the radical (hot-wire) enhancement, (iii) environmentally instable layers with (iv) amorphous/nanocrystalline structure. Studying the ammonium bromide (NH₄Br) formation is suggested for differentiating between ALD and CVD modes as well as for clarifying the deposition mechanism.

6.1 Introduction

This chapter gives insights into additional aspects of BN ALD from BBr_3 and NH_3 precursors. First, the results of the thermal-BN deposition discussed in Chapter 5 are compared with the plasma-enhanced ALD. In-situ SE results presumably indicate a different-from-thermal growth mechanism for plasma-assisted ALD. Second, two types of deposition reactors are compared, namely a hot wall versus a cold wall reactor. The latter is especially interesting for studying a reaction byproduct (ammonium bromide - NH_4Br), which is suggested for optimizing the ALD process.

Section 6.2 discusses the proposed growth mechanism based on a similar model reported in the literature and discussed earlier in Chapters 4 and 5. Section 6.3 reports the experimental results, comparing radical-enhanced and thermal deposition modes in line with the proposed deposition mechanism. Section 6.4 briefly highlights the observations made when changing the hardware from a hot-wall to a cold-wall reactor. Finally, Section 6.5 concludes this chapter.

6.2 Proposed BN growth mechanism in a radical-enhanced mode

As discussed in Chapter 1, radicals or other reactive species produced via radical enhancement methods (e.g., plasma or hot-wire) are much more reactive than their molecular counterparts, thus enabling reactions that may not be possible in thermal mode¹. This means enabling new chemical routes compared to thermal mode. Specifically, applying a radical enhancement to deposit BN is expected to alter the growth mechanism since dissociation of NH_3 into N- or H- containing radicals²⁻⁶, may enable different chemical routes, which could suppress the dominating effect of adduct assisted routes. Firstly, N- containing radicals (NH_x , $x=0-2$) can react with the surface species, causing nitridation without involving adduct formation as the intermediate step. Additionally, generated atomic hydrogen (at-H) radicals can react with surface species, e.g., with -Br, leading to their removal. This will decrease the number of available B-Br sites required for

the linkage formation via the adduct mechanism. This may imply a reduced involvement of the $\text{-NH}_2\text{-}$ bridges (linkages) into the BN growth mechanism. A schematic representation of the proposed alternations is given in Figure 6-1.

PLASMA: reacting species – NH_3 , NH_2 , NH , N and H

Figure 6-1. Proposed alternation of the BN growth with radicals involved: thermal route, reaction with NH_x radicals, removal of surface species by at-H.

It should be noted that, under optimized conditions, the use of plasma can improve film crystallinity ^{7,8}. On the other hand, non-optimized conditions (i.e., insufficient concentration of NH_x radicals, too much at-H, etc.) may lead to a lower GPC and an increased B share in the layers. Section 6.3.2 will address this issue in detail.

6.3 Plasma-enhanced ALD of BN in a hot-wall reactor

For plasma assisted deposition, in addition to pure radical enhancement, surface bombardment with energetic species (i.e., ions) can alter film properties or the growth mechanism. For example, plasma assistance has been reported to improve crystallinity, electrical behavior, and densify the layers ⁸⁻¹⁰.

6.3.1 Experimental setup

Boron nitride films were deposited on 100 nm thermally grown SiO_2 layers on Si wafers by sequentially pulsing BBr_3 and NH_3 with Ar purges in between. During the plasma-enhanced ALD (PEALD) experiments, only the NH_3 was supplied such that it passed through the plasma-generation region, the BBr_3 precursor was introduced far below and just above the substrate holder. The

depositions were performed in a Picosun Plasma R-200 reactor. Due to the technical limitations of the plasma source, it was impossible to perform the plasma-experiments at total pressures higher than 1 mbar (i.e., $P_{\text{NH}_3} = 0.12$ mbar). The total reactor gas-pressure was thus kept at 1 mbar, while the substrate temperatures (T_s) were varied between 240 and 370 °C. The typical pulse and purge times were set to 0.1-1.2 s for BBr_3 , 10-30 s for post- BBr_3 Ar-purge, 5-25 s for NH_3 , and 20-80 s for post- NH_3 Ar-purge.

The film growth was monitored in-situ by a Woollam M-2000XI spectroscopic ellipsometer (SE) served with J.A. Woollam CompleteEASE software. The approach and the SE models have been explained in Chapter 2.

6.3.2 BN ALD window and the effect of non-optimized conditions

Varying the NH_3 (Figure 6-2.a) and BBr_3 (Figure 6-2.b) pulse and purge duration caused only a slight GPC variation without any conclusive trend, consistent with an ALD growth mode.

Figure 6-2. Variation of GPC with (a) NH_3 and (b) BBr_3 pulse and purge times measured by in-situ SE. Other conditions $T_s=240$ °C and $P_{\text{NH}_3} = 0.12$ mbar ($P_{\text{tot}}=1$ mbar).

From the figure, using the shortest pulse and purge times (0.1 s of BBr_3 pulse, 10 s of post- BBr_3 purge, 5 s of NH_3 pulse and 20 s of post- NH_3 purge) seems to be long enough to achieve similar GPC values. However, an intense spectral absorption band at ~ 3.4 eV was observed for the shortest t_{NH_3} of 5 s (see Figure 6-3.a), which was earlier attributed to the appearance of a pure-B phase, as discussed

in Chapter 3. This indicated an insufficient nitridation of the surface during such short NH_3 pulses. Figure 6-3.b compares the optical function (ϵ_2) of the plasma and thermal sample deposited using 5 s of t_{NH_3} . It can be seen that the absorption band is absent in the case of thermal deposition and present if plasma assistance is used. This confirms that, in line with the expectations, plasma enhancement significantly alters the BN growth mechanism (see Figure 6-1 and the corresponding text).

Figure 6-3. The adsorption-related optical function (ϵ_2) as determined by in-situ SE for (a) various t_{NH_3} and (b) plasma-vs-thermal mode. The absorption band observed at ~ 3.4 eV is attributed to pure-B phase (see Chapter 3) and absent for thermal deposition.

The GPC vs substrate temperature exhibits no Arrhenius behavior (see Figure 6-4) in contrast with the thermal mode (recall Figure 5-4). This is another indication of altering the growth mechanism in comparison to thermal ALD and/or possibly co-existence of several parallel mechanisms with a different dependence on temperature.

Figure 6-4. Arrhenius plot for the plasma-samples. Conditions: 0.1 s of BBr_3 pulse / 30 s of Ar for post- BBr_3 purge/ 10 s of NH_3 pulse/ 20 s of Ar for post- NH_3 purge. The dashed lines are given as a guide to the eye.

6.4 BN deposition in a cold-wall reactor

All the reported earlier experiments concern deposition of BN films in a hot-wall reactor. The latter provides a vertical heating zone with a uniform temperature distribution and furnishes a good temperature control. However, due to the (large) hot surfaces, the precursors might react on the walls which could result in their depletion as well as particle/film formation on the walls ¹¹⁻¹⁵. Such effects are not desired since they can affect both reaction mechanism and material properties.

A cold-wall reactor can suppress the mentioned effects. A more efficient precursor use can be expected since the reactants are not depleted by the walls. On the other hand, heating only the substrate normally results in substrate surface temperature distribution and a strong temperature gradient. The temperature difference between the hot stage ($T \approx 1000$ °C) and the cold walls (few tens of °C) can be so high ¹⁴ that it is uncertain which reaction pathways will determine the growth. In addition, cold walls will allow increased adsorption or even condensation of precursors, water vapor or reaction byproducts. All these issues can affect the growth mechanism and film properties. The next section aims to

investigate the differences in film growth using hot-wall or cold-wall reactor designs.

6.4.1 Experimental setup

The experiments were performed in a cold-wall reactor of the home-built cluster system, using BBr_3 and NH_3 precursor pulses with Ar purges in between. For a schematic of the reactor assembly, refer to Figure 1-3. Briefly, the assembly consists of 2 reactors in series with the exhaust of the first (deposition) reactor connected to the inlet of the second (analysis) reactor. Both reactors are pumped by a shared turbo-molecular pump connected to the exhaust of the second reactor. The latter is equipped with an in-situ Fourier transform infrared spectrometer (FTIR), enabling characterization of byproducts coming from the first reactor.

6.4.2 Purely thermal mode

The depositions were conducted on Si (100) substrates at a T_s of 300 °C (as determined by in-situ SE). Initial test experiments (not shown here) were performed to verify the ALD window in terms of pulse/purge durations. XPS analysis revealed approximately 45 at.% of B, 38 at.% of N, 15 at.% of O and 2 at.% of C in the films. The relatively high oxygen share might be due to the (i) oxidation of the films upon exposure to air or (ii) oxygen being incorporated during the growth process. To differentiate between (i) and (ii), two equivalent samples were further deposited with one being in-situ capped with an a-Si protection layer and the other without capping. The XPS depth profiling (Figure 6-5), carried out on both samples after 3 days of their exposure to air, revealed 20 at. % of oxygen in the uncapped sample and 3-4 at. % of oxygen in the capped sample. This clearly confirms that the deposited layers were instable in air, presumably indicating their amorphous or nanocrystalline nature ¹⁶.

Figure 6-5. XPS sputter depth profiles of samples deposited in purely thermal mode, (a) uncapped and (b) with a-Si capping layer. Conditions: $P_{\text{tot}} = 0.5$ mbar ($P_{\text{NH}_3} \approx 0.2$ mbar), $T_s = 300$ °C, 0.1 s of BBr₃ pulse, 30 s of Ar for post-BBr₃ purge, 5 s of NH₃ pulse and 20 s of Ar for post-NH₃ purge.

6.4.3 Hot-wire-assisted mode

Further experiments were performed in the same reactor but additionally using a hot-wire (HW) radical source heated up to max. $T_{\text{HW}} = 1850$ K. Interaction of ammonia molecules with the hot tungsten surface of the HW facilitates the formation of atomic hydrogen (at-H) and NH_x (mainly NH₂) radicals^{2,3}. Generating NH₂ implies providing a corresponding flux of at-H to the surface. One should keep in mind that the at-H flux arriving at the growing surface is expected to be relatively high, due to the higher recombination rate of NH₂ compared to that of at-H. The generation, recombination and delivery of these radicals to the substrate surface were experimentally confirmed and discussed in our previous work¹, demonstrating the effective dissociation of NH₃ at HW temperatures above 1600 K.

The HW-assisted deposition led to a significant decrease in the GPC with increasing the HW temperature. Namely being 0.08 nm/cycle for the HW-off mode (i.e., HW at room temperature), the GPC decreased to 0.05 nm/cycle for the HW at 2100 K. Such a decrease was in line with the expected suppression of the adduct assisted (thermal) route while activating new chemical routes in the BN growth mechanism (see Figure 6-1 and the corresponding text).

Specifically, the experiments were performed with the HW-state changing from *off* to *on* ($T_{HW} \sim 1850$ K, out of the line-of-sight with the substrate) during deposition, otherwise using the same ALD conditions as for the purely thermal mode. The deposition started with the HW *off*, then setting the T_{HW} in steps first to ~ 800 K, ~ 1400 K and finally to ~ 1850 K. A clear effect of the T_{HW} on the GPC was observed for the T_{HW} beyond 1400 K (see Figure 6-6.a). The step-height (i.e., first increase after introducing a BBr_3 pulse) was only slightly affected ($\sim 15\%$ change) by T_{HW} while the entire GPC was changed by $\sim 50\%$. The latter is due to a pronounced decrease of the “thickness” caused by the NH_3 pulses^{***}: the higher the T_{HW} , the larger the decrease (Figure 6-6.b). This effect can be explained by increasing the dissociation degree of ammonia with T_{HW} and altering the growth mechanism due to e.g. the presence of atomic hydrogen, as discussed in Section 6.2. In this light, the use of the mentioned position of the HW, i.e. not in the line-of-sight with the substrate, ensures an effective delivery of at-H to the film surface, however preventing delivery of NH_2 radicals (see ref. ¹ for further details).

^{***} Thickness decrease after introducing an NH_3 pulse as can be seen in Figure 6-6.b for T_{HW} at 1400 K and 1850 K.

Figure 6-6. (a) GPC and (b) step-shape evolution with changing HW temperature. All measurements are performed by in-situ SE. It is important to bear in mind the considerations mentioned in Section 5.5.2 w.r.t. to the small step-variations interpreted by SE as the thickness changes.

XPS sputter-depth profiling of the HW-deposited films (see Figure 6-7) reveals (similar to the thermally deposited layers – recall Figure 6-5) near stoichiometric boron nitride with less than 3 at.% of oxygen. It can be concluded that the HW does not affect the composition, as there is no clear in-depth change observed.

Figure 6-7. XPS sputter-depth profiling of the HW-deposited sample shown in Figure 6-6.a.

It is however known that structural properties can be improved by activating radical-assisted routes. It has been reported that plasma assistance can help to improve crystallinity, electrical properties, and density of the layers⁸⁻¹⁰. Utilizing a hot-wire may be another approach to influence film properties. Importantly, a HW-process is purely chemical opposite to plasma, since energetic and charged species are excluded from the gas-surface interactions. Comparing plasma with HW in this aspect can further clarify the mechanism(s) behind the changes of the film properties.

Specifically, ref.¹⁷ reported on an improved crystallinity of silicon obtained by HWCVD. In expectation of a possible effect, transmission electron microscopy (TEM) analysis of the purely thermal and HW-deposited samples was performed. Both samples exhibited an amorphous structure of the layers. The thermal-BN easily delaminated from the substrate surface (Figure 6-8.a), indicating its poor adhesion. However, a better adhesion was observed for the HW-sample, showing no delamination (Figure 6-8.b). Both films exhibited similar densities, 2.06 g/cm³ for the thermal and 1.98 g/cm³ for the HW-deposited sample (determined by x-ray reflectometry). These values are within the range of 1.8-2.3 g/cm³ reported for amorphous BN^{18,19}.

Figure 6-8. TEM images of the films deposited in (a) purely-thermal and (b) HW-assisted modes. For the thermal sample, adhesion of the BN/a-Si stack to the protective glue layer is much larger than that to the Si substrate. This leads to the easy delamination of the complete BN/a-Si/protecting glue/a-Si/BN stack from the Si. There is no delamination observed for the HW-sample.

6.4.4 Studying the byproduct formation

Ammonium bromide (NH_4Br) forms as a byproduct of the BN formation reaction and further deposits on all cold parts of the two-reactor assembly (recall Figure 1-3) Such parts include the reactor walls, room-temperature substrates and the internal FTIR mirrors of the second downstream reactor. In ref. ²⁰, we propose to study deposition of NH_4Br for differentiating between ALD and CVD modes. This can further assist in (i) optimizing the deposition conditions and (ii) clarifying the deposition mechanism.

Briefly, rather important conclusions can be drawn from measuring the ratio of the produced amounts of NH_4Br and BN. In view of the proposed adduct formation mechanism discussed in Sections 5.3.1 and 6.2, deposition of 1 mole of BN should result in the production of 1 mole of NH_4Br , if working in an ALD mode. The NH_4Br solely appears because of the reaction between NH_3 (of the pulse) and HBr (of the byproduct). For CVD, when all the precursors are mixed, at least 3 moles of NH_4Br will be produced per 1 mole of BN. Therefore, the relative-to-BN amount of produced NH_4Br can indicate the growth mode. It can further shine light on the deposition mechanism, since the relative NH_4Br -amount can be pressure and/or temperature dependent. These issues however require further investigation and are out of the scope of this work. Further details can be found in Appendix 6.3.

The removal of ammonia from the cold-wall reactor is analyzed in Appendix 6.1. Additional results on the formation and identification of NH_4Br can be found in Appendix 6.2. The migration of NH_4Br and its removal from the reactor are briefly discussed in Appendix 6.4.

6.5 Conclusions

The effects of switching to radical enhanced modes were investigated in comparison to purely thermal deposition. The experimental results could be adequately explained by the proposed growth mechanism which involved

activating the additional-to-thermal chemical routes. The radical enhancement lead to lower GPC values and the existence of a pure-B phase. Unlike the thermal mode, the absence of Arrhenius behavior could be considered as another evidence of the altered reaction mechanism.

Further, the effects of performing depositions with a cold wall reactor (instead of a hot-wall reactor) were investigated. The material characterization revealed results similar to those obtained with a hot-wall reactor. We namely observed (i) pressure dependence of the GPC, (ii) a lower GPC in the case of the radical (HW) enhancement, (iii) environmentally instable layers with (iv) amorphous/nanocrystalline structure. Studying the ammonium bromide (NH_4Br) formation is suggested for differentiating between ALD and CVD modes as well as for clarifying the deposition mechanism.

Appendix 6.1: Ammonia-decay analysis

Ammonia decay analysis were performed using Perkin-Elmer Frontier FTIR equipment. For this analysis, NH_3 was introduced into the reactor for 5 s. The other parameters were kept similar ($T_s=300$ °C and $P_{tot}=0.5$ mbar) to the experimental conditions discussed in Section 6.4.

Although ammonia has its most intense peaks located at 965 cm^{-1} and 931 cm^{-1} and many other peaks with various intensities in the wavenumber range of $550\text{--}1250\text{ cm}^{-1}$, it is not easy to perform reliable baseline correction analysis in these ranges due to the limitations of the equipment. Therefore, to calculate the partial pressure of ammonia decay in the reactor, we selected the wavenumber range of $1300\text{--}1900\text{ cm}^{-1}$. It should be noted that this calculation is only valid for this particular reactor. The calculations were performed as follows:

- 1- Background recorded to eliminate the effects of existing molecules (i.e. water) and ammonia introduced into the reactor while FTIR signal continuously recorded.
- 2- Multiple, representative spectrum files were selected at different times
- 3- Transmittance (T) data converted to Absorbance (A) using the following equation (equation A-6.1), where I and I_o represents the intensity in the sample spectrum and intensity of the background spectrum, respectively.

$$A = -\ln(T) , \text{ where } T = \frac{I}{I_o} \quad (\text{eq. A-6.1})$$

- 4- Peak areas were calculated by integration ($\int A$ - unit cm^{-1}).
- 5- The absorption cross section (ACS - unit $\text{cm}^2/\text{molecule}$) is calculated using the HITRAN database ²¹ as a reference and multiplied with the optical pathlength of our setup.
- 6- To convert the integrated absorbance ($\int A$) to a concentration (n/V - unit $\text{molecules}/\text{cm}^3$) the following equation (equation A-6.2) is used.

$$n/V = \int A / ACS \quad (\text{eq. A-6.2})$$

- 7- The result obtained from equation A-6.2 is converted to $\text{molecules}/\text{m}^3$.

8- Following ideal gas law (equation A-6.3) pressure is calculated. In this equation P is pressure, T is temperature and k_B is the Boltzmann constant.

$$P = n/V k_B T \quad (\text{eq. A-6.3})$$

As evident from Figure A-6-1, it requires several minutes to purge ammonia below the FTIR detection limit. A complete removal of NH_3 (meaning that ammonia is not detectable by FTIR in the full range of $600\text{--}4000\text{ cm}^{-1}$) requires tens of minutes, making BN ALD impractical in this reactor.

Figure A-6-1. Ammonia pressure decay measured by FTIR by analyzing corresponding absorption bands in the range of $1300\text{--}1900\text{ cm}^{-1}$.

Appendix 6.2. Ammonium bromide identification †††

Migration of solid (but volatile) species in cold-wall reactors is a known problem for CVD and ALD processes, especially if Lewis acids and Lewis bases are used as precursors^{22,23}. These compounds tend to deposit on all available surfaces that have temperatures lower than the decomposition temperature of the solids. For the cold-wall reactor employed in Section 6.4, this includes the reactor walls and the FTIR mirrors. The latter allows the detection of the solid reaction byproduct (Figure A-6-2), which is identified as ammonium bromide (NH₄Br).

Figure A-6-2. In-situ FTIR spectrum of the solid byproduct and its comparison with a reference²⁴.

In boron nitride deposition from boron halides (i.e., BBr₃ and BCl₃), ammonium halide powders are being formed via the reaction of ammonia with available hydrogen halides (i.e., HCl, HBr). In this work, NH₄Br is being formed by reaction of HBr (byproduct of the reactions between BBr₃ and NH₃) and NH₃:

Reaction A-6.1 requires simultaneous presence of the reactants HBr and NH₃. In an ideal ALD process, both HBr and NH₃ are available during an NH₃ pulse only. As shown in Appendix 6.1, even with very long purge durations

††† Joint work of R.O. Apaydin and A.J. Onnink (University of Twente).

(minutes), the high sticking coefficient of ammonia at room temperature ²⁵ results in NH₃ adsorption on the reactor cold walls.

Appendix 6.3. In-situ study of ammonium bromide formation for optimizing boron nitride ALD from BBr₃ and NH₃ ^{†††}

The deposition of BN from boron tribromide (BBr₃) and ammonia (NH₃) was studied by *in-situ* real-time monitoring of the reactive gases and reaction byproducts, using Fourier Transform infrared (FTIR) spectroscopy and spectroscopic ellipsometry (SE) as schematically shown in Figure A-6-3.a. Depending on the chosen conditions, the deposition of BN varies between an ALD mode and a pulsed chemical vapor deposition (CVD) mode. Figures A-6-3.b and A-6-3.c show a layer of particles deposited on a cold (293 K) substrate near the exhaust, identified as ammonium bromide (NH₄Br) by the FTIR reflectance spectrum. Such a salt is a known byproduct in CVD from NH₃ and halide precursors ²⁶, forming from NH₃ and the gaseous hydrogen halide byproduct (here, HBr) and spreading through the reactor by sublimation, dissociation ²⁷ to HBr + NH₃, and redeposition.

Figure A-6-3. (a) Schematic overview of the studied reactions and the reactor (not to scale), comprising a BN deposition compartment (345 K walls) and an attachment (293 K) with *in-situ* spectroscopic ellipsometer (SE) and infrared (IR) spectrometer. The IR beam reflects between aluminum mirrors to a total path length of 26 m. **(b)** Photo of monitor wafer with a NH₄Br film (partially cleaned for contrast). **(c)** Scanning electron micrographs of NH₄Br nanoparticles on (b).

To optimize an ALD recipe, the precursor-pulse and purge durations are typically increased until the growth per cycle (GPC) saturates. This work explores a new method to optimize BN ALD based on *in-situ* monitoring by FTIR and SE of

^{†††} This section is a joint work presented at EuroCVD22-Baltic ALD16 conference by A.J. Onnink, see the list of publications at the end of this thesis.

the precursors and reaction byproducts. The idea is as follows. First, FTIR monitoring detects precursor mixing (PM) in real-time and thus assists in minimizing that effect. Second, the quantity of NH_4Br formed per cycle is expected to indicate a degree of PM. Figure A-6-4.a demonstrates the concept, which is understood by the model given below.

In absence of PM, only the fraction of HBr that is produced in the NH_3 pulse forms NH_4Br . BN ALD will thus form less NH_4Br than CVD; the amount depends on the mechanism. Based on the known mechanism of thermal ALD of aluminum nitride and the recently proposed similar pathway for gallium nitride from NH_3 and trimethylgallium²⁸, we hypothesize that ALD of BN involves formation of a $-\text{BBr}:\text{NH}_3$ 'surface adduct' complex, subsequently converted to $\text{B}-\text{NH}_2-\text{B}$ links. This reaction produces 1 mol of HBr per mol of BN in the NH_3 pulse, and so 1 mol of NH_4Br . The remaining hydrogen atoms of the $-\text{NH}_2$ -termination are released in the BBr_3 pulse (i.e., $-\text{NH}_2 + \text{BBr}_3 \rightarrow 2 \text{HBr} + -\text{N}-\text{B}-\text{Br}$) in absence of NH_3 . Alternative ALD mechanisms may yield higher NH_4Br production, but not exceeding 3 mol per mol BN. With PM, at least 3 mol NH_4Br is made per mol BN, or more if BBr_3 reacts with gases such as H_2O to form additional HBr. Therefore, the monitoring of NH_4Br production can yield information on the mode and mechanism of pulsed BN deposition.

The conditions that minimize PM in a BN deposition can be predicted by a model that describes the rise (pulse), decay (purge), and fall (reaction) in the precursor partial pressures. Figure A-6-4.b shows such a model, that also incorporates HBr and the growth of NH_4Br through parameters determined from combined *in-situ* SE and FTIR data (e.g., Figure A-6-4.a). Process 2 approaches the NH_4Br GPC of ALD, whereas process 1 is in CVD mode. An extensive purge is required to prevent PM fully; the duration may be shortened by minimizing the pulse dose and reactor volume, and maximizing the pump speed.

Figure A-6-4. (a) In-situ monitoring of partial pressures of gases (FTIR) and the effective thickness of NH_4Br (SE) near the exhaust during pulsed BN deposition. A pulse of BBr_3 (30 s) is started at $t = 3$ min with 0.01 Pa of NH_3 still present, leading to production of NH_4Br and HBr and rapid decay of P_{NH_3} . A subsequent pulse of NH_3 (5 s) in the presence of HBr similarly leads to NH_4Br production. (Partial pressures were calculated from the integrated absorbance of peaks in FTIR spectra. The effective NH_4Br thickness is calculated as layer thickness $\times$ (1-void fraction) from fits to SE data.) **(b)** Simulated pulsed depositions with different pulse and purge durations. Program 1 leads to significant PM and high NH_4Br GPC. Program 2 approaches ALD, as most HBr produced in the BBr_3 pulse is pumped off rather than reacting with NH_3 to form NH_4Br . The model calculates the NH_4Br production assuming instantaneous reactions (not treating transport or kinetics): experimentally, when either HBr or NH_3 is present in excess, the other species is not detected by in-situ FTIR, consistent with full conversion to NH_4Br . Durations in seconds (BBr_3 pulse, Ar purge, NH_3 pulse, Ar purge), program 1: 0.1-300-2-300, program 2: 0.1-300-5-600.

The monitoring of experimental trends in the NH_4Br production can further clarify the BN growth mechanism. If BN growth occurs via reversible formation of $-\text{BBr}:\text{NH}_3$ surface adducts, then the equilibrium concentration of these adducts should increase with the partial pressure of NH_3 (P_{NH_3}), enhancing the formation of $\text{B}-\text{NH}_2-\text{B}$ links. Our separately submitted results²⁹, which is also discussed in Chapter 5, indeed show the expected dependence of the BN GPC on P_{NH_3} , which is rather atypical for ALD. In support of this result, Figure A-6-5.a demonstrates that the NH_4Br production per cycle is also pressure-dependent. A lower pressure results in increased NH_4Br production, presumably because the BN growth mechanism transitions from adduct-dominated to a different regime in which more than 1 unit of HBr is produced per unit of BN during the NH_3 pulse.

Figure A-6-5 displays the surprising observation that NH_4Br deposition on the monitor wafer can be delayed to over an hour after the end of BN deposition.

Based on the absence of HBr (Figure A-6-5.a, inset) at the exhaust during the delay, we suggest that free HBr has a short lifetime when chamber surfaces have a high density of adsorbed NH_3 . Then, all NH_4Br produced after the first cycle initially deposits on cold surfaces near the deposition compartment only. Any decomposition to $\text{HBr} + \text{NH}_3$ is quickly followed by redeposition, until the density of NH_3 is sufficiently reduced to allow migration (Figure A-6-5.b).

Figure A-6-5. (a) During pulsed BN deposition with purge duration < 1 minute, NH_4Br only deposits on the monitor wafer in the first pulse-purge cycle. In subsequent cycles and until a 10-minute purge, in-situ FTIR monitoring (inset) detects NH_3 but not HBr. This figure also shows that the NH_4Br GPC on the monitor wafer increases as pressure is decreased. (b) After the BN deposition started in (a) is completed, NH_4Br migrates from the deposition chamber to the monitor wafer.

Appendix 6.4. Ammonium bromide migration and removal issues ^{§§§}

Once deposited, ammonium bromide causes multiple problems, mainly contaminating the reactor as well as the FTIR mirrors and the pumping system. One (and possibly the best) way of minimizing such contaminants is to keep the temperature of the system (including reactor walls and pumping system) above the sublimation temperature of NH_4Br . However, heating the entire system may be a difficult task. Consequently, other effective cleaning procedures must be found.

In this work, we studied multiple approaches including wet scrubbing, heating or mobilization by hot-wire and plasma. It was observed that wet scrubbing of contaminated surfaces is an efficient method on removing the contaminants. Yet, considering the complex geometries of the deposition systems, it is not possible to reach all the deposits of NH_4Br in this way. Additionally, partial cleaning of the reactor and waiting for migration of the molecules is not an effective method due to the possibility of agglomeration into bigger molecules, which makes it harder to estimate the time required for complete removal of the molecules from the reactor. In addition, because this procedure requires exposure of the reactor to ambient conditions, cleaning via wet scrubbing is impractical.

Secondly, we studied heating the reactor walls to favor the sublimation and migration of NH_4Br . It was observed that heating the walls up to 80 °C enhanced the NH_4Br migration. The relatively high activation energy (~ 0.65 eV) required for sublimation of NH_4Br ³⁰ and the low wall temperature results in a long waiting time, up to tens of days to remove all the contaminants from the reactor.

The possibility of NH_4Br removal by introducing Ar and an Ar/ H_2 mixture through HW and a microwave plasma sources has been further investigated. For this, a clean monitor wafer was placed in the downstream direction and SE was installed to follow the thickness changes on the wafer. It was observed that HW

^{§§§} Joint work of R.O. Apaydin and A.J. Onnink (University of Twente).

did not cause any removal, presumably due to a low concentration of at-H generated. On the other hand, plasma resulted in sharp thickness changes over the monitor wafer, indicating a plasma-enhanced removal. It can be seen from Figure A-6-6.a that the effect of plasma in the case of pure-Ar compared to Ar/H₂ mixture is much less pronounced. Interestingly, a removal of NH₄Br under UV/Visible light exposure (provided by SE beam) was also observed (see Figure A-6-6.b), presumably due to the local heating or photocatalytic effects.

Figure A-6-6. (a) SE measurements of NH₄Br thickness change by Ar and Ar+H₂ plasma. Rapid change in thickness in case of Ar+H₂ introduction **(b)** a picture of monitor wafer after NH₄Br deposition.

Concluding, effective cleaning can be achieved by simultaneous heating of walls and exposure to Ar/H₂ plasma. Detailed investigation of NH₄Br cleaning is however out of the scope of this work.

References

- ¹ A.Y. Kovalgin, M. Yang, S. Banerjee, R.O. Apaydin, A.A.I. Aarnink, S. Kinge, and R.A.M. Wolters, *Adv. Mater. Interfaces* **4**, 1700058 (2017).
- ² H. Umemoto, K. Ohara, D. Morita, T. Morimoto, M. Yamawaki, A. Masuda, and H. Matsumura, *Jpn. J. Appl. Phys.* **42**, 5315 (2003).
- ³ Y.J. Shi, B.D. Eustergerling, and X.M. Li, *Thin Solid Films* **516**, 506 (2008).
- ⁴ R. d'Agostino, F. Cramarossa, S. De Benedictis, and G. Ferraro, *Plasma Chem. Plasma Process.* **1**, 19 (1981).
- ⁵ G.P. Miller and J.K. Baird, *J. Phys. Chem.* **97**, 10984 (1993).
- ⁶ A. Fridman, *Plasma Chemistry* (Cambridge University Press, Cambridge, 2008).
- ⁷ M. Losurdo, M.M. Giangregorio, A. Sacchetti, P. Capezzuto, G. Bruno, G. Malandrino, and I.L. Fragalà, *Superlattices Microstruct.* **42**, 40 (2007).
- ⁸ H. Van Bui, F.B. Wiggers, A. Gupta, M.D. Nguyen, A.A.I. Aarnink, M.P. de Jong, and A.Y. Kovalgin, *J. Vac. Sci. Technol. A Vacuum, Surfaces, Film.* **33**, 01A111 (2015).
- ⁹ Y. Lee, S. Kim, J. Koo, I. Kim, J. Choi, H. Jeon, and Y. Won, *J. Electrochem. Soc.* **153**, 353 (2006).
- ¹⁰ H.B. Profijt, S.E. Potts, M.C.M. van de Sanden, and W.M.M. Kessels, *J. Vac. Sci. Technol. A Vacuum, Surfaces, Film.* **29**, 050801 (2011).
- ¹¹ M. Yang, *Hot-Wire Assisted Atomic Layer Deposition of Tungsten Films*, University of Twente, 2018.
- ¹² H. Habuka, *J. Cryst. Growth* **223**, 145 (2001).
- ¹³ N. Bondestam and S. Lindfors, *US6939579B2* (2005).
- ¹⁴ H. Arjmandi-Tash, N. Lebedev, P.M.G. van Deursen, J. Aarts, and G.F. Schneider, *Carbon N. Y.* **118**, 438 (2017).
- ¹⁵ A.R. Barron, editor, *Chemistry of Electronic Materials* (Andrew R. Barron, Houston, Texas, 2013).
- ¹⁶ C. Gómez-Aleixandre, A. Essafti, M. Fernández, J.L.G. Fierro, and J.M. Albella, *J. Phys. Chem.* **100**, 2148 (1996).
- ¹⁷ J.H. Song, B. Du Ahn, S.D. Shin, N.M. Hwang, and H.J. Kim, *Sol. Energy Mater. Sol. Cells* **93**, 324 (2009).
- ¹⁸ S. V. Nguyen, T. Nguyen, H. Treichel, and O. Spindler, *J. Electrochem. Soc.* **141**, 1633 (1994).
- ¹⁹ N.R. Glavin, C. Muratore, M.L. Jespersen, J. Hu, P.T. Hagerty, A.M. Hilton, A.T. Blake, C.A. Grabowski, M.F. Durstock, M.E. McConney, D.M. Hilgert, T.S. Fisher, and A.A. Voevodin, *Adv. Funct. Mater.* **26**, 2640 (2016).

- ²⁰ A.J. Onnink, R.O. Apaydin, J. Schmitz, and A.Y. Kovalgin, in *EuroCVD 22-Baltic ALD 16 Conf.* (Luxembourg, 2019).
- ²¹ C. Hill, I.E. Gordon, R. V. Kochanov, L. Barrett, J.S. Wilzewski, and L.S. Rothman, *J. Quant. Spectrosc. Radiat. Transf.* **177**, 4 (2016).
- ²² V. Pavlović, H.-R. Köttler, and C. Meixner, *J. Mater. Res.* **6**, 2393 (1991).
- ²³ K. Possemiers, N.R.E.N. Impens, and E.F. Vansant, *J. Chem. Soc. - Faraday Trans.* **93**, 2309 (1997).
- ²⁴ E.L. Wagner and D.F. Hornig, *J. Chem. Phys.* **18**, 305 (1950).
- ²⁵ A. de Castro, D. Alegre, and F.L. Tabarés, *Nucl. Mater. Energy* **9**, 1 (2016).
- ²⁶ B.J. Choi, D.W. Park, and D.R. Kim, *J. Mater. Sci. Lett.* **14**, 452 (1995).
- ²⁷ R.S. Zhu, J.H. Wang, and M.C. Lin, *J. Phys. Chem. C* **111**, 13831 (2007).
- ²⁸ S. Banerjee, A.J. Onnink, S. Dutta, A.A.I. Aarnink, D.J. Gravesteijn, and A.Y. Kovalgin, *J. Phys. Chem. C* **122**, 29567 (2018).
- ²⁹ R.O. Apaydin, A.A.I. Aarnink, M.P. de Jong, D.J. Gravesteijn, and A.Y. Kovalgin, in *EuroCVD 22-Baltic ALD 16 Conf.* (Luxembourg, 2019).
- ³⁰ R.F. Chaiken, D.J. Sibbett, J.E. Sutherland, D.K. Van de Mark, and A. Wheeler, *J. Chem. Phys.* **37**, 2311 (1962).

7 Growing BCN and AlBCN films from TEB and TMA

precursors

Abstract

This chapter studies the deposition of BCN and AlBCN films at 250-400 °C substrate temperatures (T_s) by giving alternating pulses of triethylborane (TEB), ammonia (NH_3) and trimethylaluminum (TMA) with argon (Ar)-purges in between. We observe that the GPC of BCN deposition increases with increasing T_s and TEB pulse time (t_{TEB}) which indicates ongoing thermal decomposition of TEB. The latter is also supported by the large thickness non-uniformity, increasing with T_s . The films deposited at different T_s exhibit similar compositions with atomic concentrations of 42 at.% of B, 41 at.% of C and 15 at.% of N. In order to enable manipulating the composition, hot-wire (HW) assistance is introduced. This results in increased C- and decreased N-shares indicating inefficient nitridation and different-to-thermal chemical routes. The attempt to increase the N-share by elongating t_{NH_3} has no conclusive effect on the composition whereas resulted in different chemical bonding environments of N atoms as determined by XPS. Namely, sp^2 hybridized carbon-nitrogen bonds are obtained at longer t_{NH_3} (30-60 s) whereas shorter t_{NH_3} (5 s) yielded sp or sp^3 carbon-nitrogen bonds. The changes in the chemical bonding environments lead to a decrease in refractive index by $\sim 10\%$. Changing other process parameters hardly has any effect.

Deposition of AlBCN films was enabled via replacing selected TEB/ NH_3 cycles by TMA/ NH_3 cycles or, in other words, realizing so-called super-cycles. The effects of the total pressure (P_{tot} of 0.2 and 10 mbar) were investigated. It was shown that the deposition kinetics is slightly pressure dependent; high P_{tot} resulted in $\sim 10\%$ higher GPC. The kinetics of deposition at 10 mbar was found to be thickness dependent; the GPC increased from 0.11 nm/cycle to 0.14 nm/cycle above ~ 10 nm of the film thickness. From XPS, the elemental compositions were determined as $\text{Al}_{34}\text{B}_{13}\text{C}_3\text{N}_{49}$ and $\text{Al}_2\text{B}_{41}\text{C}_{36}\text{N}_{15}$ at 0.2 and 10 mbar, respectively. Merely based on the XPS peak fitting analysis, the appearance of B_xC , C_yN , pure C and stoichiometric BN phases, as well as a contribution of single $\text{B}_x\text{C}_y\text{N}_z$ can be speculated for the samples. As for $\text{Al}_{34}\text{B}_{13}\text{C}_3\text{N}_{49}$, co-existence of stoichiometric AlN and BN with some small incorporations of carbon can be speculated.

7.1 Introduction

The first part of this chapter discusses the growth of boron (B), carbon (C) and nitrogen (N) containing layers from triethylborane (TEB) and ammonia (NH₃) precursors. This allowed to obtain the so-called BCN films. In the second part, the so-called super-cycles were additionally implemented by replacing selected TEB/NH₃ cycles by trimethylaluminum (TMA) and NH₃ cycles. This allowed to incorporate aluminum (Al) into the films and thus realize AlBCN material. *If not explicitly specified in the text, abbreviations BCN and AlBCN neither denote any quantitative elemental composition (i.e., give no actual shares of Al, B, C and N in the films and thus do not indicate stoichiometry) nor represent any phase information.* The depositions were performed either in thermal or hot-wire (HW) assisted modes; the latter was explored in view of possible radical enhancement.

The purpose of this work is manifold. First, considering the rather low temperature required for thermal decomposition of TEB (~250 °C, see Section 7.2.3), it is scientifically interesting to investigate whether ammonia is still able to react with a TEB-terminated surface at such low temperatures and thus provide its efficient nitridation. In this view, it is important to confirm / disprove the occurrence of a surface-adduct pathway for forming BN from TEB and NH₃ at low temperatures. Second, it is important to verify the existence of an efficient mechanism to remove carbon (of TEB) from the layers; the surface-adduct pathway may also play a role there (see, for example, ref. ¹). Third, if carbon removal is confirmed to be incomplete at low temperatures, this can be beneficial for adding C impurities to BN and thus forming BCN. Fourth, using TEB/NH₃ and TMA/NH₃ super-cycles may open a route to realize AlBN or AlBCN compounds with, depending on the elemental shares, tunable electrical and optical properties.

This chapter is organized as follows. Section 7.2 reviews the previously reported reactions between TEB and NH₃. Next, the interaction between TEB:NH₃ adducts and TMA:NH₃ adducts is discussed followed by the literature reports on decomposition of TEB in relation to BN growth. Section 7.3 discusses the experimental details and determination of an ALD window for the TEB/NH₃

precursor system. Section 7.4 reports the results of deposition of BCN films and Section 7.5 discusses the AlBCN films obtained by super-cycles. Section 7.6 concludes this chapter.

7.2 Reactions in relation to BCN growth

7.2.1 Reactions between TEB and NH₃

Since TEB ((C₂H₅)₃B) shares similar coordination characteristics with TMA (CH₃)₃Al, calculations predict that it forms an adduct already at room temperature by reacting with NH₃^{2,3}. The key importance of these adducts depends on the relative magnitude of the energy barrier to eliminate a single molecule (SM), e.g., methane (CH₄) or ethane (C₂H₆).

Several experimental⁴⁻¹⁰ and theoretical^{3,11,12} works have been reported on the decomposition of TEB and growth of BN films. Among them, Freitas et.al.³ studied the ethane elimination from a TEB:NH₃ adduct in the gas phase in relation to BN deposition by metal-organic CVD. The temperature was not specified but it is expected to be high because MOCVD was used. The adduct was considered to be the starting compound for three different reaction pathways: (i) *unimolecular*, (ii) *ammonia assisted* and (iii) *adduct assisted*. The corresponding chemical reactions are shown below³:

where TS(1), TS(2) and TS(3) stand for the transitional states.

It was reported that the ethane elimination through transitional states (reactions 7.1-7.3) might enable adduct-derived species which could potentially evolve further and eventually form BN. However, the high energies required to overcome the energy barriers of ethane elimination (see Figure 7-1) may prevent

the formation of the adduct-derived species and thus BN ³. In this case, the deposition process may be dominated by decomposition of the initial precursors close to the growth surface. To note, thermal decomposition of TEB occurs just above 250 °C ⁵.

Figure 7-1. Schematic diagrams of sequences of gas-phase reactions starting with the formation of the $(C_2H_5)_3B:NH_3$ adduct and proceeding with the removal of C_2H_6 via (a) reaction 7.1 - unimolecular reaction pathway, (b) reaction 7.2 - ammonia-assisted reaction pathway and (c) reaction 7.3 - adduct-assisted reaction pathway ³. Energy values relative to that of the starting compound are given in the images.

It is known that TEB is subjected to a so-called β -hydride elimination, meaning elimination of the β -H bond resulting in the formation of borane (BH_3) and B-containing radicals ¹⁰. The as-dehydrogenated TEB will further (dissociatively) adsorb on the surfaces as B atoms or B-containing radicals, regardless the substrate ^{3,13}. Therefore, the adsorption and decomposition of NH_3 on the deposition surface, which is terminated by B-containing molecules, will play a key role for the growth of BN. Since thermal dissociation of NH_3 occurs at high temperatures ($T > 1000$ °C) ¹⁴, lower shares of incorporated N can be expected

within the investigated temperature window of 300-400 °C. This will lead to high B- and C-shares and low N-share. For that reason, utilizing non-thermal means of energy (i.e., by a HW) can enhance N-incorporation. This will be addressed in Section 7-4.

7.2.2 Reactions between TEB:NH₃ and TMA:NH₃ adducts

ALD of AlN is known to occur via the surface adduct and -NH₂- linkages ¹⁵. To form AlBCN compounds, interactions between corresponding adduct species may play a role. Freitas et.al ³ investigated interactions between TEB:NH₃ and TMA:NH₃ ((CH₃)₃Al:NH₃) adducts and showed that the energy barrier to the SM elimination is reduced when one of the TEB:NH₃ species is replaced by a TMA:NH₃ adduct (see Figure 7-2), compared to the adduct assisted reaction pathway shown in Figure 7-1.c. Although reduced, the energy barrier to obtain a complex compound consisting of TEB:NH₃ and TMA:NH₃ derivatives remains high (~56 kcal/mol). For that reason, the formation of such intermediate species is still unlikely; other reaction pathways may therefore be expected, presumably involving thermal decomposition of TEB.

Figure 7-2. Schematic diagram of a sequence of gas-phase reactions, starting with the formation of the (C₂H₅)₃B:NH₃ adduct from the initial (C₂H₅)₃B and NH₃ precursors and proceeding with the removal of CH₄ via an (CH₃)₃Al:NH₃ adduct-assisted reaction pathway ³. Energy values relative to that of the starting compound are given in the image.

7.2.3 Thermal decomposition of TEB

It is known that metalorganic precursors with alkyl groups thermally decompose at low temperatures⁷. For example, TMA starts decomposing at $T > 330$ °C¹⁶. TEB starts decomposing at 250 °C through the so-called β -elimination reactions (reactions 7.4 - 7.6)^{5,10,11,17}, eliminating ethylene (C_2H_4) in Ar ambient and ethane (C_2H_6) in H_2 ambient. The C_2H_6 elimination occurs via reactions 7.7 - 7.9^{11,17}. The C_2H_4 elimination (reaction 7.4) was reported to occur at 300 °C. Above 400 °C, BH_3 formation was suggested via elimination of the other two ethyl groups^{11,17}. One may thus expect an increased coverage of the growth surface with TEB dissociation products, of which BH_3 is an important component, at temperatures around 400 °C or higher. If this occurs, such a process can hardly be self-limiting and will not lead to an ALD mode while depositing BN from TEB and NH_3 at $T_s > 400$ °C. As earlier proposed, the occurrence of BH_3 may lead to the formation of BN via the adduct assisted pathway. It should be noted that BH_3 can also lead to pure boron (pure-B) deposition. For further information, see Chapter 4.

Below 400 °C, the intermediate products of the β -hydride elimination reactions, namely the $B(C_2H_5)_2H$ and $B(C_2H_5)H_2$ species, are expected to lead to BN deposition. Specifically, BN may form through amine formation reactions similar to AlN and GaN (see Chapter 2). Carbon incorporation into the films can possibly originate from C_2H_4 or C_2H_2 , since these hydrocarbons can enable carbon deposits at comparable temperatures¹⁰. The C_2H_2 is being formed via H_2 elimination from ethylene^{11,18}. Incorporation of C bonded to B may occur due to unbroken C-B

bonds in TEB fragments in combination with the absence of an effective chemical reaction to remove the carbon at low deposition temperatures. An example of such a reaction is the proposed removal of CH₃ groups from TMG by the surface-adduct assisted pathway while forming GaN at 400 °C¹.

7.3 Experimental details

7.3.1 Deposition methodology

The BCN films were deposited in Reactor-3 of the home-built ALD/CVD cluster system from sequentially introduced TEB and NH₃ precursors. A detailed description of the reactor can be found in Chapter 1 and ref. ^{19,20}. The same reactor was used to additionally realize the super-cycles by replacing selected TEB/NH₃ cycles by TMA/NH₃ cycles. This allowed to incorporate Al and thus realize AIBCN films.

Prior to deposition, the substrates (i.e., Si (100) wafers) underwent the standard three-step wafer cleaning procedure detailed in Chapter 3. The films were obtained in the total pressure range of 0.2–10 mbar, at substrate temperatures between 250 and 400 °C. The precursors were introduced via alternating pulses with Ar-purges in between, to avoid gas phase reactions. The typical pulse- and purge-durations were: 0.5-2.0 s of TEB, 0.5 s of TMA, 5 s of post-TEB and 5 s of post-TMA purge, 2.0-60 s of NH₃ and 2-80 s of post-NH₃ purge.

The layers were characterized by in-situ (real time) and ex-situ spectroscopic ellipsometry (SE) (see Chapters 2 / Section 2.2 for details) and x-ray photoelectron spectroscopy (XPS) (see Chapter 3 / Section 3.2 for the equipment identification).

7.3.2 Tuning the deposition conditions

Figure 7-3 shows the effects of substrate temperature and TEB pulse time on the growth rate per cycle (GPC). There are rather small changes of the GPC for $T_s < 325$ °C, whereas beyond this temperature the GPC shows a sharp increase. This

is possibly due to the enhanced thermal dissociation of TEB if the T_s is approaching to 400 °C, as expected from the literature ⁵. Figure 7-4 shows that the GPC is not significantly affected by the NH_3 -exposure (t_{NH_3}) and post- NH_3 purge times in the range studied. Analyzing the step-wise growth per cycle by in-situ SE (see Appendix 7.1) revealed that post- NH_3 purge times longer than 20 s were required to minimize possible gas phase reactions between TEB and NH_3 at a total pressure (P_{tot}) of 5 mbar. Increasing the P_{tot} to 10 mbar required at least 60 s of the post- NH_3 purge time. The t_{TEB} was fixed at 0.5 s based on Figure 7-3.

To investigate the temperature effect on the reaction with NH_3 and the removal of carbon, T_s in the range of 325-375 °C was selected. There is only a little decomposition of TEB at the lowest T_s , whereas the highest T_s results in a significant decomposition.

Figure 7-3. Variation of GPC as a function of T_s and t_{TEB} (see the legend) at $P_{\text{tot}}=5$ mbar. Durations: post-TEB of 5 s, t_{NH_3} of 5 s for the solid and open symbols and 2 s for the half-open symbols, post- NH_3 of 40 s for the solid and 10 s for open and half-open symbols. To note: the t_{NH_3} and post- NH_3 purge durations have only a little effect on the GPC, as concluded from Figure 7-4.

Figure 7-4. Variation of GPC as a function of t_{NH_3} (see the legend) and post-NH₃ purge time at $P_{\text{tot}}=5$ mbar. Between the horizontal dashed lines, the GPC varies within 0.006 nm/cycle.

Total pressure can influence both GPC and material (i.e., optical) properties, as discussed in the earlier chapters. No film growth was observed at P_{tot} of 10^{-3} mbar. From Figure 7-5, it can be concluded that the GPC noticeably increases at $T_s=330$ - 375 °C if P_{tot} raises from 0.2 to 1 mbar and remains rather unaffected (i.e., ~ 0.012 nm/cycle) for P_{tot} in the range of 1-5 mbar. Further increase of the P_{tot} up to 10 mbar at $T_s=330$ °C results in a similar GPC value of ~ 0.011 nm/cycle. At 250 °C, the GPC gradually increases with pressure for all P_{tot} values (see Figure 7-5). However, deposition below the onset of thermal decomposition of TEB (250 °C) is impractical due to the very low GPC values (0.006 nm/cycle at 5 mbar).

Figure 7-5. Variation of GPC as a function of P_{tot} and T_s (see label). Depositions were performed at various substrate temperatures as shown in the label. Other conditions: 0.5 s of TEB pulse, 5 s of Ar for post-TEB pulse, 5 s of NH₃ pulse and 40 s of Ar for post-NH₃ purge. To note, any data reported in the graph do not correspond to GPC of zero.

Taking into account the observed temperature-pressure effects w.r.t. the deposition kinetics, we further characterize film composition and their optical properties by XPS and SE.

7.4 Deposition of BCN films

Purely thermal depositions were carried out at 330, 375 and 400 °C, see Table 7-1 for the conditions. The effect of adding a hot-wire (HW) was researched for $T_s=375$ °C. Since increasing t_{NH_3} may affect the efficiency of surface nitridation^{6,21}, the NH_3 pulse time was changed accordingly.

Table 7-1: Deposition conditions for BCN films.

Pressure (mbar)	Substrate temperature (°C)	TEB pulse / purge time (s)	NH_3 pulse time (s)	NH_3 purge time (s)
10	330	0.5 / 5	5	60
10	375	0.5 / 5	5	60
10	400	0.5 / 5	5	60
10	375 - HW (1850 K)	0.5 / 5	5	60
10	375	0.5 / 5	30	60
10	375	0.5 / 5	60	60

7.4.1 Growth aspects from SE

Figure 7-6 shows that the GPC increases with temperature, indicating the ongoing thermal decomposition of TEB. The GPC is rather unaffected by the t_{NH_3} , similar to the findings of ref. ^{6,22}, indicating that a t_{NH_3} of 5 s is enough to complete reactions between the available surface sites and NH_3 .

Since the presence of H_2 is reported to change the growth mechanism^{11,17}, adding atomic hydrogen (at-H) and NH_2 radicals generated by HW^{23,24} may facilitate alternative chemical routes, as discussed earlier in Section 7.2.3 and Chapter 4 and 6. The HW-assisted deposition (Figure 7-6) revealed only a slight

increase of the GPC. The effect of HW on the material properties will be discussed below and in Section 7.4.2.

Figure 7-6. GPC of samples deposited at various substrate temperatures and ammonia pulse durations, as measured by in-situ SE. For a comparison, HW-assisted deposition was performed at 375 °C. Other process conditions can be found in Table 7-1.

Figure 7-7 compares the shapes of individual pulses recorded by SE at various conditions. To bear in mind, the small signal variations within a cycle are interpreted by the SE optical model as thickness changes. Apart from actual thickness changes, altering optical properties as a result of surface reactions may also cause this effect. Upward steps may indicate the successful chemisorption of TEB. At higher T_s , the steps become larger, suggesting enhanced chemisorption. Turning on the HW and varying the t_{NH3} has no clear effect.

Figure 7-7. Step shapes (by in-situ SE) obtained from the samples deposited at **(a)** various substrate temperatures and **(b)** various t_{NH_3} durations. The HW-assisted deposition shows no effect on the shapes. Other process conditions can be found in Table 7-1.

The film-thickness uniformity was mapped by ex-situ SE (see Appendix 7.2). The large non-uniformity and its increase at higher T_s confirms once more (i) the absence of self-limiting surface reactions (and thus an ALD mode) and (ii) thermal decomposition of TEB, dominating the film growth. A slight decrease of the non-uniformity with increasing the t_{NH_3} may indicate some effects but needs further investigation.

The refractive index (n) of the BCN films is given in Figure 7-8. There is no significant effect of T_s on the n , suggesting similar elemental composition (see Section 7.4.2.1). A slight increase of n in case of the HW-assistance is possibly due to the 5 at.% higher share of C incorporated into the films. Changing the ammonia pulse duration has a bigger effect: the n decreases for a longer t_{NH_3} (Figure 7-8.b). Importantly, the XPS sputter-depth profiles (refer to Figure 7-9) exhibit slightly higher N content for the longer times. It should be noted that relatively small compositional changes may still cause an impact on the optical properties. For example, Lei et.al.²⁵ observed a decrease of the refractive index of their BCN films

by ~6% if going from $B_{10}C_{55}N_{35}$ to $B_{13}C_{54}N_{33}$ and further to $B_{14}C_{51}N_{35}$ stoichiometry. They attributed the effect to the increased sp^3 -binding share of B-N and C-N in the compound. Kimura et.al.²⁶ and Sota et.al.²⁷ reported a decreased optical bandgap for samples containing 13 at.% of C. The authors attributed this change to the incorporation of C atoms into the amorphous region of BCN films and suggested that formation of certain bonds, namely sp^2 C=C and C=N, may decrease the optical bandgap. Prakash et.al.²⁸ reported 15% larger bandgap for their samples exhibiting similar compositions and attributed that to changes in the chemical bonding network. Angus and Hayman²⁹, Dischler et.al.³⁰ and Robertson et.al.³¹ reported a smaller bandgap if H-content in their amorphous C:H films decreased. Similar effects of changing the composition may play a role in our case as well. This will be further discussed in the next section.

Figure 7-8. Refractive index of films deposited at various T_s (a) and t_{NH_3} (b). Other process conditions can be found in Table 7-1.

7.4.2 Compositional analysis from XPS

7.4.2.1 Sputter depth profiles

Sputter-depth profiling of a representative BCN sample is shown in Figure 7-9. In Table 7-2, the elemental shares in at.% obtained from different samples are given. The layers consisted of B, C and N. Small amounts of O (<3 at.%) and Si (<2 at.%) were also detected, not shown in the table. Varying T_s (Table 7-2) only influenced the GPC, hardly affecting the composition. The introduction of HW leads to a lower N- but higher C-share, contrary to the expected enhancement of

the removal of carbon by at-H. In this light, Chubarov et.al.³² proposed an altered surface chemistry to explain similar observations. Since at-H can promote decomposition of hydrocarbons, this can enhance deposition of carbon. Further, the attempt to increase the N incorporation by elongating the t_{NH_3} pulse hardly influenced the composition (Table 7-2). This confirmed that the time was not the limiting factor at 375 °C.

Figure 7-9. XPS sputter-depth profile of a representative $B_{0.42}C_{0.41}N_{0.15}$ sample capped with an *a*-Si layer. The given stoichiometry does not necessarily imply a single-phase material. Conditions: $T_s=330$ °C, $t_{NH_3}=5$ s. Other process conditions can be found in Table 7-1.

Table 7-2. Shares of various elements (in at.%) for samples deposited at different conditions. Other conditions can be found in Table 7-1.

Variable parameter		B	C	N
T_s	330 °C	42	41	15
	375 °C	43	40	12
	400 °C	43	42	12
HW	HW-1850 K	45	47	6
t_{NH_3}	5 s	43	40	12
	30 s	43	40	15
	60 s	42	40	16

7.4.2.2 Chemical bonding environments

The chemical nature of the BCN films was investigated by XPS. Figure 7-10 shows the representative peak fitting analysis for B 1s, C 1s and N 1s peaks.

Gaussian fitting is performed after fixing peak positions at the corresponding values in accordance with Table 7-3. For the samples of Table 7-2, there is no apparent shift detected for the B 1s and C 1s peaks neither with varying T_s and t_{NH3} nor HW-assistance. The B 1s peak is observed at approximately 189.6 eV and the fits suggest three possible binding states of boron (by neglecting the O-subpeak) centered at 187.6, 189.4 and 190.6 eV (Figure 7-10.a). Three subpeaks are needed to adequately describe the C 1s spectra (Figure 7-10.b). The N 1s spectrum is found to have a tail towards higher binding energies, when a longer t_{NH3} (30-60 s) is used, indicating a different bonding environment. Namely, the peak located at 399.3 eV is attributed to sp or sp³ hybridized carbon-nitrogen bonds whereas the peak located at 400.3 eV is assigned to sp² hybridized carbon-nitrogen bonds (for references please refer to Table 7-3). The earlier mentioned differences in the refractive index (Figure 7-8.b) can be attributed to the changes in the bonding environments. The literature-based assignment of the subpeaks is listed in Table 7-3.

Figure 7-10. Deconvolution of representative XPS peaks of a BCN film: B 1s (a), C 1s (b), N 1s with (c) and without (d) HW-assistance. For the films deposited at longer t_{NH_3} of 30-60 s, a shift towards higher binding energies was observed in the N 1s spectra, see (d).

Solely based of the subpeaks, it is difficult to conclude on a phase separation and claim the occurrence of either a composite or single-phase “BCN” material. At least two bonding environments can be suggested for N, three for C and B (the latter neglects the O-subpeak). From this, one may for example speculate the appearance of $\text{B}_x\text{C}_y\text{N}_z$, pure C and stoichiometric BN phases. It does however not exclude a contribution of a single $\text{B}_x\text{C}_y\text{N}_z$ phase as well. A detailed investigation is required in order to identify the available phases.

Table 7-3. XPS binding energies of B 1s, C 1s and N 1s peaks observed for the samples listed in Table 7-2 and peak assignment from the literature.

element	binding energy (eV)	possible bonds and compounds	references
B 1s	187.5	B-C in B ₄ C	33–36
		B-B in B ₄ C	36
		B-B in pure-B	37
	189.4	B-C in BC _{3,4}	38–40
		B-C in B _x C _y N _z	41
	190.6	B-N in BN	39,42–44
	192.7	B-O in B ₂ O ₃	45
C 1s	283.2	C-B in B ₄ C	36,38,40,46–48
	284.3	C-C in a-C	26,28,39,43,49
		C-C in BC ₂ N	50
	285.6	C-N in carbonitrides	51
N 1s	397.8	N-B in BN	38,44,49
	399.3	carbon-nitrogen bond in sp or sp ³ hybridization	38,41,43,49,52,53
	400.4	carbon-nitrogen bond in sp ² hybridizations	49,52,53

7.5 AlBCN films obtained by super-cycles

The films were deposited at T_s of 375 °C and a P_{tot} of 0.2 or 10 mbar, to investigate the total pressure effect. Each TEB/Ar/NH₃/Ar cycle was followed by a TMA/Ar/NH₃/Ar cycle. The chosen pulse durations of the first sub-cycle were: 0.5 s of TEB (t_{TEB}), 5 s of post-TEB purge, 30 s of NH₃ (t_{NH3}) and 60 s of post-NH₃ purge. For the second sub-cycle, the durations were: 0.5 s of TMA (t_{TMA}), 5 s of post-TMA purge, 10 s of NH₃ (t_{NH3}) and 5 s of post-NH₃ purge. The latter was copied from the earlier works performed in the group.

As shown in Section 7.3.2, BCN deposition at 0.2 mbar is very slow. However, AlN deposition readily occurs at this pressure ⁵⁴ and may be expected to enhance the process similar to the effect mentioned in ref. ⁵⁵. On the other hand,

at 10 mbar, both AlN and BCN can deposit. Composition of AlBCN films is therefore expected to depend on P_{tot} .

7.5.1 Growth aspects from SE

Figure 7-11 shows the dependence of GPC on P_{tot} . At 0.2 mbar, a GPC of 0.1 nm/cycle was obtained. Considering that GPC of BCN is 0.02 nm/cycle at this pressure (refer to Figure 7-5), GPC of 0.1 nm/cycle might indicate dominant AlN deposition. On the other hand, the kinetics of depositions at 10 mbar was found to be thickness dependent. Namely, a GPC of 0.11 nm/cycle was obtained for the thicknesses up to ~10 nm; above 10 nm, the GPC increased to 0.14 nm/cycle. Speculatively, it could be explained by the film closure above a critical thickness (i.e., 10 nm in this case). Alternative explanations might include (i) structural changes during deposition (as observed for TiO_2 ^{56,57} and F_{16}CuPc ⁵⁸ thin films), (ii) increased effective surface area due to surface roughening⁵⁶, (iii) establishing a preferred orientation due to film doping (see e.g. F doped ZnO⁵⁹), or (iv) increased density of reactive species on the growth surface⁵⁶ (i.e., establishing proper reaction sites). To clarify the thickness dependent GPC behavior, a detailed experimental investigation is required, which is out of the scope of this work.

Figure 7-11. (a) GPC of AlBCN films vs total pressure. At 10 mbar, two thickness dependent GPC values were measured, as indicated. For step-shape analysis refer to Figure 7-12. (b) Thickness vs number of cycles for AlBCN sample deposited at 10 mbar showing thickness dependent GPC.

The SE step-shape analysis is shown in Figure 7-12. At 0.2 mbar (Figure 7-12.a), a “thickness” change was observed following the introduction of both TMA

and TEB. The latter contributed much less compared to the former, suggesting the dominant growth of AlN once again. At 10 mbar (Figures 7-12.b and 7-12.c), introduction of TMA had no visible effect below 10 nm thickness. Above 10 nm, a small contribution due to each TMA pulse can be seen (Figure 7-12.c).

Figure 7-12. Step-shape comparison for deposition at 0.2 mbar (a) and 10 mbar (b and c). Figure (b) corresponds to thickness < 10 nm and (c) to thickness > 10 nm.

The corresponding refractive index graphs are given in Figure 7-13. There is a difference in n of less than ~20%. The n obtained at 0.2 mbar deviates from that of AlN⁵⁴ by ~10%, which can be attributed to small amounts of boron and carbon atoms present in the film (please refer to Figure 7-14). At 10 mbar, a lower n is obtained, which can be ascribed to a larger share of the BCN compound; the latter is better formed at high pressures.

Figure 7-13. Refractive index (from in-situ SE) of films deposited at P_{tot} of 0.2 (black) and 10 (red) mbar. Other conditions: 0.5-5-30-60 s durations for a TEB-Ar-NH₃-Ar sequence and 0.5-5-10-5 s durations for a TMA-Ar-NH₃-Ar sequence.

The thickness was mapped by ex-situ SE (see Appendix 7.3). It shows a high non-uniformity with a thickness variation of up to 60%, which once more (recall Appendix 7.2) confirms thermal decomposition of TEB. Deposition at 0.2 mbar results in an improved thickness uniformity compared to that at 10 mbar, presumably due to a dominant AlN growth.

7.5.2 Compositional analysis from XPS

7.5.2.1 Sputter depth profiles

Sputter-depth profiling is given in Figure 7-14. Apart from Al, B, C and N, low amounts of oxygen (less than 5 at.%) can be seen. For the deposition at a P_{tot} of 10 mbar (Figure 7-14.a), the layer mainly consists of B, C and N, with approx. 2 at.% of Al. We conclude that, at high total pressures, BCN deposition takes over AlN deposition, somehow preventing the involvement of TMA molecules. Presumably, boron and/or carbon can occupy active surface sites, preventing the chemisorption of TMA. At low pressures, 34 at.% of Al is incorporated into the film (see Figure 7-14.b). This can be explained by the inhibited growth of BCN, as earlier demonstrated in Figure 7-5.

Figure 7-14. XPS depth profiles of AlBCN samples (capped with *a*-Si layer) deposited at P_{tot} of (a) 10 mbar and (b) 0.2 mbar. The indicated stoichiometric coefficients are calculated from the peak-intensity ratios and do not necessarily imply the occurrence of a single-phase.

7.5.2.2 Chemical bonding environments

Figure 7-15 shows Gaussian fitting of Al 2p, B 1s and N 1s peaks of a sample deposited at a P_{tot} of 0.2 mbar. Positions of the subpeaks were fixed according to Table 7-4. The C 1s peak (intensity within error margin – no deconvolution performed) position shifted towards lower energies, namely to 282.0 eV, possibly due to the presence of Al. the Al 2p peak was successfully fitted by two subpeaks. Nitrogen showed two different bonding states attributed to N-Al and N-B bonds as in AlN and BN, respectively. Weak subpeaks of a N-C bond were observed at 399.0 and 400.0 eV, due to the shift in N 1s peak positions during sputtering (see Appendix 7.4), to be assigned to sp or sp^3 and sp^2 hybridizations, respectively.

Figure 7-15. Deconvolution of representative Al 2p (a), B 1s (b) and N 1s (c) XPS peaks of the $\text{Al}_{34}\text{B}_{13}\text{C}_3\text{N}_{49}$ sample of Figure 7-14.b deposited at $P_{\text{tot}} = 0.2$ mbar. 2 different peak positions were determined for N 1s clearly indicating the formation of AlN and BN compounds.

From the measured composition and the peak-deconvolution analysis, it might be speculated that the $\text{Al}_{34}\text{B}_{13}\text{C}_3\text{N}_{49}$ sample contained stoichiometric AlN and BN phases with some small incorporations of carbon.

Table 7-4. XPS binding energies of Al 2p, B 1s and N 1s peaks of the $Al_{34}B_{13}C_3N_{49}$ sample deposited at $P_{tot}=0.2$ mbar, and peak assignment from the literature.

element	binding energy (eV)	possible bonds and compounds	references
Al 2p	73.4	Al-N in AlN	60
	75.2	Al-O in Al_2O_3	61
B 1s	187.5	B-C in B_4C	33-36
		B-B in pure-B	37
	190.3	B-N in BN	42-44
N 1s	396.7	N-Al in AlN	60
	397.5	N-B in BN	38,44,49
	399.0	carbon-nitrogen bond in sp or sp^3 hybridizations	38,41,43,49,52,53
	400.0	carbon-nitrogen bond in sp^2 hybridization	49,52,53

Figure 7-16 shows the peak deconvolution of the $Al_2B_{41}C_{36}N_{15}$ sample (recall Figure 7-14.a) deposited at a P_{tot} of 10 mbar. The B 1s and C 1s spectra exhibited bonding states located at binding energies similar to those earlier measured for the BCN films discussed in Section 7.4.2.2. Further, the Al 2p peak was successfully fitted by two subpeaks (Figure 7-16.b) attributed to AlN and Al_2O_3 , similar to the 0.2 mbar case (recall Figure 7-15.a). The N 1s peak showed two different bonding states attributed to N-Al and N-B bonds as in AlN and BN, respectively (Figure 7-16.d). In addition, from deconvolution of the N 1s peak, a weak subpeak of a N-C bond might be suggested. The peak position ranges between 399.0 and 400.3 eV, depending on the vertical position of the volume probed by XPS inside the film. At the film surface, the N-C peak presumably appears at 399.0 eV, whereas it shifts to 400.3 eV while approaching the film/substrate interface (see Appendix 7.4). The shift may point out to a change in the bonding environment of nitrogen, which can be related to the change of GPC observed for the 10-mbar sample (Figure 7-11.b). Since a similar N 1s peak shift is observed for the 0.2-mbar sample as well, a change in GPC can also be expected there when approaching critical thickness. The latter is however difficult to achieve due to a low GPC at 0.2 mbar. The N 1s subpeaks at

399.0 and 400.0 eV can be assigned to sp or sp^3 and sp^2 hybridizations, respectively. Please refer to Tables 7-3 and 7-4 for further details.

Summarizing, the $Al_2B_{41}C_{36}N_{15}$ sample deposited at 10 mbar resembles, in terms of its composition and chemical bonding environments, the $B_{0.42}C_{0.41}N_{0.15}$ sample earlier discussed in Section 7.4.2.2. The similar elemental shares of B, N and C can originate from the low share of Al, making these two materials comparable. We can once again speculate the appearance of B_xC , C_yN , pure C and stoichiometric BN phases, perhaps with some additions of a single $B_xC_yN_z$ phase. As for the $Al_{34}B_{13}C_3N_{49}$ sample obtained at 0.2 mbar, co-existence of stoichiometric AlN and BN phases with some small incorporations of carbon may be speculated.

Figure 7-16. Deconvolution of representative B 1s (a), Al 2p (b), C 1s (c) and N 1s (d) XPS peaks of the $Al_2B_{41}C_{36}N_{15}$ sample of Figure 7-14.a deposited at $P_{tot}=10$ mbar. 2 different peak positions were determined for N 1s clearly indicating the formation of AlN and BN compounds.

7.6 Conclusions

This work investigated deposition of BCN and AlBCN films in view of the goals mentioned in the introduction. It was shown that, GPC of BCN films increases with T_s and t_{TEB} , indicating the ongoing thermal decomposition of TEB. The large non-uniformity exhibited by the films confirmed once more the thermal decomposition of TEB, dominating the film growth. The films deposited at different T_s comprised similar quantitative elemental compositions (QEC) of $B_{42}C_{41}N_{15}$ (values vary by ± 2), showing inefficient film nitridation. In order to facilitate nitridation, longer ammonia pulse times were applied, still hardly showing any effect on GPC. However, the t_{NH_3} influenced the N 1s bonding environment, which was changed from sp or sp^3 hybridized carbon-nitrogen bonding at $t_{NH_3}=5$ s to sp^2 hybridized carbon-nitrogen bonding at $t_{NH_3}=30-60$ s. This change had a significant effect on n which decreased by $\sim 10\%$.

To investigate alternative chemical routes, HW-assisted deposition was applied, which allowed to provide atomic hydrogen to the system among the other precursors. This lead to a lower N- and a higher C-share, yielding a QEC of $B_{45}C_{47}N_6$. The effect could be explained by the involvement of different-to-thermal chemical routes, still, however, resulting in inefficient nitridation.

The deposition of AlBCN films were found to be slightly pressure dependent, namely high P_{tot} resulted in $\sim 10\%$ higher GPC. A thickness dependent GPC was measured by in-situ SE at the high P_{tot} ; above a critical thickness ($d > 10$ nm), GPC increased by $\sim 20\%$. The films exhibited clear compositional differences. Specifically, the very different QEC of the $Al_{34}B_{13}C_3N_{49}$ and $Al_2B_{41}C_{36}N_{15}$ film deposited at 0.2 and 10 mbar, respectively, indicated the enhanced BCN deposition at higher P_{tot} whereas lower P_{tot} caused mainly AlN in the films. The $Al_2B_{41}C_{36}N_{15}$ sample deposited at 10 mbar resembled, in terms of its composition and chemical bonding environments, to the $B_{0.42}C_{0.41}N_{0.15}$ sample earlier discussed in Section 7.4.2.2. The similar elemental shares of B, N and C possibly originated from the low share of Al, making these two materials comparable.

Solely from XPS, appearance of B_xC , C_yN , pure C and stoichiometric BN phases, perhaps with some additions of a single $B_xC_yN_z$ phase can be speculated for all samples. As for the $Al_{34}B_{13}C_3N_{49}$ sample obtained at 0.2 mbar, co-existence of stoichiometric AlN and BN phases with some small incorporations of carbon may be speculated. However, a detailed investigation is required in order to identify the available phases.

Appendix 7.1: Stepwise growth of BCN films

Figure A-7-1. The effect of post-NH₃ purge time (given inside the images) on the stepwise growth of BCN films deposited at P_{tot} of 5 mbar using t_{NH_3} of (a) 2 s and (b) 5 s, as determined by in-situ SE. The graphs show that post-NH₃ purge times longer than 20 s is required to minimize possible gas phase reactions between TEB and NH₃. It is important to bear in mind the considerations mentioned in Section 5.5.2 w.r.t. to the small step-variations interpreted by SE as the thickness changes.

Appendix 7.2: Thickness variation of BCN films mapped by ex-situ SE

Figure A-7-2. (a) Representative thickness mapping of a BCN layer deposited at 375 °C, 10 mbar and t_{NH_3} of 5 s. To note, TEB is introduced from the left-hand side of the image. The thickness variations in (b) and (c) are calculated as $[(\text{max}-\text{min})/\text{max}] \times 100$.

Appendix 7.3: Thickness variation of AlBCN films mapped by ex-situ SE

Figure A-7-3. Ex-situ SE thickness maps of AlBCN samples deposited at P_{tot} of (a) 10 mbar and (b) 0.2 mbar. To note: TEB and TMA are introduced from the left-hand side, as indicated. As a result, thicker layers are formed closer to the gas inlet. Deposition at 0.2 mbar results in an improved thickness uniformity, suggesting a dominant AlN growth.

Appendix 7.4: Sputter depth profile line intensities

Figure A-7-4: Sputter depth profile line intensities of N 1s peaks for samples deposited at P_{tot} of (a) 0.2 mbar and (b) 10 mbar. The shift in N 1s peak maxima indicates different bonding environments as discussed earlier in Sections 7.4.2.2 and 7.5.2.2.

References

- ¹ S. Banerjee, A.A.I. Aarnink, D.J. Gravesteijn, and A.Y. Kovalgin, *J. Phys. Chem. C* **123**, 23214 (2019).
- ² M. Chubarov, *Chemical Vapour Deposition of Sp² Hybridised Boron Nitride*, Linköping University, 2014.
- ³ R.R.Q. Freitas, G.K. Gueorguiev, F. De Brito Mota, C.M.C. De Castilho, S. Stafström, and A. Kakanakova-Georgieva, *Chem. Phys. Lett.* **583**, 119 (2013).
- ⁴ M. Imam, C. Höglund, S. Schmidt, R. Hall-Wilton, J. Birch, and H. Pedersen, *J. Chem. Phys.* **148**, (2018).
- ⁵ A. Haider, C. Ozgit-Akgun, E. Goldenberg, A.K. Okyay, and N. Biyikli, *J. Am. Ceram. Soc.* **97**, 4052 (2014).
- ⁶ M. Snure, Q. Paduano, M. Hamilton, J. Shoaf, and J.M. Mann, *Thin Solid Films* **571**, 51 (2014).
- ⁷ O.J. Kilbury, K.S. Barrett, X. Fu, J. Yin, D.S. Dinair, C.J. Gump, A.W. Weimer, and D.M. King, *Powder Technol.* **221**, 26 (2012).
- ⁸ W. Hao, C. Marichy, and C. Journet, *2D Mater.* **6**, (2019).
- ⁹ S. Joh and G.H. Evans, in *Proc. Thirteen. Int. Conf. Chem. Vap. Depos.*, edited by T.M. Besmann, M.D. Allendorf, M. Robinson, and R.K. Ulrich (The Electrochemical Society, Inc., New Jersey, 1996), pp. 588–593.
- ¹⁰ J.S. Lewis, S. Vaidyaraman, W.J. Lackey, P.K. Agrawal, G.B. Freeman, and E.K. Barefield, *Mater. Lett.* **27**, 327 (1996).
- ¹¹ M. Imam, K. Gaul, A. Stegmüller, C. Höglund, J. Jensen, L. Hultman, J. Birch, R. Tonner, and H. Pedersen, *J. Mater. Chem. C* **3**, 10898 (2015).
- ¹² M. Imam, *CVD Chemistry of Organoborons for Boron-Carbon Thin Film Depositions*, Linköping University, 2017.
- ¹³ H. Jeong, D.Y. Kim, J. Kim, S. Moon, N. Han, S.H. Lee, O.F.N. Okello, K. Song, S.Y. Choi, and J.K. Kim, *Sci. Rep.* **9**, 1 (2019).
- ¹⁴ S.S. Liu and D.A. Stevenson, *J. Electrochem. Soc.* **125**, 1161 (1978).
- ¹⁵ M.E. Bartram, T.A. Michalske, J.W. Rogers, and R.T. Paine, *Chem. Mater.* **5**, 1424 (1993).
- ¹⁶ S. Yamashita, K. Watanuki, H. Ishii, Y. Shiba, M. Kitano, Y. Shirai, S. Sugawa, and T. Ohmi, *J. Electrochem. Soc.* **158**, H93 (2011).
- ¹⁷ H. Pedersen, C. Höglund, J. Birch, J. Jensen, and A. Henry, *Chem. Vap. Depos.* **18**, 221 (2012).
- ¹⁸ C.D. Stinespring and J.C. Wormhoudt, *J. Cryst. Growth* **87**, 481 (1988).
- ¹⁹ A.Y. Kovalgin, M. Yang, S. Banerjee, R.O. Apaydin, A.A.I. Aarnink, S. Kinge, and R.A.M. Wolters, *Adv. Mater. Interfaces* **4**, 1700058 (2017).

- ²⁰ M. Yang, Hot-Wire Assisted Atomic Layer Deposition of Tungsten Films, University of Twente, 2018.
- ²¹ X. Yang, S. Nitta, K. Nagamatsu, S.Y. Bae, H.J. Lee, Y. Liu, M. Pristovsek, Y. Honda, and H. Amano, *J. Cryst. Growth* **482**, 1 (2018).
- ²² D. Jin-Xiang, Z. Xiao-Kang, Y. Qian, W. Xu-Yang, C. Guang-Hua, and H. De-Yan, *Chinese Phys. B* **18**, 4013 (2009).
- ²³ H. Umemoto, K. Ohara, D. Morita, T. Morimoto, M. Yamawaki, A. Masuda, and H. Matsumura, *Jpn. J. Appl. Phys.* **42**, 5315 (2003).
- ²⁴ Y.J. Shi, B.D. Eustergerling, and X.M. Li, *Thin Solid Films* **516**, 506 (2008).
- ²⁵ M.K. Lei, Q. Li, Z.F. Zhou, I. Bello, C.S. Lee, and S.T. Lee, *Thin Solid Films* **389**, 194 (2001).
- ²⁶ C. Kimura, H. Sota, H. Aoki, and T. Sugino, *Diam. Relat. Mater.* **18**, 478 (2009).
- ²⁷ H. Sota, C. Kimura, H. Aoki, and T. Sugino, *Diam. Relat. Mater.* **19**, 1441 (2010).
- ²⁸ A. Prakash and K.B. Sundaram, *Appl. Surf. Sci.* **396**, 484 (2017).
- ²⁹ J.C. Angus and C.C. Hayman, *Science* (80-.). **241**, 913 (1988).
- ³⁰ B. Dischler, A. Bubenzer, and P. Koidl, *Appl. Phys. Lett.* **42**, 636 (1983).
- ³¹ J. Robertson and E.P. Oreilly, *Phys. Rev. B* **35**, 2946 (1987).
- ³² M. Chubarov, H. Pedersen, H. Högberg, J. Jensen, and A. Henry, *Cryst. Growth Des.* **12**, 3215 (2012).
- ³³ W. Cermignani, T.E. Paulson, C. Onneby, and C.G. Pantano, *Carbon N. Y.* **33**, 367 (1995).
- ³⁴ S. Jacques, A. Guette, X. Bourrat, F. Langlais, C. Guimon, and C. Labrugere, *Carbon N. Y.* **34**, 1135 (1996).
- ³⁵ Y. Sun, Q. Meng, M. Qian, B. Liu, K. Gao, Y. Ma, M. Wen, and W. Zheng, *Sci. Rep.* **6**, 1 (2016).
- ³⁶ H. Moreno Fernández, D. Rogler, G. Sauthier, M. Thomasset, R. Dietsch, V. Carlino, and E. Pellegrin, *Sci. Rep.* **8**, 1 (2018).
- ³⁷ E.A. Il'inchik, V. V. Volkov, and L.N. Mazalov, *J. Struct. Chem.* **46**, 523 (2005).
- ³⁸ M.A. Mannan, M. Nagano, K. Shigezumi, T. Kida, N. Hirao, and Y. Baba, *Am. J. Appl. Sci.* **5**, 736 (2008).
- ³⁹ M.O. Watanabe, T. Sasaki, S. Itoh, and K. Mizushima, *Thin Solid Films* **281–282**, 334 (1996).
- ⁴⁰ H. Künzli, P. Gantenbein, R. Steiner, and P. Oelhafen, *Fresenius. J. Anal. Chem.* **346**, 41 (1993).
- ⁴¹ A. Perrone, A.P. Caricato, A. Luches, M. Dinescu, C. Ghica, V. Sandu, and A. Andrei, *Appl. Surf. Sci.* **133**, 239 (1998).

- ⁴² V.S. Sulyaeva, Y.M. Rumyantsev, V.G. Kesler, and M.L. Kosinova, *Thin Solid Films* **581**, 59 (2015).
- ⁴³ T. Thamm, D. Wett, W. Böhne, E. Strub, J. Röhrich, R. Szargan, G. Marx, and W.A. Goedel, *Microchim. Acta* **156**, 53 (2006).
- ⁴⁴ V.O. Todi and K.B. Sundaram, *Electrochem. Solid-State Lett.* **14**, G49 (2011).
- ⁴⁵ A.R. Burke, C.R. Brown, W.C. Bowling, J.E. Glaub, D. Kapsch, C.M. Love, R.B. Whitaker, and W.E. Moddeman, *Surf. Interface Anal.* **11**, 353 (1988).
- ⁴⁶ L.G. Jacobsohn, R.K. Schulze, M.E.H. Maia Da Costa, and M. Nastasi, *Surf. Sci.* **572**, 418 (2004).
- ⁴⁷ C. Ronning, D. Schwen, S. Eyhusen, U. Vetter, and H. Hofsäss, *Surf. Coatings Technol.* **158–159**, 382 (2002).
- ⁴⁸ L. Liu, Y. Wang, K. Feng, Y. Li, W. Li, C. Zhao, and Y. Zhao, *Appl. Surf. Sci.* **252**, 4185 (2006).
- ⁴⁹ F. Zhou, K. Adachi, and K. Kato, *Thin Solid Films* **497**, 210 (2006).
- ⁵⁰ M.O. Watanabe, S. Itoh, K. Mizushima, and T. Sasaki, *Appl. Phys. Lett.* **68**, 2962 (1996).
- ⁵¹ A. Majumdar, J. Schäfer, P. Mishra, D. Ghose, J. Meichsner, and R. Hippler, *Surf. Coatings Technol.* **201**, 6437 (2007).
- ⁵² P. Petrov, D.B. Dimitrov, D. Papadimitriou, G. Beshkov, V. Krastev, and C. Georgiev, *Appl. Surf. Sci.* **151**, 233 (1999).
- ⁵³ E. D'Anna, M.L. De Giorgi, A. Luches, M. Martino, A. Perrone, and A. Zocco, *Thin Solid Films* **347**, 72 (1999).
- ⁵⁴ S. Banerjee, *From Radical-Enhanced to Pure Thermal ALD of Aluminium and Gallium Nitrides*, University of Twente, 2019.
- ⁵⁵ S. Banerjee, A.A.I. Aarnink, D.J. Gravesteijn, and A.Y. Kovalgin, in *EuroCVD 22-Baltic ALD 16 Conf.* (Luxembourg, 2019).
- ⁵⁶ S.K. Kim, S. Hoffmann-Eifert, M. Reiners, and R. Waser, *J. Electrochem. Soc.* **158**, 28 (2011).
- ⁵⁷ D.R.G. Mitchell, D.J. Attard, and G. Triani, *Thin Solid Films* **441**, 85 (2003).
- ⁵⁸ D.G. De Oteyza, E. Barrena, J.O. Ossó, S. Sellner, and H. Dosch, *J. Am. Chem. Soc.* **128**, 15052 (2006).
- ⁵⁹ K.-M. Kang, Y.-J. Choi, G.Y. Yeom, and H.-H. Park, *J. Vac. Sci. Technol. A Vacuum, Surfaces, Film.* **34**, 01A144 (2016).
- ⁶⁰ T. Hagio, A. Takase, and S. Umebayashi, *J. Mater. Sci. Lett.* **11**, 878 (1992).
- ⁶¹ Y.C. Kim, H.H. Park, J.S. Chun, and W.J. Lee, *Thin Solid Films* **237**, 57 (1994).

8 Conclusions and recommendations

8.1 Conclusions

This thesis addressed deposition of B-, C- and N- containing thin films by thermal and radical-enhanced methods. We explored both pulsed-deposition and ALD approaches, with the aim to comparatively study and understand the growth mechanisms, observe the occurrence of various phases in the compounds, and obtain basic material properties. Several precursor systems have been explored in view of the deposition mechanisms hypothesized and the research goals named. The approach and motivation were outlined in Chapter 1.

Chapter 2 focused on the application of SE for determining thickness, optical functions and composition of the films. The relevant optical SE models were reviewed, finally building the appropriate models used through the entire thesis for analyzing the films and composites under study. The performed literature review outlined the relevant film-growth mechanisms in terms of surface chemical reactions. The mechanisms we further confirmed / disproved to occur in the following up chapters of this thesis, in relation to the particular precursors used.

Chapter 3 experimentally verified the SE approach proposed in Chapter 2 for the films deposited from B_2H_6 and NH_3 gases. The analysis suggested the multi-phase (composite) film nature; the films were further referred to as B/BN composites. The composites exhibited refractive indices (n) strongly dependent on the pure-B fraction: a gradual increase of n from 1.7 (stoichiometric BN) to 2.9 (pure-B) was achieved by tuning the pure-B share. It was shown that the developed SE model could quantitatively describe the experimental n -values as well as the multi-phase nature of the films in terms of the B- and BN-shares. Thin pure-B films revealed a characteristic and not mentioned in the literature absorption peak at ~ 3.3 eV. The XPS measurements confirmed composite nature of the films, indicating the presence of a well-defined stoichiometric BN phase. The cross-correlation maps provided by EFTEM showed lateral homogeneity of the B- and N-elements, thereby suggesting their vertical inhomogeneity.

In Chapter 4, the growth mechanism of the B/BN composites deposited from B_2H_6 and NH_3 gases was investigated. The degree of dissociation of NH_3 was gradually changed from *zero* (purely thermal mode) through *low* by applying a hot-wire (HW) to *high* by plasma-assistance. In purely thermal mode, the growth and composition of the layers were strongly dependent on total gas pressure (P_{tot}): increasing the P_{tot} enhanced the GPC and reduced the pure-B content from ~70 vol.% to ~6 vol.%. Such a strong pressure dependence allowed to hypothesize the growth mechanism via the surface-adduct reaction pathway, analogous to the earlier suggested mechanisms for AlN and GaN. Introducing additional means to dissociate NH_3 significantly affected the growth behavior, film properties and thus the mechanism. The best results were obtained with plasma, which provided near stoichiometric, crystalline and stable in air BN films at approx. 300 °C.

Applicability of the surface-adduct mechanism to ALD of BN from BBr_3 and NH_3 was further addressed in Chapter 5 and 6. Chapter 5 showed that the hypothesized role of the $BBr_3:NH_3$ surface adduct in the ALD mechanism could adequately explain the experimental observations. In addition, the kinetics of surface-adduct formation and its conversion to $-NH_2-$ linkages were simulated using a Mathcad code. The results showed a dependence of the adduct surface coverage on ammonia partial pressure, in line with the experimental observations.

Alternative approaches to growing BN from BBr_3 and NH_3 , such as the radical assistance and the use of a cold-wall reactor instead of a hot-wall reactor, were discussed in Chapter 6. The radical (plasma) assistance led to lower GPC values and the occurrence of a pure-B phase, clearly indicating the involvement of additional-to-thermal chemical routes. A change of the film growth mechanism was suggested. Use of a hot-wire instead of plasma revealed similar results, although less pronounced in view of a lower dissociation degree of ammonia by HW compared to plasma. The cold-wall reactor enabled studying the reaction byproducts, namely NH_4Br , which was suggested for differentiating between ALD and CVD modes and verifying film-growth mechanism.

Chapter 7 discussed growth of BCN and AlBCN films from metalorganic precursors. Due to the low temperature required for thermal decomposition of triethylborane (TEB, ~ 250 °C), ammonia was not able to react with a TEB-terminated surface at such low temperatures and thus provide its efficient nitridation. The attempt to enhance this process by activating the surface-adduct pathway was unsuccessful since thermal decomposition of TEB still led the process. Decomposition suppressed the removal of carbon (of TEB) from the layers, which in turn appeared to be beneficial for adding C impurities to BN and thus forming BCN. Giving TEB/ NH_3 and TMA/ NH_3 super-cycles resulted in AlBN or AlBCN compounds, depending on total gas pressure. From XPS, appearance of B_xC , C_yN , pure C as well as stoichiometric AlN and BN phases might be speculated, perhaps with some additions of a $\text{B}_x\text{C}_y\text{N}_z$ phase.

8.2 Recommendations

The broad experimental work conducted in this thesis provides many opportunities for additional research. This will be briefly addressed in this section.

The formation of surface adducts of $\text{BH}_3\text{:NH}_3$, $\text{BBr}_3\text{:NH}_3$ and TEB:NH_3 , and their conversion to $-\text{NH}_2$ - linkages is crucial for explaining the film deposition mechanism. The adduct occurrence shall be experimentally confirmed or disproved by using appropriate surface analysis techniques, such as FTIR and XPS.

Additional studies are required to verify the application feasibility of the materials investigated in this thesis. Concerning the B/BN composites with tunable refractive index (Chapter 3), it would be interesting to characterize these films in terms of their electronic properties. *Can the B/BN lead to bandgap engineering, thus opening new routes towards the applications in electronics?*

The plasma assisted depositions from B_2H_6 and NH_3 resulted in hexagonal boron nitride films with crystal planes stacked perpendicular to the substrate surface (Chapter 4). The high thermal conductivity of BN together with the wide bandgap makes it an attractive material for certain applications. *Can h-BN*

outperform the existing gate dielectric materials and be a suitable material for graphene-based devices? The properties of h-BN can additionally suggest using it as a *protective layer for EUV pellicles*. Further, investigation of substrate effects in relation to area selective growth of h-BN can enable many potential applications, and is therefore an interesting route to explore.

The byproduct characterization suggested in Chapter 6 is practically attractive for the efficient and fast optimization of deposition processes, and scientifically interesting to enable differentiation between ALD and CVD modes as well as verification of film-growth mechanism. Exploring this promising approach has just been started in this work and can be addressed in a future research.

Deposition of BCN and AlBCN films attempted in Chapter 7 is at the beginning stage and will certainly require a continuation. Further experiments are needed to shine light on the (co)-existence of phases as well as on structural, optical and electrical properties of these films. Practically, the ability to manipulate the optical and electronic properties by varying composition and/or chemical bonding environments may lead to specific applications in, for example, (opto)electronics.

Summary

This thesis focused on the deposition of B-, C- and N-containing thin films from several precursor systems. We explored both pulsed-deposition and ALD approaches, with the aim to comparatively understand the growth mechanisms and investigate the effects of a variety of activation techniques; namely, thermal-, hot-wire- (HW-) and plasma-assistance. Furthermore, this thesis aims to clarify the occurrence of various phases in the compounds, and obtain the material properties.

The research started with developing recipes for the deposition of BN layers, giving alternating pulses of B_2H_6 and NH_3 . The results suggested the multi-phase (composite) film nature, consisting of pure-B and BN. These films exhibited refractive indices (n) strongly dependent on the pure-B fraction. It was found that the growth and composition of these layers were strongly dependent on total gas pressure (P_{tot}): enhanced GPC and reduced pure-B were achieved by increasing the P_{tot} . This strong pressure dependence allowed to hypothesize the growth mechanism via the surface-adduct reaction pathway analogous to previously reported AlN and GaN. Introducing additional means of activation (i.e. HW and plasma) affected the growth behavior, film properties and therefore the growth mechanism. Plasma-assistance provided near-stoichiometric, crystalline BN film at ~ 300 °C. These insights established the groundwork towards understanding the growth via the surface-adduct reaction pathway for the ALD of BN from BBr_3 and NH_3 precursor system. It was shown that, the experimental results could be adequately explained by the suggested reaction mechanism. Moreover, the results showed the influence of alternative approaches: the occurrence of pure-B phase and lower GPC in the case of plasma-assistance indicated the different-from-thermal growth mechanism. Switching to a cold-wall reactor enabled studying the reaction byproducts, which was suggested for differentiating between ALD and CVD modes.

The deposition of BCN and AlBN layers was subsequently explored from TEB and NH_3 . The results suggested ineffective nitridation of TEB-terminated surfaces in thermal deposition mode. Utilizing additional means of activation to enable manipulating the composition was unsuccessful due to the low temperature required for thermal decomposition of TEB, which dominated the process. This, however in turn, appeared to be beneficial for the formation of BCN. Giving TEB/ NH_3 and TMA/ NH_3 super-cycles resulted in AlBN or AlBCN compounds, depending on total gas pressure.

Dit proefschrift behandelt de depositie van B-, C- en N-bevattende dunne films met verschillende precursors. We hebben zowel gepulste depositie als ALD technieken onderzocht, met als doel om de groeimechanismen te kunnen vergelijken en begrijpen, en om de effecten van een aantal activatietechnieken in kaart te brengen, namelijk thermische, hot-wire (HW) en plasma activatie. Verder beschrijft dit proefschrift de materiaaleigenschappen en het voorkomen van verschillende fasen in de films.

Het onderzoek begon aanvankelijk met het ontwikkelen van recepten voor BN lagen, gebruik makend van afwisselende pulsen van B_2H_6 en NH_3 . De resultaten duiden de aanwezigheid van meerdere fasen aan, puur B en BN. De brekingsindices (n) van deze films waren sterk afhankelijk van de hoeveelheid puur B in de films. De groei en samenstelling van deze lagen bleek sterk af te hangen van de totale gasdruk (P_{tot}): een verhoogde GPC en een verlaagde hoeveelheid puur B resulteerden door het verhogen van P_{tot} . Deze sterke drukafhankelijkheid heeft geleid tot de hypothese dat in het groeimechanisme reacties van oppervlakte-adducten een rol spelen, analoog aan eerder beschreven groei van AlN en GaN. Het introduceren van toegevoegde activatiemiddelen (HW en plasma) beïnvloedden de groei, de eigenschappen van de films, en dus het groeimechanisme. Plasma-assistentie resulteerde in vrijwel stoichiometrisch, kristallijn BN bij ~ 300 °C. Deze inzichten legden de basis voor het begrijpen van ALD van BN, gebruik maken van BBr_3 en NH_3 precursors, via een oppervlakte-adduct mechanisme. De resultaten van de experimenten konden adequaat worden verklaard met dit mechanisme. Ook lieten de resultaten de invloed van alternatieve benaderingen zien: Het voorkomen van een puur-B fase en een lagere GPC in het geval van plasma-assistentie suggereerden een groeimechanisme afwijkend van thermische groei. Overschakelen naar een cold-wall reactor maakte het bestuderen van nevenproducten van de reacties mogelijk, hetgeen voorgesteld was om onderscheid te kunnen maken tussen ALD en CVD modes.

Vervolgens is de depositie van BCN en ALBN lagen bestudeerd, gebruik makend van TEB en NH_3 . De resultaten suggereerden onvolledige nitridatie van TEB-getermineerde oppervlakken tijdens thermische depositie. Het gebruiken van toegevoegde activatiemiddelen om de samenstelling te manipuleren was niet succesvol vanwege de lage temperatuur voor thermische decompositie van TEB, waardoor dit laatste het groeiproces domineerde. Dit bleek echter voordelig voor het vormen van BCN. Het gebruiken van TEB/ NH_3 en TMA/ NH_3 super-cycli resulteerde in AlBN of AlBCN verbindingen, afhankelijk van de totale gasdruk.

List of Publications

Journals

Ramazan O. Apaydin, Arnoud J. Onnink, Antonius A.I. Aarnink, Michel P. de Jong, Dirk J. Gravesteijn and Alexey Y. Kovalgin, "*Multi-Phase Nature of Tunable-Refractive-Index B/BN Films Confirmed by Photoelectron Spectroscopy and Quantified by Ellipsometry*", submitted to Journal of Vacuum Science and Technology A.

Ramazan O. Apaydin, Arnoud J. Onnink, Xingyu Liu, Antonius A.I. Aarnink, Michel P. de Jong, Dirk J. Gravesteijn and Alexey Y. Kovalgin, "*A Comparative Study of Thermal and Radical-Enhanced Methods for Growing Boron Nitride Films from Diborane and Ammonia*", submitted to Journal of Vacuum Science and Technology A.

Alexey Y. Kovalgin, Mengdi Yang, Sourish Banerjee, **Ramazan O. Apaydin**, Antonius A. I. Aarnink, Sachin Kinge, Rob A. M. Wolters, "*Hot-Wire Assisted ALD: A Study Powered by In Situ Spectroscopic Ellipsometry*", Adv. Mater. Interfaces, 4, 2017, 1700058, Invited.

Conferences

R.O. Apaydin, A.J. Onnink, X. Liu, A.A.I. Aarnink, M.P. de Jong, D. J. Gravesteijn and A.Y. Kovalgin, "*Deposition of boron nitride films from B₂H₆ and NH₃*", PRORISC&SAFE conference, Eindhoven, July 2019, poster presentation.

R.O. Apaydin, A.A.I. Aarnink, M. P. de Jong, D.J. Gravesteijn, A.Y. Kovalgin, "*A comparative study of low-temperature BN ALD in thermal and plasma-enhanced modes*", EuroCVD 22 – Baltic ALD 16, Luxembourg, June 2019, oral presentation.

Arnoud J. Onnink, **R. Oguzhan Apaydin**, Jurriaan Schmitz and Alexey Y. Kovalgin, "*In-situ study of ammonium bromide formation for optimizing boron nitride ALD from BBr₃ and NH₃*", EuroCVD 22 – Baltic ALD 16, Luxembourg, June 2019, oral presentation, co-author.

Sourish Banerjee, **Ramazan O. Apaydin** and Alexey Y. Kovalgin, "*A comparative study of low-temperature III-V nitrides ALD in thermal and radical-enhanced modes*", ECS 234 meeting (AiMES 2018), Cancun, 2018, oral presentation, co-author.

A.J. Onnink, **R.O. Apaydin**, J. Schmitz and A.Y. Kovalgin, "*Monitoring of hotwire-assisted layer deposition and etching*", MESA+ Day, September 2018, Enschede, shared first authorship.

A.J. Onnink, **R.O. Apaydin**, J. Schmitz, M.P. de Jong, A.Y. Kovalgin, *“Strategies to Mitigate the Ammonium Halide Contamination of an ALD/CVD Reactor”*, SAFE conference, Enschede, June 2018, poster and oral presentation, *shared first authorship*.

X. Liu, **R.O. Apaydin**, S. Banerjee, A.A.I. Aarnink, A. Y. Kovalgin, L.K. Nanver, *“Electrical measurement of the conduction along the interface of negatively-charged CVD/ALD depositions on silicon”*, EuroCVD 21 – Baltic ALD 15, Linköping, June 2017, poster presentation, *co-author*.

Sourish Banerjee, **Ramazan O. Apaydin**, Antonius A. I. Aarnink, Jurriaan Schmitz, Dirk J. Gravesteijn, Michel P. de Jong and Alexey Y. Kovalgin, *“Hot wire technique as a radical source for atomic layer deposition of metal and metal nitride films”*, EuroCVD 21 – Baltic ALD 15, Linköping, June 2017, oral presentation, *co-author*.

Acknowledgements

The four-year PhD life was a long, challenging but also a nice journey to me. I have always wanted to do it and here we are. I made my dream come true. Obviously, no single study can be done without the help of valuable contributions of others. Therefore, I would like to take my time here to send my acknowledgements to those who helped me in many different ways through my PhD study. I will do my best on remembering everybody but if I missed someone, please accept my apologies.

First and foremost, I would like to mention the brief story of how ended up with my PhD project. I actually applied for another project for which I was invited for an interview. Following the interviews, I received an e-mail from Jurriaan saying that “We look back on a very good interview round with you. After a team discussion about your application to our group, we wanted to investigate if you would fit the position, we have for a PhD student on two-dimensional semiconductor growth”. After thinking for a few days, I decided to say yes. Herewith, I would like to thank Prof. Dr. Jurriaan Schmitz for offering me the PhD position and giving me this great opportunity to do research with valuable scientists. Jurriaan, thank you for everything you have done for me.

I will always be thankful to my daily supervisors and also my promotor, Dr. Alexey Y. Kovalgin and Dr.ir. Michel P. de Jong for their guidance, patience, motivation and enthusiasm. I remember a lot of times being lost in trivial experiments and data analysis from which you dragged me out and guided me for a better goal in the project. You could stop me wasting time in less meaningful work. When I was frustrated with the results, you could still come up with an idea that allowed us transferring the results into scientific publications. I learned from Alexey and Michel that, sometimes, you just need to take a look at the results from a different perspective. Thank you very much for spending enormous time on guiding me and helping me to improve my scientific skills. In addition, special thanks to Michel for translating the summary of my thesis.

Besides Alexey and Michel, I would like to acknowledge Prof. Dr. Dirk Gravesteyn. Thank you for your kind support and valuable contribution. Also thank you for being positive all the time.

Apart from my supervisors, I would like to thank to the graduation committee members for taking the time from their busy schedule to evaluate this work.

I would like to thank to my former colleagues at IDS group. First of all, I am very thankful to Remke Assink and Susan Janse-Godschalk (former secretaries of IDS group) for helping with organizing all kinds of paper works till the last moment of their employment in our group.

My special thanks to our dedicated senior engineer Tom. Tom, I cannot think of enough words to thank you for your support and concern in both scientific and personal life. Thank you for creating the perfect atmosphere for us. I will always remember you with your positive, enthusiastic and beer loving personality. I am also thankful to my officemates, colleagues and friends in the second floor. Thank you all for your willingness to help and all the fun we had. Arnoud, thank you for being a really good friend, for your help and more importantly for accepting the tough duty of being my paranymph. Thanks to Kevin (from IDS) for his technical support during my study and thanks to all other IDS members for their kind help.

I also would like thank to Wilfred and Floris for their kind contributions to my work. Besides, I would like to thank to Johnny and all other NE members for their help during our group meetings, for being such good and helpful friends to me.

Let's take a chance to acknowledge some individuals for the fruitful discussions and their contribution. From MESA+: Gerard Kip, Rico Keim, Peter Linders, Marion Nijhuis, Huib van Vossen, Christiaan Bruinink, Robert Wijn, Mike Dijkers and from XUV optics group: Airat Shafikov, Seda Kizir, Marko Sturm, Bart Schurink and Wesley van den Beld.

Next, I would like to thank to the International Human Resources staff. Special thanks to Maureen S. Melisie and Dagmar J. Keuken for handling all the official works for me and helping me out for communicating with IND.

I would like to take the chance to send my special thanks to the dearest Turkish friends with whom I had great time during the last 4 years. Special thanks to our dedicated group member Muharrem and his family. I am grateful for all your help. Apart from them, I would like to thank to my friends Derya, Güner, Yiğitcan, Cihan, Seda, Pelin, Devrim, Deniz, Derya, Burcu, Akın, Sinem, Armağan, Elif, Özlem, Ozan, Yusuf, Mehmet and Damla. Thank you, guys, for being such good friends. Special thanks to Burcu for designing the cover of my thesis. Next, I owe my deepest gratitude to Yiğitcan for being a really good friend and accepting the responsibility of being my paranymp. Besides, I would like to thank to all other friends in the Turkish community. It was my pleasure meeting you all and I wish you all the best.

I would like to acknowledge my girlfriend for being extremely supportive especially during the last part of my PhD. Thank you for being such an understanding person. Thank you for your support whenever I needed and for helping me out for all sorts of things.

I would like to acknowledge my relatives who supported me during my life in the Netherlands. Among all, I am eternally grateful to my dear father, mother, brother, sister in law and lovely niece Nehir. I am thankful to you with all my heart for your confidence. I would be no match for something like this without your unlimited support. I felt safe and strong with your love and support and I am grateful to have you as my family. You were the ones I missed the most.

I would like to ask your kind understanding here since I would like to write the next paragraph in Turkish and dedicate it to my family.

“Annem, babam, ağabeyim, ablam ve güzel yeğenim Nehir; sizlere nasıl teşekkür edeceğimi bilemiyorum, keza hiçbir kelime bunu gerçekleştirmek için yeterli olmayacaktır. Sizlerin desteği olmadan böyle bir sürecin altından

kalkamazdım. Zaman zaman belli etmemiş ya da edememiş olsam da, burada bulunduğum süreç boyunca en çok özlediğim sizler oldunuz. Sizlerin hayatının uzağında kalmak, uzakta olmak ve güzel yeğenimin büyüdüğünü görememek belki de bu kararımın en ağır sonuçlarından birisiydi. Sevginiz ve desteğiniz sayesinde kendimi güvende ve güçlü hissettim. Sizin gibi bir aileye sahip olduğum için kendimi çok şanslı hissediyorum. Sizleri çok seviyorum.”

My apologies to whom I might have forgotten to mention here. You will always be in my heart and I will always be grateful for your support.

Sincerely,

R. Oğuzhan APAYDIN

Author's Biography

Ramazan Oğuzhan APAYDIN was born in Samsun, Turkey, on April 29th, 1988. He obtained his B.Sc. degree from Department of Metallurgical and Materials Engineering at Istanbul Technical University (ITU), Istanbul, Turkey, in 2011. Following, he obtained his M.Sc. degree from Department of Materials Science and Engineering at Istanbul Technical University (ITU), Istanbul, Turkey, in 2013. He carried out his B.Sc. work on “Design of A System to Manufacture Boron-Fiber Reinforced Aluminum Matrix Composites” under the supervision of Prof. Dr. Ismail DUMAN. He carried out his M.Sc. work on “Production of Copper-Nickel (CuNi) and Copper-Nickel-Indium (CuNiIn) Alloy Nanoparticles by Ultrasonic Spray Pyrolysis (USP) and Hydrogen Reduction (HR) Method” under the supervision of Prof. Dr. Sebahattin GURMEN. He joined the groups of Integrated Devices and Systems and NanoElectronics at University of Twente in June 2015 as a PhD candidate and worked on the project named “Ultra-thin Layers and Their Stacks for Next-generation Electronics and Energy Storage Devices” under the supervision of Dr. Alexey Y. KOVALGIN and Dr. Ir. Michel P. de JONG. His doctoral research is described in this thesis.

ERRATA for

“Thermal and Radical Enhanced Atomic Layer Deposition of Films Containing Boron, Nitrogen and Carbon”

PhD Thesis, Ramazan Oğuzhan Apaydın

March 30th, 2020

Page 53: typo

The sentence:

Namely, for $P_{\text{tot}} > 1$ mbar, the $P_{B_2H_6}$ was kept in the range of 10^{-3} - 10^{-2} mbar, whereas the P_{NH_3} was changing between 10^{-2} and 10^{-1} mbar.

should instead be:

Namely, for $P_{\text{tot}} > 1$ mbar, the $P_{B_2H_6}$ was kept in the range of 10^{-2} - 10^{-1} mbar, whereas the P_{NH_3} was changing between 10^{-1} and 2 mbar.