Time-Resolved CVD of Group 13-Nitrides

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Cover: Transmission electron microscope (TEM) image of epitaxial wurtzite GaN on 4H-SiC substrate together with the structure of the triazenide ligand.

Back side: Pole figure of epitaxial wurtzite InN on 4H-SiC substrate.

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

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This thesis is dedicated to my mom and dad, Amireh and Abdulkhallaq Rouf

Abstract

Group 13 nitrides (AlN, GaN and InN) and their alloys are semiconductor materials with a wide bandgap span covering from UV down to IR range. Their excellent electronic properties make them extremely attractive materials for light emitting diodes (LEDs) and different kind of transistor structures, especially high electron mobility transistors (HEMTs). These materials are routinely deposited by chemical vapor deposition (CVD) at high temperatures. The most sought-after material among the group 13 nitrides is InN due to its high electron mobility making it extremely useful in transistor structures. InN needs to be deposited at low temperatures as it decomposes at high temperatures. This does not only limit the deposition temperature for InN growth but also for all the other materials that will be deposited on top of InN. In this thesis the deposition of group 13 nitrides is investigated by low temperature atomic layer deposition (ALD) via both a thermal and plasma route. This was conducted by both process development and by improving the deposition chemistry by developing new precursors.

Carbon impurities is one of the greater challenges when using the standard aluminum precursor trimethylaluminum (TMA) in ALD due to the strong Al–C bonds in the molecule. An in-situ removal of carbon impurities was investigated by introducing a cleaning pulse, after the TMA pulse. The cleaning pulse consisted of an H₂, N₂ or Ar gas pulse perpendicular to the surface. The introduction of the cleaning pulse reduced the carbon impurity in the AlN film from 3 at% down to under 1 at%. This made it possible to deposit AlN at higher temperature to obtain better crystalline quality and on the same time reduce the impurity levels. Kinetic simulations showed that the cleaning pulse cleans the surface from desorbed methyl groups resulting in a suppressed reabsorption pathway.

To further reduce carbon impurities, the strong M–C bonded precursors was replaced with a M–N bonded one. The precursor used were tris(dimethylamido)gallium together with ammonia (NH₃) plasma to deposit GaN. The precursor showed ALD behavior and the resulting GaN film possessed significantly lower carbon impurities compared to M–C bonded precursor at low deposition temperatures. This precursor could also produce epitaxial GaN directly on 4H–SiC without a need of a seed layer. To further investigate the precursor impact on deposition chemistry and ultimately the film quality, three indium precursors were evaluated, indium(III)guanidinate, indium(III)amidinate and indium(III)formamidinate. All

three precursors have the same structure, only difference being the size of the substituent on the endocyclic carbon position (-NMe₂, -Me and -H respectively). Experimental results showed that smaller groups on the endocyclic carbon position improved the InN film quality in terms of crystallinity, morphology, stoichiometry, and optical properties. Density functional theory (DFT) calculations showed that smaller moieties on the endocyclic position will lead to less surface and steric repulsion with the exocyclic position. As the size is decreased the exocyclic groups can fold up closer towards the endocyclic position leading to elongated metal-ligand bonds which will result in easier removal of the ligand for the upcoming NH₃ plasma pulse.

From these results a new ligand was developed to further improve the deposition chemistry where the endocyclic carbon atom in the ligand backbone of the foramidinate ligand was replaced by a N atom to form a triazenide ligand (iPr-N=N=N-iPr). The triazenide ligand possess no moiety on the endocyclic position compared to the ligands used previously and hence should result in improved material quality if extrapolated from our previous study. The ligand was placed on indium and gallium forming In(III)triazenide and Ga(III)triazenide respectively. Both precursors showed excellent thermal properties making them good ALD precursors. Their use for depositing InN and GaN was investigated with NH₃ plasma. The resulting films showed excellent quality where no carbon could be detected for either InN nor GaN using XPS and ERDA. Both InN and GaN showed epitaxial growth behavior on 4H-SiC at deposition temperature of 350 °C, a factor of three lower deposition temperature compared to CVD. Interestingly, several linear growth regimes (ALD windows) upon changing the temperature were observed, two and three for InN and GaN respectively. This indicated that the precursors decomposed upon increasing the temperature to form smaller fragments which increased the growth rate but on the same time the smaller precursor fragments saturated the surface. This was further confirmed by DFT calculations.

The In(III)triazenide and Ga(III)triazenide was further used to deposit the ternary InGaN phase. A new method was developed where both precursors were mixed in the bubbler and co-sublimed into the reactor via a single pulse. The composition of the films could be tuned via bubbler temperature, deposition temperature and premixed ratio of the precursors in the bubbler. Near In_{0.5}Ga_{0.5}N could be obtained at low deposition temperatures confirmed by both XPS, ERDA and bandgap measurement. Deposition at 350 °C on 4H-SiC resulted in epitaxial In_{1-x}Ga_xN without a need of a seed layer.

Populärvetenskaplig Sammanfattning

De flesta materialen runt omkring oss finns inte naturligt ute i naturen utan måste syntetiseras. Ett sätt att syntetisera dessa material är i form av en beläggning, ett tunt skikt av material. En beläggning har olika egenskaper och ändamål men huvuduppgiften är att förändra ytan där beläggning ska läggas. En sorts beläggning som finns runt omkring oss är färg på till exempel bilar där beläggningens uppgift är att skydda metallen från korrosion. En beläggningsslag som varit på frammarsch de senaste decennierna heter atomic layer deposition (ALD) på engelska och som kan översättas till atomlagerdeponering. Denna metod används för att göra väldigt tunna skikt av ett önskat material. Metoden bygger på att man har källmolekyler som innehåller de atomer man vill att sitt tunna skikt ska innehålla. Dessa källmolekyler värms för att producera en ånga (om de inte är i gasfas vid rumstemperatur) och sedan förs ångan in i en depositions-kammare där de får reagera på en yta och bilda ett fast material. Då man oftast behöver två källmolekyler så pulser man in respektive källmolekyl med en inert spolagas mellan varje puls. När man har gått ett helt varv och pulsat in båda källmolekylerna så börjar man om och fortsätter på samma sätt tills man fått en film med den tjockleken som man önskar. Då man pulser in en källmolekyl i taget så kommer substratyten att mätts med respektive källmolekyl. Detta innebär att man växer det tunna skiktet av material ett atomlager i taget, vilket namnet också refererar till. Denna metod gör att man kan växa sina tunna skikt vid låga temperaturer samtidigt som man har extremt bra kontroll på tjockleken.

Grupp 13 nitrid, aluminiumnitrid (AlN), galliumnitrid (GaN) och indiumnitrid (InN) består av en metallatom från grupp 13 i det periodiska systemet (Al, Ga eller In) som är bundet till en kväveatom (N). Dessa material är så kallade halvledare vilket betyder att deras elektriska ledningsförmåga ligger mellan en ledare och en isolator. Deras egenskaper gör de till användbara material för bland annat ljusdioder (LED) och transistorer. All tre materialen sänder ut ljus med en viss våglängd i sina grundtillstånd men genom att binda två metaller tillsammans med kväve så kan man exempelvis bilda InGaN (kallas ternär fas). Genom att ändra In till Ga förhållandet så kan man också finjustera färgen (våglängden) som materialet emitterar. I denna avhandling så undersöktes möjligheten att deponera Al-, Ga-, samt InN med ALD vid låga temperaturer. Olika källmolekyler studerades, både kommersiella som trimetylaluminium (TMA) och tris(dimetylamido)gallium samt egenutvecklade molekyler. De olika källmolekylerna undersöktes för att få en bättre uppfattning gällande beläggningsslag samt hur molekylernas design påverkar materialens egenskaper. Som kvävekälla användes

ammoniak (NH_3), både termiskt och plasma för att få reaktivare NH_3 fragment. De tunna skikten (filmerna) undersöktes med hjälp av olika analystekniker för att få en uppfattning om kristalliniteten, sammansättningen, morfologin samt de elektriska och optiska egenskaperna. Resultaten från dessa studier har gett bättre förståelse av beläggningsskemin samt sambandet mellan källmolekylstrukturen och den slutliga filmen.

När TMA används för att tillverka AlN med ALD vid temperaturer $>330\text{ }^\circ\text{C}$ återfinns höga halter av kol (C) i filmen vilket inte är önskvärt då detta påverkar egenskaperna av materialet på ett negativt sätt. För att få bukt med detta problem introducerades en ny process där en puls med en inert gas pulsades efter TMA pulsen för att frigöra ytan från kolinnehållande fragment. Det visade sig att denna extra puls reducerar kolhalten i AlN från 3 at% (atomprocent) ner till 1 at% och möjliggör deponering även vid högre temperaturer utan att riskera höga kolhalter i filmen. Kinetiska beräkningar och modelleringar påvisade att den extra pulsen gjorde så att de kolfragment som desorberades från ytan från TMA kunde ”spolas” bort och förhindra att de hamnade där igen.

För att analysera om bindningen mellan metallen och resten av källmolekylen har en påverkan på beläggningsskemin så användes en källmolekyl med svagare bindningar. Källmolekyler som TMA har metal-kol (M–C) bindningar som är relativt starka men genom att välja en molekyl med svagare bindningar som metal-kväve (M–N) så kan deponeringsskemin gynnas. Tris(dimethylamido)gallium som har Ga–N bindningar användes tillsammans med NH_3 plasma för att undersöka deras förmåga att deponera GaN filmer. Denna källmolekyl funkade utmärkt för att deponera GaN vid låga temperaturer och samtidigt så visade analyser att lägre kolhalt fanns i GaN filmen jämfört med andra studier som använts sig av M–C bindande källmolekyler. Dessutom så kunde GaN med riktigt bra kvalitet fås med avseende på sammansättning, kristallinitet och morfologi.

För att vidare utforska M–N bindande källmolekyler så undersöktes tre indium molekyler med In–N bindningar; In(guanidinat), In(amidinat) och In(formamidinat). Dessa källmolekyler har mer eller mindre samma struktur, det enda som skiljer dem åt är substituenten på den endocykliska kolatomen i molekylen. De grupper som sitter på den endocykliska positionen minskar från $-\text{NMe}_2$ (dimetylkväve), $-\text{Me}$ (metyl) och $-\text{H}$ (väte) för respektive In(guanidinat), In(amidinat) och In(formamidinat). Deponering med dessa källmolekyler tillsammans med NH_3 plasma producerade InN men intressant nog så kunde bättre InN kvalitet fås med avseende på kristallinitet, sammansättning, morfologi och optiska egenskaper när mindre

grupper satt på den endocykliska positionen. Kvantmekaniska beräkningar visade att ju mindre grupp som sitter på den endocykliska positionen desto större rörelsefrihet har resten av molekylen. Detta innebär att bindningen sträcks ut mellan metallen och resten av molekylen vilket leder till att bindningen blir svagare. På så sätt kommer det bli lättare för den efterföljande NH_3 plasmapulsen att reagera och bilda InN.

För att reducera storleken på gruppen på den endocykliska positionen ännu mer designades en helt ny molekyl där kolatomen byttes ut mot en kväveatom, som bildar en bindning mindre än kol och därmed behövs ingen substituent alls, då bildades en triazenid. Denna molekyl sattes därefter på indium och gallium för att bilda In(triazenid) och Ga(triazenid). Båda dessa källmolekyler användes tillsammans med NH_3 plasma för att växa InN och GaN vid låga temperaturer med ALD. InN och GaN filmerna visade en mycket låg koncentration av kol, under detektionsgränsen för analysmetoderna XPS (X-ray photoelectron spectroscopy) och ERDA (elastic recoil detection analysis). Dessutom så hade filmerna mycket bra kristallinitet, atomär sammansättning och ytmorfologi. De här två källmolekylerna användes också till för att göra den ternära indiumgalliumnitrid (InGaN) fasen genom en nyutvecklad process. I denna process blandades båda källmolekylerna i samma uppvärmda behållare för att producera ånga av båda källmolekylerna som med en enda puls kunde föras in i depositions-kammaren. Genom att ändra olika processparametrar som temperatur kunde också sammansättning av den ternära fasen kontrolleras till en viss del. Vid låga temperaturer kunde InGaN produceras med lika mängd In och Ga ($\text{In}_{0.5}\text{Ga}_{0.5}\text{N}$) vilket tidigare har varit svårt att åstadkomma p.g.a. termodynamiska hinder. Analyser visade bra filmkvalité med avseende på kristallinitet, morfologi och dessutom så kunde ingen fassetparation påvisas vilket är väldigt sällsynt när det kommer till InGaN deponering.

Preface

This thesis concludes 4 years of research at the chemistry division of the Department of Physics, Chemistry and Biology (IFM) at Linköping University. The thesis summarizes my research on atomic layer deposition (ALD) mainly on group 13 nitrides. The focus of this work has been both on process development with existing precursors but also implementing newly developed precursors to improve the deposition chemistry and in turn the material quality.

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Papers Included in the Thesis and Contribution

Paper I:

Reduction of Carbon Impurities in Aluminium Nitride from Time-Resolved Chemical Vapour Deposition Using Trimethylaluminum

Polla Rouf, Pitsiri Sukkaew, Lars Ojamäe and Henrik Pedersen

J. Phys. Chem. C **2020**, *124* (26), 1–6.

I planned and conducted all the depositions. I performed and analyzed all the characterisations of the material (XRD, XPS and SEM). I wrote the first draft of the manuscript and finalized it after comments and discussion with the co-authors.

Paper II:

Epitaxial GaN Using Ga(NMe₂)₃ and NH₃ plasma by Atomic Layer Deposition

Polla Rouf, Nathan J. O'Brien, Sydney C. Buttera, Ivan Martinovic, Babak Bakhit, Erik Martinsson, Justinas Palisaitis, Chih-Wei Hsu and Henrik Pedersen

J. Mater. Chem. C **2020**, *8* (25), 8457–8465.

I synthesised the precursor together with a co-author and conducted all the depositions. I performed XRD, XPS and SEM. I analysed the XRD, XPS, SEM and absorption data. I wrote the first draft of the manuscript and finalized it after comments and discussion with the co-authors.

Paper III:

The Endocyclic Carbon Substituent of Guanidinate and Amidinate Precursors Controlling Atomic Layer Deposition of InN Films

Polla Rouf, Nathan J. O'Brien, Karl Rönby, Rouzbeh Samii, Ivan G. Ivanov, Lars Ojamäe and Henrik Pedersen

J. Phys. Chem. C **2019**, *123* (42), 25691–25700.

I helped synthesising the precursors together with co-authors and conducted all the depositions. I performed XRD, XPS and SEM. I analysed the XRD, XPS and SEM data. I wrote the first draft of the manuscript together with a co-author and finalized it after comments and discussion with the co-authors.

Paper IV:

***In Situ* Activation of an Indium(III) Triazenide Precursor for Epitaxial Growth of Indium Nitride by Atomic Layer Deposition**

Nathan J. O'Brien, **Polla Rouf**, Rouzbeh Samii, Karl Rönby, Sydney C. Buttera, Chih-Wei Hsu, Ivan G. Ivanov, Vadim Kessler, Lars Ojamäe and Henrik Pedersen
Chem. Mater. **2020**, 32 (11), 4481–4489.

I helped synthesising the precursor together with co-authors and conducted all the depositions. I performed XRD, XPS and SEM. I analysed the XRD, XPS and SEM data. I helped writing the first draft of the manuscript.

Paper V:

Hexacoordinated Gallium(III) Triazenide Precursor for Epitaxial Gallium Nitride by Atomic Layer Deposition

Polla Rouf, Rouzbeh Samii, Karl Rönby, Babak Bakht, Sydney C. Buttera, Ivan Martinovic, Lars Ojamäe, Chih-Wei Hsu, Justinas Palisaitis, Vadim Kessler, Henrik Pedersen and Nathan J. O'Brien
Chem. Mater. **2021**, 33 (9), 3266–3275.

I helped synthesising the precursor together with co-authors and conducted all the depositions. I performed XRD, XPS and SEM. I analyzed the XRD, XPS and SEM data. I helped writing the first draft of the manuscript.

Paper VI:

In_{0.5}Ga_{0.5}N Layers by Atomic Layer Deposition

Polla Rouf, Justinas Palisaitis, Babak Bakht, Nathan J. O'Brien and Henrik Pedersen
Submitted

I helped synthesising the precursor together with co-author and conducted all the depositions. I performed XRD, XPS, SEM and TEM sample preparation. I analysed the XRD, XPS, SEM, TEM and absorption data. I wrote the first draft of the manuscript and finalized it after comments and discussion with co-authors.

Papers not Included in the Thesis

Paper VII:

Atomic Layer Deposition of InN Using Trimethylindium and Ammonia Plasma

Petro Deminskyi, **Polla Rouf**, Ivan G. Ivanov and Henrik Pedersen

J. Vac. Sci. Technol. A **2019**, 37 (2), 0220926.

Paper VIII:

Methylamines as Nitrogen Precursors in Chemical Vapor Deposition of Gallium Nitride

Karl Rönby, Sydney C. Buttera, **Polla Rouf**, Séan T. Barry, Lars Ojamäe and Henrik Pedersen

J. Phys. Chem. C **2019**, 123 (11), 6701–6710.

Paper IX:

Chemical vapor deposition of metallic films using plasma electrons as reducing agents

Hama Nadhom, Daniel Lundin, **Polla Rouf** and Henrik Pedersen

J. Vac. Sci. Technol. A **2020**, 38 (3), 033402.

Paper X:

Surface ligand removal in atomic layer deposition of GaN using triethylgallium

Petro Deminskyi, Chih-Wei Hsu, Babak Bakhit, **Polla Rouf** and Henrik Pedersen

J. Vac. Sci. Technol. A **2021**, 39 (1), 012411.

Paper XI:

Resolving impurities in atomic layer deposited aluminum nitride through low cost, high Efficiency precursor design

Sydney C. Buttera, **Polla Rouf**, Petro Deminskyi, Nathan J. O'Brien, Henrik Pedersen and Séan T. Barry

Inorg. Chem. **2021**, 60 (15), 11025–11031.

Paper XII:

Area Selective Deposition of Metals from the Electrical Resistivity of the Substrate

Hama Nadhom, Robert Boyd, **Polla Rouf**, Daniel Lundin and Henrik Pedersen

J. Phys. Chem. Lett. **2021**, 12 (17), 4130–4133.

Paper XIII:

Solar-driven photoelectrochemical performance of novel ZnO/Ag₂WO₄/AgBr nanorods-Based photoelectrodes

Elfatih Mustafa, Rania E. Adam, **Polla Rouf**, Magnus Willander and Omer Nur
Nanoscale Res. Lett. **2021**

Paper XIV:

Area selective deposition of metal films using temperature sensitive masking materials and plasma electrons as reducing agents

Hama Nadhom, Yusheng Yuan, **Polla Rouf**, Niclas Solin and Henrik Pedersen
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Chapter 1—Introduction

Many materials around us can be found in nature, however, most of them must be synthesised. One synthesis route is to deposit these materials as coatings or thin films. Coatings or thin films are thin layers or multilayers of materials, usually in the nm to μm thickness range, placed on a substrate and the goal is to change the properties of the substrate by the deposited thin film. The purposes of the coatings are many, it's all around us, one example being paint. The paint that is brushed onto the wood panels of houses have the purpose to protect the wood from moisture and sunlight, which will increase the lifetime of the wood. The first evidence of a coating is dated all the way back to the Egyptians and some 5000 years where gold coatings were used for decoration purposes.¹ However, even though coatings are not something newly invented its real development and breakthrough started with the development of vacuum systems as the majority of thin film depositions are performed in a vacuum system.²

There are many different deposition techniques however, the main ones being physical vapor deposition (PVD) and chemical vapor deposition (CVD). In PVD a solid source, containing the wanted material or metal, is bombarded with ions which forms a vapor and then produces a thin film on a substrate.³ In CVD, vapours of two or more precursors are introduced into the reaction chamber where they react with the substrate and form a thin film.^{4,5} The precursors contain the atoms of the desired thin film, i.e., Al from trimethylaluminum (TMA) and N from ammonia (NH_3) to deposit AlN. When the precursor gases are introduced into the chamber, where they could react with each other in the gas phase as two or more precursors are introduced simultaneously, a diffusion of the gases towards the substrate surface will occur. Upon arrival towards the surface, they will react (chemisorb) on the surface and further diffuse. The surface reactions will lead to desorption of parts of the precursor and any other volatile species created from the surface reactions. The diffusion of the atoms on the surface will lead to nucleation and a thin film will start to grow on the surface, see Fig. 1.

Figure 1: Schematic overview of deposition processes occurring in CVD during film growth.

As CVD uses gaseous precursors and relies on surface chemistry makes it possible to deposit materials on complex shapes in comparison to PVD which is a line-of-sight technique. These characteristics of CVD have made the technique suitable for many applications such as hard coatings and microelectronics.^{6,7}

As the electronic devices and components became smaller and smaller over the years, a deposition technique which were able to deposit thin films in the nm range with exceptional conformality were needed. To be able to keep up with the electronic revolution and always make smaller but at the same time more powerful devices, atomic layer deposition (ALD) was employed. Because ALD have monolayer control of the thickness and the ability to conformally deposit features kept the electronic minimization alive. Furthermore, ALD opened the doors for new materialsystem due to the low deposition temperature required and made it possible to coat temperature sensitive substrates which had been hindered before.

Chapter 2—ALD

2.1—Fundamental ALD Characteristics

Atomic layer deposition (ALD) is a subset of CVD, the difference being that the precursors are introduced separately and not simultaneously, which is sometimes referred to as time-resolved CVD.^{8,9,10} This results in that ALD doesn't rely on gas phase reactions but is solely a surface-based technique making it possible to deposit the same material system as in CVD, but at lower temperatures. The characteristics of ALD is that each pulse of precursor should saturate the surface, meaning that all the reaction sites available on the surface must be occupied after each precursor pulse. When the first pulse has occupied all the available reactions sites, the chamber is purged with an inert gas to remove excess precursor and surface products, making it "clean" for the introduction of the next precursor. The purge pulse will also make sure that only one precursor is in the chamber at the time and that there is no overlap between them, see Fig. 2. When both precursors have been introduced to the surface, an ALD cycle is finished, and this cycling is repeated several times (hundreds or thousands of cycles) to obtain the desired thickness of the film. The key parameter for a well functional ALD process is that the pulse time for each precursor, is long enough for the precursor to completely occupy all the available sites on the surface. When all the reaction sites are occupied, one monolayer is formed, no more reactions can occur even if there is precursor in the chamber.¹¹ For example, if it's required three seconds for a precursor to occupy all the reaction sites and the pulse time is set to five or six seconds, it will not affect the growth because the precursor have saturated the surface after three seconds and no more reaction sites are available after that. The saturation time needed for each precursor is determined by observing the thickness when the pulse time is changed, Fig. 3a. The pulse time for one precursor is changed at a time while the other deposition parameters is unchanged, and the thickness of the resulting film is measured. When the thickness of the thin film has been measured, the thickness is divided by the number of cycles used in the process to obtain the growth rate. The growth rate will then be ascribed as growth per cycle with Ångström/cycle (Å/cycle) as a unit which is commonly used in ALD literature. When the thickness does not change, i.e., a plateau in the growth upon changes in the pulse time, means that saturation have been achieved and from such a curve the minimum required pulse time will also be observed to obtain saturation.

The saturation can also be determined more conveniently in-situ with a quartz crystal microbalance (QCM).^{11,12}

Figure 2: Schematic overview of one ALD cycle where each precursor is separated by a purge pulse making the process solely rely on surface chemistry.

To further evaluate the robustness of the process, the pulse time for each precursor is kept constant while the temperature is changed. In most ALD processes there will be a temperature region where the growth is constant, saturation of the growth with respect to the temperature, which is commonly denoted as “ALD window” in the literature, Fig. 3b.^{13,11} The ALD window indicates in which temperature range the process with a specific pulse time can operate without starting to desorb or decompose the precursor molecules.

However, it should be noted that even though theoretically a monolayer growth should be obtained after each pulse this is not the case. The steric hinderance and the kinetics of the precursor is the limiting factor and rather sub-monolayer growth are achieved.^{14,15} This is further discussed in the precursor section (chapter 3).

Figure 3: Schematic overview of a) growth rate behaviour when changing the pulse time where a plateau indicates a saturated growth. b) Growth rate behaviour upon changing the deposition temperature showing the different growth regimes where constant growth indicates an ALD window.

In an ideal ALD process, the mass gain, the film deposited on the surface, should be constant after every cycle meaning that each ALD cycle provides a certain thickness. This behaviour is seen by changing the number of ALD cycles while measuring the thickness which results in a linear thickness increase upon increasing the number of cycles, see Fig. 4. However, in the real world nothing is ideal so a linear growth will sometimes take several ALD cycles before it's observed.¹⁶ In the majority of the cases this delay in the linear growth is due to that it takes time, some ALD cycles, before the material starts to nucleate on the surface. It needs to form an ideal surface for growth before the linear behaviour starts. This delay on linear growth is typically a sign of poor chemisorption of the precursors.¹⁷ This phenomenon can be observed by that the linear behaviour of the growth does not start immediately but rather after some ALD cycles, see Fig. 4. The nucleation delay is best observed with a QCM where even small mass gains can be observed.^{11,18,17} The nucleation delay is not a constant number of ALD cycles for all the process but it's rather heavily fluctuating depending on the material system that is being deposited, the surface (substrate) used, the crystal match between the deposited film/substrate and precursors used in the process.^{19,20,21}

Figure 4: The linear ALD behaviour of the growth upon increasing the number of ALD cycles for a theoretically ideal process and a process with nucleation delay.

2.2–Plasma ALD

There are two main routes to produce a thin film via ALD: either thermal or plasma. In the thermal route, energy in the form of thermal energy (heat) is provided to activate the reactions on the surface. In many cases the thermal energy tolerated by the system is not enough for the reactions to occur or for the deposited material to crystalize. The only way forward is then to replace the precursors with more reactive molecules. The thermal route can also be limited by the stability of the precursor as some precursors decompose at certain temperatures.^{22,23} To be able to solve this problem a plasma source is used in the ALD system. The plasma provides energy to the system via reactive species making plasma processes to generally require lower deposition temperatures. The plasma source is used in conjunction with the non-metal precursor to provide a more reactive co-reactant. When the non-metal precursor is passed through a plasma source it generally becomes ionized making the compound significantly more reactive. The created ionized gas contains negatively, neutral, and positively charged fragments in the form of electrons, radicals, and ions. In a ALD system, the species are usually weakly ionized together with having a low temperature.²⁴ The plasma can be generated via different methods, with the hollow cathode and inductively coupled configuration being the most common.^{24,25,26,27} Fig. 5. shows the NH₃ plasma generated from an inductively coupled plasma configuration from our ALD tool.

The distance between the plasma source and the substrate can be configured differently so that the species reaching the substrate can be controlled. The plasma can be located close to or in contact with the substrate which will expose the substrate to high energy ions. This plasma configuration is called “direct plasma”. By having a longer distance between the plasma source and the substrate will result in that most of the species that reaches the substrate is radicals, usually called remote plasma. In this configuration the impact of high energy ions is significantly reduced. The plasma can also be generated separately from the substrate zone where only the neutral plasma species are introduced to the substrate. This configuration is called radical enhanced plasma.²⁸

Figure 5: Image of the NH_3 plasma (NH_3/Ar mixture) in our Picosun R-200 tool.

The plasma will not only have an impact on the precursor but also the resulting film. In several material systems and processes the thermally deposited film is different compared to the plasma. The films deposited with plasma generally show higher growth rate, better crystalline quality, lower levels of impurities and higher density.^{15,28,29,30} The addition of a plasma also gives two key process benefits which are more precursor freedom, further discussed in the precursor section (chapter 3), and the ability to deposit at lower temperatures.¹⁵

However, there are also some disadvantages with using a plasma compared to a thermal process where the conformality might be limited. As radicals and other plasma species recombine, the further they travel away from the sources, the more difficult it will be for the species to survive. This together with their reactivity will make it difficult to penetrate plasma species deep down into trenches and voids with high aspect ratios resulting in non-conformal growth. Another disadvantage with plasma processes is that the surface reactions occurring are more complicated and possible damage to the film.²⁸ The damages on the material that the plasma could cause are often creation of defects or unwanted changes in the composition.³¹

2.3–ALD Reactor Types

There are several types of ALD reactors available. They all have their own advantages and targets different needs. The reactors that are mainly used have a continuous flow of inert gas into the reactor however, this reactor type is not efficient if depositions on featured substrates with high aspect ratio are needed. This would mean that long exposure times must be applied

which would be both time consuming and a lot of precursors would be wasted. A reactor with the ability to stop the flow (stop flow process) would be more advantageous for deposition on high aspect ratio substrates. In this set-up, the precursor is pulsed into the reactor and then all the valves are closed leaving only the precursor left in the reactor. This will give more time for the precursor to diffuse into the voids and trenches of the featured substrate and to deposit a conformal thin film.²⁸

There are also reactors with several precursor lines entering the reactor and eventually reaching the substrate. There are systems with a single injection line above the substrate and showerhead configuration where the gases pass through an array of injectors which will cover the whole substrate surface. The later configuration being better suited for deposition on full wafers. In the recent years coating nanoparticles or other small molecules have increased in interest. As the surface area increases dramatically when depositing on nanoparticles, the reactor design must meet those needs. The two reactor types typically used to deposit nanoparticles are denoted fluidized bed and rotary drums, respectively.³²

As ALD is a key technique in many industrial settings, the reactor type must be designed to access those needs. The common reactor type in the industry are batch reactors, with different configuration, which can deposit thin films on up to hundreds of wafers simultaneously.²⁸

Throughout this thesis, a Picosun R-200 equipped with a Litmas plasma source was used for all the ALD depositions, see Fig. 6. The plasma source is located approximately 70 cm from the substrate holder making it a remote plasma. The tool has one specially made bubbler inlet for precursors with insufficient vapor pressure at room temperature which can be heated up to 200 °C.

Figure 6: Image of our Picosun R-200 ALD equipment, close-up of the deposition chamber and the plasma source on the right-hand side.

2.4–Advantages and Disadvantages of ALD

The ability to deposit different materials at lower temperatures with ALD compared to other deposition techniques such as CVD opens a much bigger playing field. With ALD a much higher variety of substrate materials can be used to deposit on which have previously been hindered by CVD due to the high temperatures required. By employing ALD, and especially plasma ALD, materials can be deposited at even room temperature making it possible to deposit on temperature sensitive materials/substrates such as polymers and biological materials.^{15,33,34}

The saturation of the surface after each precursor pulse gives ALD tremendous advantage in thickness control and conformality. Everything from large wafers to complex structures, spheres, trenches, and voids can be conformally coated if the precursor pulses are long enough to ensure saturation of the surface and that the precursors react with all the reaction sites. By being able to adjust the number of ALD cycles the thickness of the deposited film onto the features can be controlled down to nanometre level. This is a huge advantage when constructing electronic devices (transistors, capacitors, etc.) where they are becoming smaller

and smaller each year while the performance is enhanced. These devices typically require thickness conformality on complex structures which ALD can provide. One company that have taken advantage of conformality of ALD is Samsung where they could reduce the thickness of the dielectric layer, making it possible to reduce the size of their dynamic random-access memory (DRAM) from 20 nm to 10 nm and at the same time enhance the performance.²⁸ The extraordinary conformality of ALD has also opened up the doors to produce more efficient catalytical thin films.²¹ However, ALD is not only used in the typical coating industries but due to the ability to deposit material at low temperatures makes it also suitable for pharmaceutical applications.^{35,36}

ALD is not perfect, and it has its own drawbacks as everything else. ALD have a very low deposition rate compared to other techniques and are time consuming as it requires most often several hours to obtain some tens of nm film. There is also the need of suitable precursors (see chapter 3) which sometimes it's difficult to come across so new ones must be invented and synthesised.

Chapter 3—Precursors

3.1—Precursor Requirements

The most crucial aspect of an ALD process are the precursors. Without suitable precursors the desired material will not be able to grow. Most often, the desired metal atom is not volatile by itself at moderate temperatures. By combining the metal with different types of ligands, a new volatile compound could be formed. There are several key features that the precursor must possess to be considered a good ALD precursor. First, the precursor must be volatile so that the vapor can be transported into the chamber. Most of the precursors need thermal energy (heat) to help vapourise it. However, heating of the precursor should be minimized as much as possible as this affects the deposition temperature. The precursor can both be a liquid or a solid, but solid precursors usually require higher temperatures to achieve sufficient vapor pressure. It is extremely important to have a constant vapor pressure in the precursor container to ensure a constant amount is introduced into the chamber to saturate the surface. When the precursor has been vapourised and makes its way into the chamber it should not decompose. The precursor should reach the surface intact requiring the precursor to have high thermal stability. If the precursor has a low thermal stability, a lower deposition temperature must usually be used to avoid decomposition. There is also the risk of gas phase reactions, which is characteristic of a CVD process rather than an ALD process. A precursor with a wide range between its evaporation/sublimation and decomposition temperature allows it to be used over a wider deposition temperature. However, the precursor should possess enough reactivity to react with the substrate surface (species adsorbed on the surface) and with the co-reactant. A precursor with high reactivity will most often require a lower deposition temperature, have faster surface reactions (faster kinetics), which leads faster surface saturation, shorter pulses and ultimately a shorter deposition time.^{14,37} All these criteria must be fulfilled in order for a molecule to be considered appropriate as an ALD precursor. Further advantages are obtained if the precursor is a liquid at room temperature or has a low melting point. A liquid precursor will improve the vapor pressure where a more constant pressure is achieved compared to a solid precursor.

3.2–Precursor Design

Precursor design can be used to obtain a molecule with the desired properties. The size of the precursor or its ligands plays a vital role in the outcome of its volatility. Generally, by reducing the size of the ligand the volatility of the precursor will be improved. The volatility is also connected to intermolecular forces and if these forces can be reduced it will have a positive outcome on the volatility. Thermal stability of the precursor can be tuned by controlling the bond strength of the ligand to the metal centre. However, predicting the thermal stability of an ALD precursor is not straight forward and requires fine tuning to obtain the desired property. The thermal stability of the precursor must be high enough to undergo volatilization and travel thorough the deposition chamber onto the surface without decomposing. However, if the thermal stability is too high the precursor will stay intact upon arrival at the substrate, where it will be prevented to react with the substrate surface and no film can be grown. The ideal precursor must have high enough thermal stability so it does not decompose but at the same time low enough stability that it can react with the substrate surface. Due to this trade off makes the ability to find the “sweet spot” for the thermal stability more of a “trial and error” effort.

The reactivity is also an important parameter for precursor optimization and has the same trade off as thermal stability. The reactivity of the precursor must be high enough so it can react with the surface and produce a stable monolayer. At the same time it should not react in the gas phase or the deposited precursor surface species before the non-metal precursor pulse arrives.^{15,37,38} It is difficult to have all these properties tuned in a precursor and sometimes compromises have to be made when designing the precursor.

The size or the bulk of the precursor/ligand does not only play a part in the precursor properties but also the surface chemistry and the resulting film. Having a precursor with bulky ligands will make its reaction with the surface difficult and the deposited surface species will sterically hinder unreacted surface sites. The latter is a problem upon removing the ligands that terminate the surface with the second pulse as it will eventually lead to much smaller terminated species. This size reduction of the species on the surface will also reveal the previously unaccusable surface sites blocked by the bulky ligands which will lead to sub-monolayer growth. When the next metal precursor pulse is introduced to the surface it will both react with the terminated surface as well as the newly revealed surface sites that were previously blocked by the bulky ligands, see Fig. 7.

Figure 7: Schematic illustration of the effect of bulky ligands on the deposition chemistry. The bigger black spheres indicate larger ligands, taking up more surface sites compared to Fig. 1.

3.2–Precursor Handling

Many precursors used in ALD are air and moisture sensitive, which requires specialised handling. Even the standard trimethyl precursors, such as trimethyl aluminium (TMA), needs to be handled with care as they are flammable upon exposure to air.³⁹

Precursor synthesis typically requires air and moisture free environment and therefore all reactions and manipulations are undertaken in a glove box or using Schlenk line techniques.⁴⁰ The air sensitive precursors also require transportation to the reactor with minimized air exposure as they will otherwise decompose. To achieve that, the bubbler was filled with the desired precursor in an inert atmosphere using the glovebox. The top was covered with layers of parafilm upon transportation between the glovebox and the ALD tool.

The bubbler used for synthesized precursors in our ALD tool consisted of a glass vial, which were filled with precursors, Fig. 8. That glass vial was then placed in a stainless-steel container and the whole package was connected to the ALD tool via a special port which could heat the bubbler. The bubbler does not have a dip tube design, which is normally found for bubbler, for the incoming carrier gas. The system uses pressure difference between the bubbler and the reaction chamber to move the precursor.

Figure 8: Image of the bubbler used in the ALD equipment for synthesized precursors.

3.3–Non-Metal Precursors

Most of the precursor development has been undertaken on metal precursors, however, little work has been carried out on the non-metal precursors. There are some alternatives for the standard non-metal precursors such as N_2H_4 (hydrazine) as a replacement for NH_3 and ozone as a replacement for oxygen or water.^{15,41,42} The difficulty in developing a suitable non-metal precursor with better properties is extremely challenging. The ability of employing energy enhanced ALD methods, such as a plasma, have made the standard non-metal precursors more reactive without the need for designing new ones. This has shifted the focus more towards the metal precursors development as it is the main limiting factor precursor wise. The introduction of a plasma has also led to more of a precursor freedom (metal precursor) where the chemisorption onto the surface is the crucial part because the upcoming plasma pulse is reactive enough to react with most terminated surfaces.

Chapter 4—Group 13-Nitrides

4.1—Binary Nitrides

Al-, Ga-, and InN are semiconductors with bandgaps varying from 6.2 eV, 3.4 eV and down to 0.7 eV respectively, spanning the whole region from UV to IR.^{46,47} They all crystallize into the wurtzite hexagonal crystal structure which is the most stable structure for these materials.⁴³ However, they can also form the metastable cubic zincblende crystal structure under some specific conditions, Fig. 9. Both crystal structures have 4:4 coordination between cation and the anion. However, they differ in the crystal stacking of the atoms where the cubic crystal structure has a ABCABCABC type stacking along the (111) direction while the hexagonal have a ABABAB along the (0001) direction. There are some differences in the physical properties as well such as bandgap between the different crystal structures.⁴⁴ The bonds in the crystal structure between the metal (Al, Ga or In) and the nitrogen are relatively strong and the resulting III-nitride possess high melting points, good mechanical strength and chemical resistance.⁴⁵ The lattice constant, the length of a side of a unit cell in the crystal lattice, is 3.112, 3.189 and 3.545 Å for the wurtzite structure of Al-, Ga- and InN, respectively.⁴⁴

Figure 9: The two crystal structures for Al-, Ga-, and InN, the metastable cubic a) and the stable wurtzite b) [Image source: Wikimedia Commons, free to re-use].

They all have a direct bandgap meaning that the electrons positioned at the conduction band minima and the holes positioned at the valence band maxima possess the same momentum. At room temperature the theoretically maximum electron mobility value is 1000 and 4400

$\text{cm}^2\text{V}^{-1}\text{s}^{-1}$ for GaN and InN respectively.⁴⁸ As the bandgap dramatically increases for AlN (compared to GaN and InN) and nearly makes it an insulator the mobility will also decrease, theoretical calculations have shown that phonon limited electron mobility for AlN is $300 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$.⁴⁸ The thermal conductivity for AlN, GaN and InN are $320 \text{ Wm}^{-1}\text{K}^{-1}$, $253 \text{ Wm}^{-1}\text{K}^{-1}$ and $176 \text{ Wm}^{-1}\text{K}^{-1}$ respectively.^{49,50,51}

4.2–Ternary Nitrides

Ternary nitrides, $\text{A}_x\text{B}_y\text{N}$ (A and B being either Al, Ga or In), are an alloy of the binary nitrides. The bandgap of the ternary nitrides can be tuned by changing the compositional relationship between the metals and this will bridge the bandgap of the binary nitrides together, Fig. 10.

Figure 10: Schematic overview of the lattice constant and bandgaps for binary and ternary nitrides.

The most challenging ternary nitride to deposit is InGaIn. As previously mentioned, the thermal stability of binary InN is low as it decomposes at around 500°C making deposition of InGaIn at high temperatures not ideal. It has also been shown theoretically that InGaIn, at thermodynamic equilibrium, is a meta stable phase with only small amount of the metals, In

or Ga, Fig 11.⁵³ When higher amount of the metals is incorporated into the ternary phase it becomes unstable and decompose into the binary phases.

Figure 11: Schematic overview of the phase diagram for InGaN.

4.3–Applications

The properties of group 13-nitrides makes them excellent materials for optoelectronic application such as light emitting diodes (LED) where the bandgap tuning makes it possible to obtain a variety of colours.^{45,47,52,54,55,56} The good thermal conductivity and mobility also makes these materials good for high frequency and high-power applications. The noble prize in physics 2014 was awarded to research conducted on blue LEDs which were based on GaN.

4.3.1–HEMT Structure

One common structure containing these materials are high electron mobility transistor (HEMT) which is a multilayer of GaN, AlN and their alloys. A HEMT structure based on group 13 nitrides usually consists of a nucleation layer (often AlN because of its lattice match to the substrate), a buffer layer (GaN) and a barrier (AlGaIn), Fig. 12. As each Ga atom in the GaN layer is bonded to four N atoms giving rise to a spontaneous polarization in the system due to the electronegativity of the elements. The crystal structure of the materials can also develop dipole moments as they get strained due to the lattice mismatch between the materials. If a crystal can sustain such a dipole moment, then it's called piezoelectric. The difference in bandgap between the top two materials (AlGaIn and GaN in Fig. 12.) together

with the polarisation and the piezoelectric effect will push the electrons towards the AlGa_N/Ga_N interface which will result in the formation of an electron dense region called 2-dimensional electron gas, 2DEG, Fig. 12.^{57,58,59,60,61} The 2DEG formation is spontaneous and the need for doping the materials in order to add electrons are not needed.⁵⁴ These HEMT structures can also be constructed in different ways to obtain the desired properties and functions.

Figure 12: Schematic overview of a HEMT structure based on group 13 nitrides.

Chapter 5—Thin film Deposition of Group 13-Nitrides

5.1–PVD

Deposition of group 13 nitrides using sputtering usually consists of Ar and N₂ plasma, the positive ions created in the plasma is accelerated towards the target which have a negative voltage. The target is usually a metal disc (Al, Ga or In metal disc) and upon collision of the accelerated ions on the target, metal atoms gets sputtered. The sputtered metal from the target together with N from the plasma will produce a metal-N film on a substrate.^{62,63,64} However, as Ga metal have a low melting point (~29 °C) makes pure Ga metal target challenging to handle.⁶³ An alternative is to use a GaAs target.^{65,66}

5.2–CVD

When depositing group 13 nitrides with CVD the metal chloride precursors was used in the beginning together with NH₃, usually at a deposition temperature of 1000 °C.^{67,68,69,70,71,72,73} However, lower deposition temperature were used for the deposition of InN, around 500-700 °C.^{72,73} The by-products of the chloride based precursors are corrosive (HCl) which can damage the reactor and the resulting film. To avoid the hazardous by-products, the chloride-based precursors was replaced by metal organic ones, trimethyl (TMA, TMG and TMI, Fig. 13a.) or triethyl metal precursors.^{45,74,75,76,77,78} The deposition temperature used for the trimethyl or triethyl precursors was in the same region as the chloride precursors. AlN and GaN have also been deposited with CVD using the tris(dimethylamido)-metal (Al and Ga) precursor, Fig. 13b. Upon using this precursor, the deposition temperature could substantially be decreased to as low as 200 °C however, the films were X-ray amorphous.⁷⁹

5.3–ALD

The same trend in terms of precursors were seen for ALD as for CVD, first the use of chloride based metal precursors^{80,81,82,83,84,85,86} which later were replaced by trimethyl (TMA, TMG and TMI, Fig. 13a.) or triethyl metal precursors.^{27,46,87,88,89,90,91,92,93} These metal precursors are most widely used due to its availability and its high vapor pressure at room temperature which requires no heating of the precursor container. However, using these metal precursors have shown some unwanted features in the resulting film. The strong metal-carbon bonds present in the precursor molecule will require high energy to break and to form a bond with the non-

metal molecule.⁹⁴ As the deposition temperatures are much lower in ALD compared to CVD, these strong bonds could lead to incomplete removal of the ligands on the surface and result in films containing high amount of carbon impurities which is undesired especially for semiconductor applications.^{25,27,95,96} To solve these problems precursor with weaker bonds between the metal and the ligands have been explored. By replacing the metal-carbon (M–C) bonded precursor with especially metal-nitrogen (M–N) bonded precursor the bond strength is decreased and theoretically the surface chemistry could be improved where it would be easier for the non-metal precursor to remove the ligands terminating the surface.

Figure 13: Schematic overview of a) the trimethyl metal precursors (TMA, TMG and TMI) where M represents the Al, Ga or In atom and b) tris(dimethylamido)gallium(III).

The commercially available tris(dimethylamido)-metal precursor has been used because of its M–N bonds but also due to its low melting point, resulting in a good and even vapor pressure. It has been shown that the carbon impurities in the film can be significantly reduced compared to the use of M–C bonded precursors.⁹⁷ The Al and Ga dimerize precursors can be used for depositing AlN and GaN however, for In it polymerize which makes it non-volatile and not useful for depositions.^{79,98,99} To further improve the quality of the films better precursors are required where their properties are tuned. This is achieved by synthesising new ligands in the lab which possess superior properties than commercially available. One ligand systems, with different moiety on the endocyclic carbon position, that have recently been developed is the guanidinate and amidinate which have shown promising results for several metals including In, Fig. 14.^{100,101,102,103}

Even though amidinate and guanidinate based group 13 metal precursors have shown improvements compared to the M–C bonded precursors it's still not ideal due to their slow kinetics, volatility and relatively low thermal stability.^{103,104} This makes the need for improved Al, Ga and In precursors huge in order to be able to deposit high quality Al-, Ga- and InN with low level of impurities.

Figure 14: Schematic overview of the In(III)-guanidinate, -amidinate and -formamidinate, **1**, **2** and **3** respectively.

One major problem in the group 13 nitride field is InN, its desired electronic properties make it a sought-after material however its low thermal stability makes realization of its difficulty. The implementation of InN into HEMT structures as a channel layer have shown theoretically to have several advantages such as higher density and mobility of the 2 DEG.¹⁰⁵

As mentioned before, high temperatures will lead to decomposition of InN into In metal and N_2 . This will limit the deposition temperature ($< 500\text{ }^\circ\text{C}$) for both the growth of InN and all the other materials deposited on top of it in a device structure. CVD is not favourable to be used for this purpose due to the requirement of high temperatures to deposit group 13 nitrides with the existing precursors. However, by employing ALD this problem could potentially be solved. It has been shown previously that all the group 13 nitrides can be deposited at low temperature using ALD. However, the quality of the materials that is wanted in device structure needs to be impeccable which is still somewhat lacking for ALD of group 13 nitrides both in terms of crystallinity and purity (high carbon and oxygen impurities). The other limiting factor that is holding ALD back in terms of implementing it in HEMT structures is the ability to deposit ternary nitrides.

5.4–Ternary Nitrides by ALD

As ALD is a self-limiting surface saturated process makes the possibility to grow ternary nitrides somewhat challenging. To be able to deposit ternary material systems with ALD a supercycle approach is employed where the process for two binary materials are combined into

one, see Fig 15.^{25,106,107,108,109} For example if InGaN is desired then layers of InN and GaN is grown on top of each other. By alternating the supercycles different composition of the ternary material can be obtained. However, this method require that the deposited two binary materials will diffuse enough to form a homogenous ternary phase. The same approach is used in ALD today to deposit multilayer and doping of materials.

Figure 15: Schematic overview of how two binary ALD processes are used to make ternary material systems as well as multilayers and doping.

Experimentally InGaN have been made with an In content of maximum 20 at% with vapor deposition techniques.^{75,76,77,110,111,112} However, previously used CVD methods all requires high temperatures, > 500 °C. This has led to spinodal decomposition of the InGaN phase and in many cases In metal droplets have been observed on the surface of the film.^{76,77,112} To be able to successfully deposit InGaN, a low temperature technique is required and the ability to move far away from the thermodynamic equilibrium. ALD could be the solutions as it is a low temperature deposition technique and indeed InGaN have been explored by ALD.¹¹² However, as discussed above the saturation behaviour makes true mixture difficult as the binary InN and GaN are deposited sequentially which then have to diffuse into the ternary InGaN.

Chapter 6—Substrates and Crystal Growth

6.1—Substrate

To obtain good thin film properties, the foundation needs to be optimal and in this case the foundation is the substrate. The crystal structure and lattice parameter of the substrate heavily dictates the growth of the film. This makes the choice of substrate crucial. This is especially important when epitaxial film growth is desired, see chapter 6.2. Si (100) is often used in ALD for process development, when investigating new materials or precursors, as Si substrate is a relatively cheap substrate, compared to the other substrates such as SiC. Si (100) has a cubic lattice which is not ideal for group 13 nitrides due to their hexagonal crystal structure. However, Si substrate have been used to obtain the metastable cubic phases of group 13 nitrides.^{113,114,115} In order to be able to obtain epitaxial growth suitable substrates are needed, the most used ones being different polytypes of SiC and different cuts of sapphire however other substrates have also been explored such as GaAs (111) and GaN (bulk).¹²¹ The choice of substrate are heavily determined by minimizing the lattice mismatch.

6.2—Epitaxial Growth

Epitaxy is defined as a crystalline material deposited upon a crystalline substrate which imposes an order on the orientation of the deposited material. This basically means that the substrates force the deposited film to grow in a certain direction. There are two types of epitaxy, homo and hetero. Homoepitaxy indicates that the deposited material and the substrate are the same material i.e., SiC on SiC substrate. Heteroepitaxy means that the deposited material and the substrate are not the same i.e., GaN on SiC substrate. In heteroepitaxy, the deposited thin film will be strained due to the lattice mismatch between the substrate and the film. The deposited film can either possess compressive or tensile stress depending on if the lattice parameter is larger or smaller for the film compared to the substrate, Fig. 16. Upon epitaxial growth, the lattice parameter of the film will change (compared to the relaxed state) as the deposited film is influenced by stress from the substrate.

Figure 16: Illustration of epitaxial growth and the effect of stress on the deposited film depending on lattice parameter, where a_F and a_S is the lattice parameter for the film and the substrate respectively.

There are also some concerns with epitaxial growth. As the film possess stress, upon growing thicker layers the materials cannot couple with the stress and will at some point start to relax. This relaxation, stress relieve, will induce dislocations and other defects in the film.^{117,118} The stress in the film could also lead to cracks and buckling of the thin film material.^{119,120}

Group 13 nitrides materials implemented into different device structures, such as HEMT, needs to be epitaxially grown as that will improve the electrical and optical properties.¹²¹ In this thesis, 4H-SiC was used as the potential substrate to grow epitaxial films of group 13 nitrides. The choice of SiC, beside its good lattice match with group 13 nitride films, were due to its promising application as substrate in high-frequency, power electronics and HEMT structures.¹¹⁶ The lattice mismatch between the films (Al-, Ga- and InN) and 4H-SiC ($3.080\text{\AA}$)¹²² are 1.04%, 3.54% and 15.1% for Al-, Ga- and InN, respectively. Theoretically, this means that 4H-SiC is a good substrate to grow epitaxial film for AlN and GaN as the lattice mismatch is small while the substrate is less optimal for InN. This also means that epitaxial AlN on 4H-SiC will possess minimal stress and less dislocations related to

relaxation. This is also one of the reasons AlN often is used as nucleation layer in different structures.^{123,124,125} As all the three materials have a lattice constant that is larger than the substrate (see chapter 4.1) leads to compressive stress upon epitaxial growth on 4H-SiC, Fig.16.

6.2–Growth Mode for Epitaxy

The substrate isn’t the only factor that plays an important role in epitaxial growth but also the growth mode, how the film nucleates and grows on the substrate.^{126,127} The optimal epitaxial growth mode is the layer-by-layer growth also known as Frank-van der Merwe (2D layer nucleation). The growth mode depends on the surface energy of the substrate, film, and interface. If the surface energy of the deposited film and interface is larger than the substrate then the film will “lump up” rather than spreading out on the substrate. This growth mode is called 3D island growth also known as Volmer-Weber. The opposite is happening for Frank-van der Merwe growth where the surface energy of the substrate and deposited film are the same making the film to spread out on the substrate, see Fig. 17. There is also the possibility of a growth which is between the 3D and 2D film growth known as Stranski-Krastanov growth mode.¹²⁸

Figure 17: Schematic overview of 3D island and 2D film growth.

Chapter 7—Characterisation

7.1–X-Ray Diffraction

X-ray diffraction (XRD) is a technique used to determine mainly the crystallinity of a material however, thickness and density can also be obtained.

The technique is based on the interaction between X-rays and electrons. The X-rays have a wavelength of approximately 0.5-50 Å with energies ranging from 250 eV-25 keV. In our XRD equipment, Cu (is used as the anode material to produce the X-rays with a wavelength of 1.54 Å. Other anode materials can be used such as Cr, Mo, Fe, W, Ni, Co.¹²⁹

When X-rays, electromagnetic waves, with a certain wavelength interacts with an electron, the electron will produce electromagnetic wave (scattered X-ray), spherical waves with the same wavelength as the incoming X-ray. For crystalline materials, the atoms are arranged in a specific 3D periodic pattern, a crystal structure. The atoms are arranged at fixed positions with a specific spacing between each plane. The electrons in each atom in the crystal structure will be a source of scattering for the incoming X-ray. The scattered electromagnetic waves from the crystal structure can either have destructive interference (no peak in the spectrum) or constructive interference (a peak in the spectrum), Fig. 18. At a certain angle the scattered X-rays comes out in phase (constructive interference) which is determined by Bragg's Law¹³⁰:

$$\lambda = 2d_{hkl}\sin\theta$$

where d_{hkl} is the interplanar distance between the crystalline planes, θ is the Bragg angle and λ is the wavelength of the incoming X-rays.

The planes of a crystal can more conveniently be described in the reciprocal space where the plane in real space is converted to reciprocal vector via Fourier transformation and presented as spheres/points with coordinates. The scattering vector (Q) in the reciprocal space are the difference between the diffracted wavevector (K) and incident wavevector (K_o):

$$Q = K - K_o$$

Figure 18: A diffractogram with diffraction angle (2θ) and intensity for InN thin film on 4H-SiC substrate.

XRD can be executed in different configurations to obtain different information regarding the crystallinity however, the most common configuration is θ - 2θ . In a θ - 2θ measurement the incident (K_o) and scattered (K) X-ray beam angles are the same and both angles move simultaneously. This will result in that the scattering vector is always perpendicular with respect to the sample surface meaning that all the planes parallel with the surface will be detected as illustrated in Fig. 19.

Figure 19: The schematic illustration of a θ - 2θ measurement.

7.1.2–Grazing Incidence X-ray Diffraction

In some situations when the deposited film is thin and θ - 2θ measurement shows no or small peaks which is hard to distinguish other XRD configuration can be used. One configuration that can be used is grazing incidence XRD (GIXRD).¹³¹ In this configuration the incident and diffracted X-ray beam are not the same nor moved simultaneously. The incidence angle (θ) are kept constant at a low angle (approximately 0.5 - 5°) while the detector (2θ) is moved. Depending on the incident angle the peaks from the substrate can be completely avoided and most of the diffraction comes from the actual film. In this configuration the scattering vector is not perpendicular to the surface but rather moves with the moving of the 2θ detecting planes that are tilted, Fig. 20. In all the papers GIXRD have been used to analyse the crystallinity of the films and to detect any tilted planes.

Figure 20: Schematic illustration of GIXRD configuration.

7.1.3–Texture Analysis

When the crystalline quality of the film increases the θ - 2θ and GIXRD measurements is not enough to describe the crystallinity of the film, in-plane information about the crystal orientation is required. That is the case for textured films where the crystal of the film is aligned with the substrate. To obtain the full overview of the crystallinity of such films, texture analysis must be obtained which will reveal how the films is growing with respect to the substrate. The texture analysis is conducted by fixing the diffraction angle (2θ) to a set of lattice planes and then the intensity of these lattice planes is measured in all possible directions of the sample by rotating the angles ϕ and Ψ , Fig. 21. This measurement is often presented graphically as a pole figure which is based on the stereographic projection of the

crystal planes. For a complete description of the orientation of the crystallites several pole figures are needed from both the film and the substrate. If the measured pole figures show rings, then this indicates that the film have a random in-plane orientation, known as fibre texture. However, if instead of rings there are spots (poles) in the pole figure displays that the film has a certain in-plane orientation better known as epitaxy, Fig. 22. Depending on the symmetry of the crystal structure certain number of poles will be present in a pole figure. For hexagonal AlN, GaN and InN six poles are present in a pole figure when measuring lattice planes that are not in the growth direction.

Figure 21: Schematic illustration of a pole figure measurement set-up with ϕ and Ψ angles.

To be able to conduct such measurements a more advanced XRD equipment are required equipped with a Eulerian cradle. This equipment has the possibility to move the sample stage not only in the x-y direction but also orthogonal in the z-direction. Also, the sample stage can be rotated around the surface normal (ϕ axis) and tilt the surface normal with respect to the z-direction (Ψ axis), Fig. 21.

Figure 22: Illustration of pole figure measurements showing a) fibre texture and b) epitaxial growth of a hexagonal material.

7.1.4–X-ray Reflectivity

XRD is not only limited to determine the crystallinity of materials but for thin films it can also be used to measure the thickness and roughness by X-ray reflectivity (XRR) configuration. XRR relies on the interference of X-rays reflected at interfaces between layers with different indices of refraction. The same set-up is used as in a θ - 2θ measurement however, in XRR only a small range of diffraction angles are measured usually between 0 - 10° . When the incident X-ray beam hits the sample, part of the beam will be reflected by the surface and each interface. The reflected beams will interfere resulting in a diffractogram with the characteristic Kiessig Fringes. There are two ways to determine the thickness of the film from the Kiessig Fringes, either via modelling or using Bragg's modified law. However, by modelling the data more information can be extracted beside the thickness such as density and surface roughness. The advantages with XRR are that it's ideal for ALD thin films (thickness of 5 - 100 nm) and it can be used on amorphous films as well. The disadvantages are that it cannot be used for thick films (>100 nm), data modelling can be complex especially for multilayers, high surface and interface roughness is not suitable for this technique.

Also, below a critical angle the effect of total reflection will occur which will be seen as a sharp drop of intensity in the diffractogram. The critical angle depends on the electron density of the film and the substrate making XRR not possible on film/substrate with similar electron density. Throughout this thesis XRR have been used to determine the thickness of the thin films.

7.2–X-ray Photoelectron Spectroscopy

X-ray photoelectron spectroscopy (XPS) is a spectroscopic analysis method used to determine the composition of a compound and the chemical environment of each atom.^{132,133,134} The method is based on the photoelectric effect where electromagnetic radiation in form of X-rays (usually from an Al source with a fixed wavelength) interacts with the surface of the sample. If the photon energy is higher than the ionization energy, then a core electron will be emitted from the compound. The core electrons ejected are then analysed via a detector and a peak appears, Fig. 23. The kinetic energy of the electron that has been emitted is measured during the analysis process, however by using the Einstein equation (1) the binding energy E_B can be obtained. During the interaction between the photons and the material, Auger electrons are also emitted from the surface.

$$E_b = h\nu - E_k \quad (1)$$

Each element in the periodic table has a unique electronic structure making electrons that is ejected by the X-ray to have a specifically defined kinetic energy. This will result in a specific set of peaks for each element, “fingerprint”. The obtained spectrum can be compared to reference data and each element present in the sample can be identified making elemental composition possible.

Figure 23: Schematic overview of XPS.

Depending on the nearest bonding atom to each element it can be easier or tougher to create a photoelectron. When an atom is bonded to a more electronegative element (e.g., gallium, aluminium, or indium bonded to oxygen) a shift in the peak will be seen in the spectra. The reason for this is that it takes certain amount of energy to create a core hole and the energy

required is higher for a metal bonded to a more electronegative element. When the metal is bonded to an element with high electronegativity a reduction of the negative valence charge density occurs which will result in poor screening of the core hole left after photoionization. So, when a photoelectron is emitted from this site the Coulomb attraction that it will experience is stronger which will result in lower kinetic energy (higher binding energy) upon arrival to the detector. This will result in a chemical shift in the spectra giving valuable information regarding the chemical environment of each element. Table 1 shows the binding energies used to analyse the films.

Table 1: The reported peak position of AlN and InN.

Core level	Chemical bond	Binding energy (eV)	Reference
Al 2p	Al-N	74.7-73.5	136,137,138
	Al-O	75.6-74.5	136,137,138
N 1s	N-Al	397.9-396.8	136,137,139
	N-O	398.5-398.4	136,140
In 3d_{5/2}	In-N	444.0-443.7	27,141,142
	In-O	445.0-444.3	27,141,142
N 1s	N-In	396.8-395.9	27,141,142
	N-O	396.8-398.0	141,142

To obtain this information high resolution XPS (HR-XPS) must be conducted where only a small region (binding energy) is scanned several times for each desired element. If the HR-XPS spectrum is asymmetric, the peak must be fitted to acquire the chemical environment for each element. Throughout this thesis the HR-XPS spectrum have been fitted using Gaussian-Lorentzian (GL) function together with Shirley background. For AlN and InN usually both the metal and nitrogen HR-XPS spectrum was fitted with two GL curves reassembling the chemical shift for each element where the GL curve at higher binding energy corresponds to M-O bond while the one at lower binding energy corresponding to M-N bond, Fig 24.

Figure 24: Schematic overview of XPS fitting showing the chemical shift between M-N and M-O bonds.

Since the ALD system is not connect to an XPS directly and the sample is exposed to air during transportation between the deposition chamber and the XPS system, the surface of the sample usually forms surfaces oxide and other contaminations. These contaminations formed on the surface from air exposure do not represent the true nature of the deposited film. Thereby all the analysed samples are sputtered to remove the oxide and other contaminations from the air exposure. The sputtering is conducted by Ar in the XPS equipment and different sputtering energies can be used. However, preferential sputtering where the lighter and smaller atoms are sputtered more compared to the heavier atoms occurs during the cleaning of the surface.¹³⁵ This can cause problem when determining the composition of the sample. This effect cannot be avoided; however, it can be minimized by using the lowest sputtering energy available which in our case is 0.5 keV.

XPS have some limitations where hydrogen and helium are not detectable, the material/sample that is analysed must be UHV (ultra-high vacuum) compatible and there is a detection limit of 0.1-1 at. % depending on the element. A drawback with using XPS (with an Al x-ray source) for analysis on group 13 nitrides is that for GaN the Ga auger peaks overlaps with the N 1s spectrum. This makes analysis regarding composition unreliable due to the broadening of the N 1s peak that the Ga auger peaks causes. This will result in a highly

overcompensated N contribution and the true composition of the film cannot be obtained using this technique.

7.3–Elastic recoil detection analysis

To be able to obtain the composition of the GaN films elastic recoil detection analysis (ERDA)¹⁴³ has to be employed which is an ion beam technique. In this method an ion with high energy (MeV range) is accelerated towards the sample and penetrates it while target atoms are recoiled from the sample which is then analysed.¹⁴⁴ Via this technique all the element can analysed even hydrogen and helium with high mass resolution. Because the high energy ion penetrates the whole sample there is no need for sputtering (compared to XPS) and a composition along the whole film thickness is obtained. Different ions can be used as projectile however in our case $^{127}\text{I}^{8+}$ with an energy of 36 MeV was used when analysing GaN.

7.4–Electron microscopy

Electron microscopy is a widely used tool to image different objects and its surface with usually several 100 000x magnification. However, it can also be used to obtain information about the crystallinity, composition and interface between the deposited film and the substrate.¹⁴⁵ As the name implies electrons are used to bombard the surface and when they penetrate the material a series of collisions will occur, Fig. 25.

Figure 25: Schematic illustration of electron collisions occurring when electrons hit and penetrates the sample.

7.4.1–Scanning Electron Microscopy

When desired to image the sample surface and obtain information about the topography of the surface, scanning electron microscopy (SEM) is used. In SEM the electrons produced in the electron gun (energy of 0.2-20 keV)¹⁴⁶ are scanned over the surface and only the secondary and back scattered electrons are collected in the detector depending on the detector mode. In the back scattered mode, the electrons that have a protective towards the detector will be detected while a positive potential will be applied in the secondary mode which will attract electrons over larger area towards the detector. Depending on the material that is being analysed different contrast will appear in the image where larger atomic number give rise to more back scattered electrons and eventually brighter areas in the image. Beside imaging the surface SEM can be used to determine the thickness of thin films where XRR have an upper thickness limitation while SEM is a good alternative for thicknesses >100 nm. Fig. 26 shows a SEM image of InN thin film on 4H-SiC.

Figure 26: SEM image of InN deposited on 4H-SiC.

7.4.2–Transmission Electron Microscopy

Higher resolution is required to obtain further information about the material and here the transmitted electrons are analysed, transmission electron microscopy (TEM). Compared to SEM, in TEM higher electron energies are needed (100-400 keV)¹⁴⁷ together with extensive sample preparation in order to penetrate the sample. To obtain electron transparency the sample have to be <100 nm thick and this is achieved with various mechanical and chemical techniques.¹⁴⁷

The atomic resolution makes TEM powerful in obtaining information about local microstructure, interfaces, and diffraction pattern (crystallinity). The high magnification also makes imperfections in the crystalline material visible making it possible to determine defects in the sample. TEM can be used in different configuration such as high resolution TEM (HRTEM), scanning TEM (STEM) and diffraction can be obtaining from a specific area (selected area electron diffraction, SAED).

For our purposes we have used TEM to investigate the microstructure, diffraction patterns of different areas of the films and the interfaces between substrate and film, Fig. 27. This have given us the possibility to observe how the film grows at the start and how the lattice behaves further away from the interface. TEM have also been used to investigate the epitaxial relationship between film/substrate to confirm the pole figures obtained by XRD. Because TEM only gives information from a small area and pole figure covers a larger area makes the combination of them valuable in determination of epitaxial relationship.

TEM is extremely helpful and necessary in material science and especially for thin film however, the biggest drawback is the sample preparation which can take days up to a week to complete depending on experience.

Figure 27: TEM image of GaN deposited on 4H-SiC together with the diffraction patterns (SAED).

Chapter 8—Contribution to the Field

My contribution to the field of ALD and group 13 nitrides have been using standard precursors and optimizing their use by investigating their deposition chemistry. But primarily it has been the transition from the standard precursors towards investigating newly developed ligands for group 13 metals to be used in ALD depositions and further understand their deposition chemistry. From the deposition chemistry observations of the existing ligands, a new in-house ligand was developed which had excellent precursor properties resulting in superior film properties. The focus has been to move away from the strong M–C bonded precursors to weaker M–N bonded precursors to investigate their ability to improve the deposition chemistry and the resulting film.

8.1–Process Development with Known Precursors

As previously mentioned, when using the standard metal-organic precursors such as TMA the resulting film possesses high amount of carbon impurities. It has been shown that when trying to deposit AlN with TMA at higher temperature the carbon amount also increases in the film due to the decomposition of TMA. To be able to deposit AlN at higher temperature to obtain better crystalline quality but at the same time reduce the carbon content an ABC type ALD process was investigated. The deposition was made at 480 °C and 400 °C where a cleaning pulse was introduced after the TMA pulse to remove any unwanted products on the surface before the NH₃ was introduced, Fig. 28. The cleaning pulse was either H₂, N₂ or Ar gas and the difference between a cleaning pulse and a purge pulse were that the cleaning pulse was introduced perpendicular to the surface while the purge came in horizontally. We could see that when a cleaning pulse was introduced the carbon impurities was reduced by almost a factor of three compared to when no cleaning pulse was used. The crystallinity of the AlN also improved upon the introduction of a cleaning pulse. To further investigate this behaviour kinetic simulations were performed to understand the surface chemistry of the process. The simulations showed that surface methyl groups (–CH₃) is being desorbed from the surface and the desorption increases with increasing temperature. When no cleaning pulse is introduced (just TMA and NH₃) the desorbed methyl groups can re-adsorb back onto the empty surface sites or form ethane gas (C₂H₆) resulting in films with high carbon content. However, when a cleaning pulse of inert gas is introduced between the TMA and NH₃ the re-adsorption of

methyl groups is suppressed, and the surface will be cleaned from any carbon molecules resulting in less carbon impurities in the film.

Figure 28: Illustration of the cleaning pulse removing carbon species from the surface before the introduction of NH_3 .

To investigate if a M-N bonded precursor could potentially be a better alternative than a M-C bonded one, the commercially available tris(dimethylamido)gallium(III) dimer was used together with NH_3 plasma. The ALD process showed self-limiting behaviour with a growth rate of $1.4 \text{ \AA/cycle}$ which is considerably higher than previously reported for GaN using the M-C bonded precursors. A wide “ALD window” could be observed between $130 - 250 \text{ }^\circ\text{C}$ and the films were all crystalline with a preferred orientation along the c-axis in this temperature region. The composition of the GaN film analysed with RBS/ERDA showed 45.7 at% Ga, 47.2 at% N, 2.8 at% C, 3.1 at% O and 1.2 at% H giving a slightly under-stoichiometric composition. Absorption measurement showed that the GaN film have an optical bandgap of 3.42 eV which is close to the theoretical of 3.4 eV . When replacing the cubic Si substrate to SiC (more suitable in terms of crystal structure and lattice mismatch) the GaN could be grown epitaxially without a need of a nucleation layer. The epitaxial relationship was found to be $\text{GaN } [0002] \parallel \text{SiC } [0004]$ and $\text{GaN } [10\bar{1}3] \parallel \text{SiC } [10\bar{1}2]$ confirmed with XRD and pole figure measurement. The GaN epitaxy was further confirmed by TEM showing a sharp interface between the film and the substrate, Fig. 29. A thermal route was also examined in the temperature range $150 - 400 \text{ }^\circ\text{C}$ which resulted in x-ray amorphous films with carbon and oxygen content of 4 at% and 15 at% respectively. This indicated the importance of plasma and its ability to reduce impurities in the film.

Figure 29: TEM image of epitaxial GaN deposited on 4H-SiC using the tris(dimethylamido)gallium(III).

The same approach was made for InN where M–N precursors were used for deposition, this time we used indium guanidinate (**1**), amidinate (**2**) and formamidinate (**3**) as precursor together with NH_3 plasma. All three precursors have almost the same structure, only the substituent on the endocyclic carbon position differs where the substituent decreases in size from $-\text{NMe}_2$ to $-\text{Me}$ and lastly $-\text{H}$ for **1**, **2** and **3** respectively. InN could be obtained with all three precursors, but the lack of thermal stability made **1** to decompose in the bubbler due to heating. Lowering the bubbler temperature was not a good solution due to the low vapor pressure of the guanidinate precursor which resulted in no film growth. The amidinate and formamidinate however, both showed saturation and an ALD process could be confirmed. The stability of the formed monolayers on the surface of **2** and **3** differed, where the “ALD window” could be obtained for **3** compared to **2**. The InN properties for all the precursors differed where both crystallinity, composition and optical properties improved upon decreasing the size of the substituent on the endocyclic carbon position, going from precursor **1**→**3**. DFT calculations were employed to further understand the surface chemistry of these precursors. The calculations showed that bond dissociation enthalpy between the In and its ligand is

decreasing with decreasing size of the substituent. Decreasing the size will also lead to reduced steric repulsion between the exocyclic N-iPr groups and the substituent on the endocyclic position but also towards the surface, Fig. 30. This will give more freedom for the exocyclic groups to move, and the ability to fold up further away from the surface and closer to the moiety on the endocyclic position. When the exocyclic groups can fold up closer to the substituent on the endocyclic position will lead to a more exposed metal centre upon which the NH₃ species could react easier with it and remove the ligand. However, these precursors were not ideal due to their slow kinetics (**3** and **2**) and low thermal stability (**1**).

Figure 30: Illustration of how the steric repulsion changes upon decreasing the size of the moiety on the endocyclic carbon position.

8.2–Development of New Precursors

Could the properties of the precursors become better if the substituent on the endocyclic position is reduced even more? To investigate this the -CH on the formamidinate backbone was replaced with only N to form a triazenide ligand, Fig. 31. The triazenide ligand was placed on In to form In(III)triazenide which was used together with NH₃ plasma to deposit InN. The precursor was found to be volatile with a sublimation temperature of 80 °C (0.5 mbar) and TGA showed a single step volatilization with only 2% residual mass left. The precursor showed no sign of slow kinetics as only one pulse was used in contrast to the amidinate and formamidinate where multiple pulses was needed. Interestingly, two intervals were found where the growth was independent of the temperature, interval 1 at 220-250 °C with a growth rate of 0.4 Å/cycle and interval 2 at 300-350 °C with a growth rate of 1.2 Å/cycle. Both intervals showed saturation for both the In precursor and NH₃ plasma

confirming ALD behaviour. XRD, GIXRD and pole figure measurements showed epitaxial InN growth on SiC (0001) without any nucleation layer with in-plane relations $\text{InN } [10\bar{1}1] \parallel \text{SiC } [10\bar{1}1]$ and $\text{InN } [10\bar{1}2] \parallel \text{SiC } [10\bar{1}2]$. The composition of the films was investigated by XPS showing no detectable C and 48.7 at% In, 48.6 at% N, 2.7at% O with a AlN capping layer. To obtain a better understanding of the two growth intervals, DFT calculations were conducted on the thermal decomposition of the precursor. The calculations showed that the precursor can decompose into significantly smaller fragments compared to the original structure by the release of propane and N_2 . This indicates that at lower deposition temperatures the In precursor stays intact and the growth rate is slow whilst the precursor will decompose into a smaller molecule upon increasing the temperature leading to a more reactive species resulting in higher growth rate. However, even though the precursor decomposes the resulting smaller molecule still saturates the surface with no detectable carbon impurities.

Figure 31: Schematic of the synthesis of In(III)triazenide precursor.

The same ligand system was reacted with GaCl_3 to form Ga(III)triazenide which was used for ALD together with NH_3 plasma. The precursor was volatile with a sublimation temperature of 90°C (0.5 mbar) and the TGA analysis showed single step volatilisation from $155\text{--}225^\circ\text{C}$ with only 1% residual mass left. The same ALD behaviour was found for this precursor as the In with several regions where the growth was constant upon temperature changes. Three intervals were found for the Ga precursor, interval I between $150\text{--}275^\circ\text{C}$ ($0.25\text{ \AA/cycle}$), interval II between $300\text{--}350^\circ\text{C}$ ($0.31\text{ \AA/cycle}$) and interval III between $375\text{--}450^\circ\text{C}$ ($0.70\text{ \AA/cycle}$). Saturation could be obtained for both the precursor and NH_3 in all three temperature intervals. However, the films in interval I was X-ray amorphous while crystalline film was obtained in interval II and III. The small growth rate difference between interval I and II could be the transformation from amorphous to crystalline GaN. Similar decomposition products were found for the Ga precursor as in the In(triazenide) case where the precursor

decomposes into smaller molecules upon heating making it more reactive. This was the suggested reason for the different growth rate at different temperature regions. XRD of the films on SiC (0001) showed epitaxial GaN without the need of a nucleation layer. The epitaxial relationship was found to be GaN $[10\bar{1}3] \parallel$ SiC $[10\bar{1}2]$ and the heteroepitaxy was further confirmed by TEM analysis. The TEM also revealed a sharp GaN/SiC interface without any sign of curved lattice in contrast to the commercially available Ga(NMe₂)₃ precursor. The composition of the films was investigated in both interval II and III by RBS and ERDA showing no detectable C, 48.8 at% Ga, 46.4 at% N, 3.0 at% O, 1.8 at% H for interval II and 44.0 at% Ga, 49.1 at% N, 6.0 at%, 0.5 at% H and 0.4 at% C for interval III. Absorption measurement showed that the GaN film have a bandgap of 3.41 eV. The low carbon content shows that the new triazenide precursor have superior surface chemistry compared to the other available Ga precursors.

8.3–ALD of Ternary Phases

Both the In- and Ga(triazenide) was used to deposit the ternary InGa_xN phase. A different approach was used, instead of using the supercycle process approach to deposit the ternary nitride a novel method was developed. Both metal precursors were placed in the bubbler and mixed, the bubbler was heated and from a single pulse both metals could be transported to the reaction chamber via co-sublimation, Fig. 32. This method gives true mixing of the metals both in the growth and in-plane direction compared to the supercycles approach, see section 5.4. The composition of the InGa_xN films could be tuned via bubbler temperature, deposition temperature and the premixed ratio between each metal precursor. XPS together with RBS and ERDA analysis showed that near In_{0.5}Ga_{0.5}N could be obtained at a deposition temperature of 200-250 °C on Si substrate. From absorption measurement a Tauc plot was constructed to determine the bandgap of the near In_{0.50}Ga_{0.50}N. The bandgap was determined to be 1.94 eV and by using Vegard's Law the bandgap were correlated to In_{0.55}Ga_{0.45}N which is in good agreement with the compositional determination from XPS. Deposition on the more suited (in terms of lattice match and crystal structure) SiC (0001) substrate showed epitaxial In_{1-x}Ga_xN without a need of a seed layer. The epitaxial relationship was InGa_xN $[0002] \parallel$ SiC $[0001]$ and InGa_xN $[10-11] \parallel$ SiC $[10-11]$. XRD analysis also revealed that the In_{1-x}Ga_xN (0002) peak was broad indicating a compositional difference along the growth direction. To further investigate the microstructure TEM was employed. The TEM analysis showed a smooth and sharp interface between the film and the substrate. EDX showed a complete

mixture of both the metals with no sign of segregation into the binary phases or indium droplet formation. SAED confirmed the epitaxial behavior between the film and substrate but also revealed that the diffraction points were elongated indicating compositional difference at different regions of the film along the growth direction. To further investigate the compositional difference electron energy loss spectroscopy (EELS) was employed where the plasmon peaks were collected for the different region of the films. There was a shift of the plasmon peaks revealing a composition close to the interface to be gallium rich ($\text{In}_{0.18}\text{Ga}_{0.82}\text{N}$) while further away from the interface an indium rich ($\text{In}_{0.82}\text{Ga}_{0.18}\text{N}$) composition was calculated.

Figure 32: Illustration of the newly developed deposition route based on co-sublimation (evaporation). This method was used to deposit $\text{In}_{1-x}\text{Ga}_x\text{N}$ using the In(III)triazenide and Ga(III)triazenide precursors.

Chapter 9—Outlook

Through the research conducted in this thesis of group 13 nitrides, further questions have been awakened. The possible implementation of InN into HEMT structures being one, where we have demonstrated the ability to deposit high quality InN at low temperatures. By applying the developed processes, can InN be successfully integrated into these structures, and will the improvement of the device be of such significant magnitude as described theoretically?

As demonstrated, low temperature deposition of GaN and ternary phases of group 13 nitrides have also been realized making the ability to deposit the whole HEMT structure in a single tool possible. The development of a whole structure in a single ALD tool would be of huge interest. This possibility could also introduce new material configurations in the HEMT structures such as near $\text{In}_{50}\text{Ga}_{50}\text{N}$ or In-rich InGaN which have previously been hindered.

The newly developed deposition process for ternary materials (paper VI) based on co-sublimation (evaporation) have only marginally been explored in this thesis. Further development and understanding of this process is needed as it is brand-new. This method could be the possible solution for several problems in the ALD field, one being doping of materials. We have also shown that there is a possibility to deposit ternary phases with different composition along the growth direction. Further investigation into this area is needed as this could present new ways to engineer stress in the film arising from lattice mismatch between the film and substrate. As only one ternary phase has been investigated ($\text{In}_{1-x}\text{Ga}_x\text{N}$), further research on depositing other material systems (ternary or quaternary) should be conducted to broaden the use of this method.

Throughout the work conducted in this thesis, development of new precursors has mainly been due to minimizing carbon impurities in the film. This has been solved; however, oxygen impurities are still a challenge. The development of new precursors did not show a significant improvement, but could the configuration of the reactor be the solution? Could the implementation of a load-lock, which would minimize the exposure of oxygen into the deposition chamber, or a turbo pump be a solution? Or does the oxygen issue arise from the quartz tube in the plasma and could changing the quartz to another material help? These ideas would be of interest to study to further improve the quality of the materials.

A challenge that remains is the ability to deposit these materials via a thermal route. Devices and structures become smaller, but the area is still the same if not increased via different 3D features to improve the performance. These features need to be conformally coated which can be a challenge for plasma processes especially if the aspect ratio is high. A solution for the implementation of a thermal route could be to use an alternative nitrogen source such as hydrazine or development of new ones. Other ways to solve these problems could be to use our developed precursors in a thermal CVD process. I actually were able to successfully deposited InN with the In(III)triazene by converting the ALD tool into a CVD (not published). Only one run was made at 400 °C using NH₃ plasma before the ALD valves clogged and these endangers were banned by the boss. However, the deposit film was indeed InN and crystalline. This could be a potential route to explore for thermal processes.

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