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Doping of high-Al-content AlGaN grown by MOCVD

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Abstract

The high-Al-content $\text{Al}_x\text{Ga}_{1-x}\text{N}$, $x > 0.70$, is the principal wide-band-gap alloy system to enable the development of light-emitting diodes operating at the short wavelengths in the deep-ultraviolet, $\lambda < 280$ nm. The development of the deep-ultraviolet light-emitting diodes (DUV LEDs) is driven by the social and market impact expected from their implementation in portable units for water/surface disinfection and based on the damaging effect of the deep-ultraviolet radiation on the DNA of various microorganisms. Internationally, intense research and technology developments occur in the past few years, yet, the external quantum efficiency of the DUV LEDs is typically below 1%.

One of the main material issues in the development of the DUV LEDs is the achievement of *n*- and *p*-type high-Al-content $\text{Al}_x\text{Ga}_{1-x}\text{N}$ layers with low resistivity, which is required for the electrical pumping of the diodes. The doping process becomes significantly more complex with increasing the Al content and the electrical resistivity is as high as 10^1 - 10^2 Ωcm for *n*-type AlN doped by silicon, and 10^7 - 10^8 Ωcm for *p*-type AlN doped by magnesium.

The present study was therefore focused on gaining a better understanding of the constraints in the doping process of the high-Al-content $\text{Al}_x\text{Ga}_{1-x}\text{N}$ alloys, involving mainly silicon. For this purpose, the epitaxial growth of the high-Al-content $\text{Al}_x\text{Ga}_{1-x}\text{N}$ and AlN by implementing the distinct hot-wall MOCVD was developed in order to achieve layers of good structural and morphological properties, and with low content of residual impurities, particularly oxygen and carbon. Substitutional point defects O_N and C_N may have a profound impact on the doping by their involvement in effects of *n*-type carrier compensation. The process temperature was varied between 1000 and up to 1400 °C, which is a principal advantage in order to optimize the material properties of the high-Al-content $\text{Al}_x\text{Ga}_{1-x}\text{N}$ and AlN. The epitaxial growth of the high-Al-content $\text{Al}_x\text{Ga}_{1-x}\text{N}$ and AlN was largely performed on 4H-SiC substrates motivated by (i) the lattice mismatch of $\sim 1\%$ along the basal plane (the smallest among other available substrates including Si and sapphire), (ii) the good thermal conductivity of $3.7 \text{ W cm}^{-1} \text{ K}^{-1}$, which is essential to minimize the self-heating during the operation of any light-emitting diode, and (iii) the limited access to true-bulk AlN wafers. The Si doping was investigated over a large range of $[\text{Si}] \sim 1 \times 10^{17} \text{ cm}^{-3} - 1 \times 10^{20} \text{ cm}^{-3}$. Only the high doping range of $[\text{Mg}] \sim (1\text{-}3) \times 10^{19} \text{ cm}^{-3}$ was targeted motivated by the large thermal ionization energy of this common acceptor (from 200 meV in GaN to about 630 meV in AlN). The material characterization involved extensive implementation of atomic force microscopy (AFM), x-ray diffraction (XRD), cathodoluminescence (CL), secondary ion mass spectrometry (SIMS), capacitance-voltage measurements, as well as measurements of the conductivity of the layers by contactless microwave-based technique. The possibility to perform electron paramagnetic resonance (EPR) measurements on the Si-doped high-Al-content $\text{Al}_x\text{Ga}_{1-x}\text{N}$ was essential in order to establish any effect of self-compensation of the shallow donor state of silicon through the related so-called DX state. The EPR measurements corroborated the study of the incorporation kinetics of silicon and oxygen at various process temperatures and growth rates.

The outcome of this study is accordingly summarized and presents our understanding for (i) the complex impact of silicon and oxygen on the *n*-type conductivity of $\text{Al}_{0.77}\text{Ga}_{0.23}\text{N}$, representative for the alloy composition at which a drastic reduction of the *n*-type conductivity of $\text{Al}_x\text{Ga}_{1-x}\text{N}$ is commonly reported (**paper 1**); (ii) the strain and morphology compliance during the intentional

doping by silicon and magnesium, and its correlation with the resistivity of highly doped layers of $\text{Al}_{0.82}\text{Ga}_{0.18}\text{N}$ alloy composition (**paper 2**); (iii) the n -type conductivity of highly Si-doped $\text{Al}_{0.72}\text{Ga}_{0.28}\text{N}$ as bound by the process temperature (**paper 3**); and (iv) the shallow donor or DX behavior of silicon in conductive $\text{Al}_x\text{Ga}_{1-x}\text{N}$ layers with $0.63 \leq x \leq 1$ (**paper 4**). It is noted that the measured n -type conductivity in reference layers of $\text{Al}_{0.77}\text{Ga}_{0.23}\text{N}$, alternatively $\text{Al}_{0.72}\text{Ga}_{0.28}\text{N}$, alloy composition is on par with the state-of-the-art values, i.e. $\leq 0.05 \, \Omega\text{cm}$, and $0.012 \, \Omega\text{cm}$, respectively. A room-temperature resistivity of $7 \, \text{k}\Omega\text{cm}$ was measured in Mg-doped layers of $\text{Al}_{0.85}\text{Ga}_{0.15}\text{N}$ alloy composition, which is superior to the state-of-art values (**paper 5**). The performance of the transport properties of the high-Al-content $\text{Al}_x\text{Ga}_{1-x}\text{N}$ layers can further improve by improving the crystalline quality of the AlN-on-SiC template and by implementing true-bulk AlN substrates. The AlN heteroepitaxial growth at the process temperatures of 1100 and 1200 °C is therefore investigated (**paper 6**). The lattice parameters, structural and optical properties of true-bulk, homoepitaxial and heteroepitaxial AlN material grown at high process temperatures of up to 1400 °C is further reported (**paper 7**).

Populärvetenskaplig sammanfattning

Aluminium-gallium-nitrid ($\text{Al}_x\text{Ga}_{1-x}\text{N}$) med hög Aluminium halt ($x > 0.7$) är en legering som tillhör materialklassen halvledare och har ett enormt brett och direkt band-gap upp till 6.2 eV för AlN. Denna egenskap gör denna legering optimal för att tillverka mycket små och effektiva optoelektroniska komponenter, så som till exempel lysdioder och laserdioder, som kan emittera ultraviolett (UV) ljus med en våglängder kortare än 280 nm. UV ljus med denna våglängd skadar cellers DNA molekyler och kan därför användas för desinfektion av förorenat vatten och luft. Denna viktiga tillämpning har starkt drivit utvecklingen av detta material system framåt, men än så länge är effektiviteten hos dessa komponenter mycket lägre än för till exempel lysdioder som emitterar blått eller rött ljus.

För att utnyttja dessa unika materialetegenskaper för optoelektroniska tillämpningar är det nödvändigt att erhålla en mycket hög kristallkvalitet och att kunna kontrollera dess elektriska ledningsförmåga genom att tillsätta små koncentrationer av föroreningar eller så kallat störämne. Denna process kallas dopning. Störämnena som avger en extra elektron till materialet kallas donatorer (bidrar till n-typ konduktivitet) medan störämnena som binder en extra elektron och bildar elektriskt ledande ”hål” kallas acceptorer (p-typ konduktivitet). När elektroner och hål möts kan energi frigöras genom att bland annat emittera UV ljus. Vanligen används störämnena Si (donator) och Mg (acceptor) för att kontrollera konduktiviteten hos GaN och AlGaIn. Men vid höga Aluminium halter är det svårt att kontrollera den elektroniska ledningsförmågan till den grad som krävs för att tillverka effektiva ultraviolettera lysdioder. Därför är det viktigt att utforska och förstå de grundläggande egenskaperna hos störatomer samt hur de påverkar tillväxt processen av AlGaIn.

I denna avhandling har dopning processen av AlGaIn med hög Aluminium halt studerats ($x > 0.6$). Den tillväxt process som har används i detta arbete är, *metalorganic chemical vapor deposition* (MOCVD), som idag är den dominerande tillväxt metoden för optoelektroniska komponent-strukturer. För att odla AlGaIn med MOCVD används vanligtvis de metalorganiska föreningarna Trimetylaluminium ($\text{Al}(\text{CH}_3)_3$) och Trimetylgallium ($\text{Ga}(\text{CH}_3)_3$) samt gasen ammoniak (NH_3). Dessa föreningar flödar sedan tillsammans med stora mängder vätgas över ett kiselkarbid- (SiC) eller AlN-substrat som har värmts upp till en temperatur av $\sim 1000\text{--}1500^\circ\text{C}$ under ett lågt processtryck av 50 mbar. De kemiska föreningarna reagerar över det varma substratet och formar AlGaIn. Under detta projekt studerades initialt tillväxten av AlN, för att erhålla den höga kristallkvalité och de låga bakgrunds nivåer av föroreningar så som syre och kol, som krävs för att kunna erhålla kontrollerad dopning. Detta kan uppnås bland annat genom att använda relativt höga tillväxt temperaturer och låga tillväxthastigheter. Dopning och dess inverkan på den elektriska ledningsförmågan och materialkvaliteten studerades sedan i detalj genom att växa dopad AlGaIn på dessa högkvalitativa AlN filmer. Genom att tillsätta små flöden av Si och Mg innehållande föreningar till MOCVD processen kan materialet dopas med önskade koncentrationer med Si eller Mg. Hur dessa atomer inkorporeras i kristallen och hur den elektriska konduktiviteten påverkakas av tillväxtparameterar så som tillväxthastighet, dopning koncentration och processstemperatur har undersökts. Arbetet har resulterat i kontrollerad konduktivitet vid Aluminium halter upp till 80-85 % för både n-typ och p-typ dopad AlGaIn vilket möjliggör tillverkning av UV emitterande optoelektroniska komponenter med extremt korta våglängder, $\lambda \sim 230\text{--}240\text{ nm}$. Vi har också presenterat en möjlig förklaring för den låga n-typ konduktiviteten observerad hos

AlN, där vi föreslår att Si bildar en stabil djup donatornivå (DX-center) som kräver en relativt hög termiskenergi för att frigöra de donator bundna elektronerna.

Preface

This thesis is based on my PhD studies conducted from May 2009 to May 2014 in the Division of Semiconductor Materials, Department of Physics, Chemistry and Biology (IFM), Linköping University. Financial support was provided by the Swedish Research Council (VR) and Swedish Foundation for Strategic Research (SSF).

Papers included in the thesis

1. **The complex impact of silicon and oxygen on the n-type conductivity of high-Al-content AlGa_N**
A. Kakanakova-Georgieva, D. Nilsson, X. T. Trinh, U. Forsberg, N. T. Son, and E. Janzén
Applied Physics Letters 102 (2013) 132113
2. **Strain and morphology compliance during the intentional doping of high-Al-content AlGa_N layers**
D. Nilsson, E. Janzén, and A. Kakanakova-Georgieva
submitted
3. **Highly Si-doped Al_{0.72}Ga_{0.28}N layers: n-type conductivity bound by the process temperature**
D. Nilsson, X. T. Trinh, N. T. Son, E. Janzén, S.-L. Lata, M. J. Kappers, C. J. Humphreys, and A. Kakanakova-Georgieva
Manuscript
4. **On the behavior of the silicon donor in conductive Al_xGa_{1-x}N (0.63 ≤ x ≤ 1) layers**
D. Nilsson, X. T. Trinh, E. Janzén, N. T. Son, and A. Kakanakova-Georgieva
Manuscript in final preparation
5. **Mg-doped Al_{0.85}Ga_{0.15}N layers grown by hot-wall MOCVD with low resistivity at room temperature**
A. Kakanakova-Georgieva, D. Nilsson, M. Stattin, U. Forsberg, Å. Haglund, A. Larsson, and E. Janzén
Physica Status Solidi - Rapid Research Letters 4 (2010) 311
6. **High-quality AlN layers grown by hot-wall MOCVD at reduced temperatures**
A. Kakanakova-Georgieva, D. Nilsson, and E. Janzén
Journal of Crystal Growth 338 (2012) 52
7. **Lattice parameters, structural and optical properties of AlN true bulk, homoepitaxial and heteroepitaxial material grown at high temperatures of up to 1400 °C**
D. Nilsson, E. Janzén, and A. Kakanakova-Georgieva
Manuscript

My contribution to the papers

Paper 1. I performed the growth, AFM and electrical characterization, and took part in the CL-SEM measurements. I participated in the analysis and discussions of the data, and in the writing of the paper.

Paper 2. I planned and performed the growth, AFM and XRD characterization. I participated in the analysis and discussions of the data, and in the writing of the manuscript.

Paper 3. I planned and performed the growth, AFM, XRD, and electrical characterization. I participated in the analysis and discussions of the data, and in the writing of the manuscript.

Paper 4. I planned and performed the growth, AFM, XRD, and electrical characterization. I wrote the manuscript after discussions and inputs from the co-authors.

Paper 5. I performed the AFM characterization and took part in the growth. I participated in the analysis and discussions of the data, and in the writing of the paper.

Paper 6. I performed the AFM characterization and took part in the CL-SEM measurements. I participated in the discussions of the data, and in the writing of the paper.

Paper 7. I planned and performed a major part of the growth. I performed the XRD and CL-SEM characterization. I wrote the manuscript draft.

Papers related to the thesis

8. **Silicon and oxygen in high-Al-content AlGa_N: incorporation kinetics and electron paramagnetic resonance study**
A. Kakanakova-Georgieva, D. Nilsson, X.T. Trinh, N.T. Son, and E. Janzén
Diffusion and Defect Data Pt.B: Solid State Phenomena 205-206 (2014) 441
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12. **Controlled growth of hexagonal Ga_N pyramids by hot-wall MOCVD**
A. Lundskog, C.W. Hsu, D. Nilsson, K.F. Karlsson, U. Forsberg, P.O. Holtz, and E. Janzén
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Daniel Nilsson
Linköping May 2014

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Part I – Introduction to the field

1 Introduction

Wide band-gap semiconductors have been extensively studied the last decades due to their superior material properties, which out-compete the traditional semiconductor materials in many areas of applications such as ultraviolet (UV) optoelectronics [1,2], high temperature microelectronics and high power electronics [3].

Aluminum Gallium Nitride (AlGa_N) has a continuous wide direct band-gap (E_G), ranging from 3.5 eV for GaN to 6.2 eV for AlN, and making this material system most suitable for manufacturing of light-emitting diodes (LEDs) operating in the ultraviolet (UV) spectral region between 210-365 nm. High-Al-content AlGa_N material development has been strongly driven by the fact that deep UV radiation is damaging for bacteria, yeast and viruses [4], which opens up for important fields of applications for deep UV radiation (<285 nm), namely, water- and air-purification that have enormous market opportunities [2].

Potential material systems for deep UV optoelectronic applications are listed in Table 1.1. Hexagonal BN has a wide direct band-gap giving rise to intense luminescence at 215 nm [5]. However, the different crystal structure and growth conditions have made BN difficult to integrate with the rest of III-Nitrides. Diamond on the other hand is a indirect band-gap semiconductor. Even so, diamond-based deep UV LEDs have been demonstrated, but with a relative low efficiency [6]. The AlGa_N and AlIn_N alloys are the only alloy systems with direct and tunable band-gap in the UV region. Growth of high quality AlIn_N is very challenging since the optimal growth temperature for InN is significantly lower (~600 °C) compare to AlN (~1200-1600 °C) and GaN (~1100 °C) [7,8]. In contrast, high quality AlGa_N can be obtained at growth temperatures of ~1100-1200 °C [9].

In order to utilize the large band-gap of AlGa_N for optoelectronic applications it is essential to control the electrical conductivity by intentionally adding impurities into the crystal lattice in order to form a *pn*-junction. AlN was for a long time considered as an electrical insulator rather than a semiconductor. However, it was shown that both *n*- and *p*-type conductivity can be obtained in AlN by using Si and Mg doping, respectively, as the first AlN based LED was demonstrated in 2006 [10]. At that time, both the *n*- and *p*-type conductivity was very poor and the doping is still today one of the most challenging issues in this field in order to achieve high-performance devices.

Table 1.1 Band-gap energy and crystal structure of wide band-gap semiconductors with potential for UV optoelectronic applications.

	crystal structure	E_G (eV)	LED wavelength (nm)
Al _x Ga _{1-x} N	wurtzite	3.5 – 6.2 (direct)	~210-365
Al _x In _{1-x} N	wurtzite	0.6 – 6.2 (direct)	~210-2067
BN	hexagonal	6.0 (direct)	215
Diamond	diamond	5.5 (indirect)	235

Figure 1.1 External quantum efficiency of state-of-art deep UV LEDs (●) [12–16] and commercially available InGaN based LEDs from Nichia and Sora (◆) emitting at 365 nm and 410 nm, respectively [12,17]. State-of-the-art deep UV LED based on Diamond (in-direct band-gap) is given for comparison (□)[6].

Deep UV LEDs emitting at 210-280 nm have been demonstrated. However the external quantum efficiency (EQE) decreases for LEDs operating at shorter wavelengths, Figure 1.1 [11–16]. The commercially available InGaN-based LEDs have a high EQE of about 40-60% [12] whereas the efficiency drastically decreases for AlGaN-based LEDs and the highest reported EQE for the AlN-based LEDs is very low ~0.0001% [13]. The drop in EQE is closely linked to the material quality but depends also on the light extraction efficiency and the design of the device [2]. High dislocation densities in epitaxial layers have been shown to negatively influence the device performance [12]. A schematic sketch of AlGaN-based LED is presented in Figure 1.2 and the specific issues posed by each individual layer are indicated.

Figure 1.2 Schematic sketch of AlGaN-based LED structure and issues related to each individual layer.

This thesis focuses on the growth and intentional doping of high-Al-content $\text{Al}_x\text{Ga}_{1-x}\text{N}$ ($x > 0.6$). The first part of this thesis gives an introduction to the field. The fundamental material properties of AlGaN will be described (chapter 2), and the basic principles of MOCVD are described (chapter 3). The doping properties of AlGaN are presented and put into a perspective (chapter 4). Finally, brief description of the experimental techniques and methods, which were used during this work is given (chapter 5). The second part of the thesis includes **papers 1-7**.

2 Properties of AlGaN

2.1 Crystal structure

AlGaN has a thermodynamically stable hexagonal wurtzite and a metastable cubic zincblende crystal structure [18]. Both structures are based on tetrahedral atomic coordination where the cation (Al/Ga) atom is surrounded by four anion (N) atoms. The structures differ in the stacking order of the close packed diatomic planes [Figure 2.1]. The wurtzite structure has a stacking order of AaBbAa... along the [0001] while the zincblende structure has a stacking order of AaBbCcAa... along the [111]. A, B, C (a, b, c) denote the cation (anion) atoms. One fundamental difference between these two structures is the interaction with the third nearest neighbor, A and a [Figure 2.1(a)]. In the wurtzite structure third nearest neighbor is a pair of the cation and anion atoms which coulomb interaction tends to stabilize the wurtzite structure.

Figure 2.2 (a) shows the tetrahedron that builds up the crystal structure and the characteristic angles α and β . For ideal tetrahedron the bond length is equivalent for all bonds and $\alpha = \beta \approx 109.47^\circ$. The wurtzite structure is characterized by the a and c lattice constants and the internal parameter u defined as the bond distance between the cation and anion atoms divided by the c lattice constant. For AlGaN, the wurtzite structure is distorted from the ideal values as can be seen from the smaller c/a ratio [Table 2.1]. This can be understood as distortion of the bond angles, while the bond lengths of the strong tetrahedral bonds are almost constant, $\sim uc$. Since N is the most electronegative group V element the covalent sp^3 hybrid bonds in AlGaN has higher degree of ionicity compared to other III-V semiconductors such as AlGaAs, which results in strong chemical bonds affecting many of the properties of AlGaN.

Figure 2.1 Atomic structure and stacking sequence of (a) wurtzite and (b) zincblende crystal structures. The white and black spheres indicate the cation and anion atoms while the bonds are indicated with a solid line. A, B, C (a, b, c) denote the cation (anion) position and indicate the difference in stacking sequence between the two structures.

Figure 2.2 (a) tetrahedron with the characteristic angles which are $\alpha = \beta \approx 109.47^\circ$ in an ideal tetrahedron and (b) the wurtzite structure with the characteristic a and c lattice constants and the internal parameter u marked in the figure. For AlN the c/a ratio is substantially smaller than the ideal value of $c/a \approx 1.633$, which was attributed to the large β angle ($>109.47^\circ$) and with unchanged bond length.

The metastable zincblende structure can be stabilized and grown under certain growth conditions using cubic substrates [19] but the majority of the studies, as well as the work presented in this thesis, treat the hexagonal wurtzite structure.

2.2 Polarization

Wurtzite structures have spontaneous polarization along the $-c$ -axis [18]. One consequence of the distorted lattice configuration is that the polarization along the $-c$ -axis strongly enhances compared to what would be expected for the ideal wurtzite structure [20]. This polarization is also affected by strain in the film, an effect that is referred as piezoelectric polarization. The induced polarization will introduce an electrostatic field along the c -axis, which strongly affects the properties of optoelectronic devices. For instance, the electric field leads to separation of the electrons and holes in the quantum well (active layer) in optoelectronic devices grown along the c -axis, which results in low recombination efficiency [21]. Therefore, epitaxial growth along non-polar crystal directions, such as $[1\bar{1}00]$ direction, is widely studied [21]. One advantage of the polarization is that the electric field can be utilized for creating polarization induced electron or hole gas [22,23] that can be used to overcome the difficulty in obtaining highly conductive AlGaIn. A doping free (“polarization doped”) AlGaIn-based LED was recently demonstrated [24]. In this work the growth and doping along c -axis oriented substrates was studied.

Table 2.1 Structural parameters of wurtzite AlN and GaN compared to the ideal values for the wurtzite crystal structure at 300 K [18].

	a (Å)	c (Å)	c/a	u	uc (Å)
Ideal			≈ 1.633	0.375	1.868
AlN	3.112	4.982	1.601	0.380	1.893
GaN	3.189	5.185	1.626	0.376	1.950

2.3 Mechanical properties

For small deformations, crystals are elastic and there is a linear relationship between the applied load (stress) and lattice displacement (strain) that is given by Hook's law. Hook's law can be expressed as $\sigma_{ij}=C_{ijkl} \epsilon_{kl}$ where σ , C and ϵ are the stress, elastic stiffness moduli and strain tensors, respectively [25]. Due to the crystal symmetry the relation between strain and stress tensor in hexagonal crystals can be written using a matrix representation [26]:

$$\begin{pmatrix} \sigma_{xx} \\ \sigma_{yy} \\ \sigma_{zz} \\ \sigma_{yz} \\ \sigma_{xz} \\ \sigma_{xy} \end{pmatrix} = \begin{pmatrix} C_{11} & C_{12} & C_{13} & 0 & 0 & 0 \\ C_{12} & C_{11} & C_{13} & 0 & 0 & 0 \\ C_{13} & C_{13} & C_{33} & 0 & 0 & 0 \\ 0 & 0 & 0 & C_{44} & 0 & 0 \\ 0 & 0 & 0 & 0 & C_{44} & 0 \\ 0 & 0 & 0 & 0 & 0 & (C_{11} - C_{12})/2 \end{pmatrix} \begin{pmatrix} \epsilon_{xx} \\ \epsilon_{yy} \\ \epsilon_{zz} \\ 2\epsilon_{yz} \\ 2\epsilon_{xz} \\ 2\epsilon_{xy} \end{pmatrix},$$

where C_{ij} is the elastic stiffness constants, which have the dimension of pressure. The x-, y- and z-axis are represented by the $[1\bar{1}20]$, $[\bar{1}100]$, and $[0001]$ directions, respectively. This gives the useful expressions between stress and strain:

$$\begin{aligned} \sigma_{xx} &= C_{11}\epsilon_{xx} + C_{12}\epsilon_{yy} + C_{13}\epsilon_{zz}, \\ \sigma_{yy} &= C_{12}\epsilon_{xx} + C_{11}\epsilon_{yy} + C_{13}\epsilon_{zz}, \\ \sigma_{zz} &= C_{13}\epsilon_{xx} + C_{13}\epsilon_{yy} + C_{33}\epsilon_{zz}, \\ \sigma_{yz} &= 2C_{44}\epsilon_{yz}, \\ \sigma_{xz} &= 2C_{44}\epsilon_{xz}, \\ \sigma_{xy} &= (C_{11} - C_{12})\epsilon_{xy} \end{aligned} \quad (2.1)$$

For heteroepitaxial layers grown along $[0001]$ direction, the stress can be assume to be dominated by isotropic biaxial in-plane stress ($\sigma_{xx} = \sigma_{yy}$) and all other strains are negligibly small. For fully strained epitaxial layers, the external stress is mainly related to the film/substrate interface whereas the layer is free to expand along the $[0001]$ direction ($\sigma_{zz} = 0$), giving the following equation:

$$\sigma_{zz} = 0 = C_{13}\epsilon_{xx} + C_{13}\epsilon_{yy} + C_{33}\epsilon_{zz}. \quad (2.2)$$

Since isotropic in-plane stress is assumed ($\epsilon_{xx} = \epsilon_{yy}$), we can rewrite (2.2) on the form:

$$\epsilon_{zz} \equiv -\frac{2C_{13}}{C_{33}}\epsilon_{xx} = R_B\epsilon_{xx}, \quad (2.3)$$

where R_B is the biaxial strain relaxation coefficient and ϵ_{xx} and ϵ_{zz} are the in-plane and out-of-plane strain, respectively, which are defined as:

$$\epsilon_{xx} \equiv \frac{a - a_0}{a_0}, \quad \epsilon_{zz} \equiv \frac{c - c_0}{c_0}, \quad (2.4)$$

As we will see in chapter 5.1, the expression above, Eq. (2.3), can be used in order to determine the Al content in strained AlGaN layers or the strain in AlN grown on the c-axis substrates. It is therefore important that the R_B and the relaxed lattice constants are known. However, in the literature both the relaxed lattice constants and R_B widely scatter [27–30]. These quantities are discussed and determined in **paper 7**. In Table 2.2 the elastic stiffness constants and R_B are given for GaN and AlN. These values were used in this work to calculate the Al content of AlGaN and strain for AlN.

Table 2.2 Elastic stiffness constants for wurtzite AlN and GaN [30]

	C_{11} (GPa)	C_{12} (GPa)	C_{13} (GPa)	C_{33} (GPa)	C_{44} (GPa)	R_B ($= -2C_{13}/C_{33}$)
GaN	374	138	101	395	98	-0.511
AlN	395	137	107	404	117	-0.530
AlN (This work)						-0.556±0.021

3 MOCVD of AlGaN

Successful growth of GaN and AlN by metal-organic chemical vapor deposition (MOCVD) was first reported by Manasevit, Erdmann, and Simpson in 1971 [31]. Although the precursors and growth temperature were similar to the one used today, the process was incapable of producing device quality materials due to the low purity of the precursors and low quality of the epitaxial films. The breakthrough for the MOCVD technique came 1978 as Dupuis and Dapkus showed that device quality AlGaAs could be obtained by MOCVD by the demonstration of the first working AlGaAs-based laser diode [32]. This result encouraged the development of various semiconductor material systems for various applications. Nevertheless, it was not until the beginning of the 1990s that the GaN-based material system was mature enough to be used for device applications. The pioneering work, by Akasaki et al.[33], and Nakamura et al. [34], on the development of the MOCVD of the GaN-based material system led to reliable and efficient InGaN based blue light emitting diodes (LEDs) and laser diodes (LDs) [35] that have strongly stimulated the worldwide research efforts and development of the III-Nitrides. Today, basically all epitaxially grown AlGaN-based optoelectronic and electronic device structures on the market are produced using MOCVD. The research focus has now expanded towards the high aluminum and indium containing alloys and nanostructures.

3.1 General principles of MOCVD

CVD describes the process where solid material is deposited on a substrate by chemical reactions of vapor phase precursors [36]. The chemical reactions are activated by an external energy source such as heat, plasma or photons. In MOCVD, metal-organic compounds are used as precursors, often together with a hydride gas, such as AsH₃ or NH₃. It is desirable that the metal-organic precursors are volatile, stable during storage and of high purity [37].

The CVD involves the following sequential steps; (i) transport of precursors to the growth zone, (ii) Gas-phase reactions of the precursors in the hot zone to form reactive intermediates or by-products, (iii) Transport of the precursors and the reactants to the substrate, (iv) adsorption of reactants on the substrate, (v) surface diffusion, nucleation and surface reactions on the surface leading to the growth, and (vi) desorption and transport of by-products away from the surface [36].

Figure 3.1 Schematic view of the CVD process.

MOCVD systems normally operate at pressures in the range of a few millibars up to atmospheric pressure. At these pressures the molecules are close enough to meet and interact which means that the gas can be described by the laws of gas dynamics. In order to control the growth, the MOCVD reactor is designed to keep a *laminar gas flow* above substrate i.e. the fluid flows in parallel layers above the substrate with no mixing perpendicular to the flow direction. In contrast, turbulent gas flows are characterized by chaotic flow patterns that must be avoided to control a smooth distribution of reactant on the substrate.

In the laminar flow regime, the transfer of the reactants to the substrate happens through gas phase diffusion. The velocity profile of gas flowing over a flat plate is show in Figure 3.2. The velocity of the gas at the reactor walls is zero, due to the frictional forces at the surface [38], and gradually increases to u_0 far away from the walls. The layer, for which the gas velocity is lower than u_0 , is defined as the *boundary layer*, and its thickness $\delta(x)$ is inversely proportional to the square root of the gas velocity:

$$\delta(x) \propto \sqrt{\frac{\nu x}{u_0}}, \quad (3.1)$$

where ν is the kinematic viscosity of the gas and x is the horizontal position along the plate and u_0 is the velocity of the gas at infinite distance above the plate. Thus the thickness of the boundary layer can be controlled by the gas velocity and the viscosity of the carrier gas. The boundary layer is of importance for the growth since the molecules and radicals need to diffuse through this layer to react on the surface and contribute to the growth.

The growth rate in thermal CVD is determined by several factors and can be generalized into three limiting modes according to different temperature regimes as illustrated in Figure 3.3:

(1) At low growth temperatures the growth rate decreases exponentially with the reciprocal process temperature ($1/T$). In this temperature region the growth rate is limited by the reaction kinetics, namely the slowest reaction in the gas phase or at the surface. The slope of the curve gives the *activation energy* for the rate limiting process. Since the growth rate is sensitive to the process conditions in this growth window it is challenging to control the growth and get reproducible results over time.

Figure 3.2 Profile of the gas velocity above a flat plate and the formation of a boundary layer that is marked with a dashed line. u_0 is the undisturbed gas velocity and $\delta(x)$ is the thickness of the boundary layer.

(2) At medium growth temperatures the growth rate becomes insensitive to the growth temperature. In this region the growth rate is limited by the transport of the reactants to the surface and is therefore called, transport limited growth (or diffusion limited growth). By increasing the precursor concentration or by reducing the thickness of the boundary layer the growth rate can be well controlled and giving reproducible results. (3) At very high growth temperatures the growth rate decreases which can be due to several of factors such as decomposition of the film, parasitic reactions between the precursors in gas phase and desorption of precursors from the surface.

In the mass transport limited regime the growth rate is limited by the diffusion of reactants through the boundary layer. The flux, J , of reactants that diffuse through the boundary layer can be expressed as,

$$J = \frac{D(P - P_i)}{RT\delta} \propto \text{Growth rate} , \quad (3.2)$$

where P is the partial pressure of reactant in the gas phase and P_i is the partial pressure at the interface. T is the temperature at the substrate, D is the diffusion coefficient of the reactant in the carrier gas and R is the gas constant. The growth rate is proportional to the flux J in the mass transport limited growth region. Therefore, in principle, the growth rate can be increased by reducing the pressure since this will reduce the boundary layer [Eq. (3.1)] and increase the diffusivity (D).

Figure 3.3 Different growth regimes as function of reciprocal process temperature.

3.2 Aspects of the reactor design

Figure 3.4 Schematic of a horizontal hot-wall MOCVD system.

The MOCVD system [Figure 3.1] can be divided into three main subsystems, gas delivery system, pump system and heating system, which are shortly presented below:

The *gas delivery system* controls the supply of precursors to the growth chamber. The metal-organic precursors are stored in stainless steel containers, called bubblers, which are kept in a thermostat bath where the temperature of the bath controls the vapor pressure of the metal-organics. The carrier gas flows through the liquid metal-organics, and deliver the metal-organic compound to the hot zone inside the growth chamber where the growth takes place. The gas flows are precisely controlled by mass flow controllers (MFCs) and pneumatic valves that can accurately switch the gas flow from the growth chamber to the vent. The precise control allows growth of atomically flat and abrupt heterostructures.

In the *pump system*, the pressure in the growth chamber is measured by a pressure gauge and the pumping speed regulates by a valve in order to keep a constant pressure in the cell. Before each run a turbo pump can evacuate the growth chamber in order to reduce the amount of residual vapors and to ensure that the growth chamber is leak tight.

Finally, there is heating system that has a water cooled radio-frequency (RF) coil that inductively heats the graphite susceptor to a certain growth temperature. A pyrometer measures the temperature in order for the system to regulate a stable process temperature. Porous graphite purged with nitrogen is used as an insulator in order to effectively heat the susceptor and to protect the quartz tube from the heat.

Figure 3.5 (a) Drawing of the horizontal hot-wall MOCVD chamber (b) Cross sectional sketch of the growth chamber including the up-stream quartz liners and the precursors used for the growth of AlGaN.

In this work a horizontal gas flow hot-wall MOCVD reactor (GaN VP508GFR, Aixtron AB) that has a growth capacity of $1 \times 4''$ (alternatively $3 \times 2''$) wafers per growth run has been used [39]. The hot-wall MOCVD is new concept for III-nitride growth that was originally designed for growth of SiC [40]. In the hot-wall MOCVD system the susceptor is wrapped around the substrate as can be seen in Figure 3.5. The heating of the hot-wall MOCVD system gives more uniform heat profiles in gas-phase compared to a cold wall reactor. This leads to a more efficient cracking of the precursors and reduced thermal gradients that will introduce less wafer-bowing [41]. Since the system was developed for SiC growth, which is usually performed at much higher temperatures, compared to the III-Nitrides. Thus the concept of hot-wall MOCVD makes it possible to study growth of III-Nitrides in a very wide temperature range 700-1600 °C. Particularly, high growth temperatures of 1600°C benefit achievement of high-quality AlN layers [8].

The MOCVD growth of AlGaN is challenging since the strong Al-N bond induces a low surface mobility of Al containing species [9]. In order to obtain flat surface morphologies, high growth temperatures are needed to facilitate the surface diffusion. Heteroepitaxial GaN layers with atomically smooth surfaces have been obtained using a growth temperature between ~ 1000 -1100 °C [42] while the optimized growth temperature for AlN is much higher (>1200 °C) [8,43]. Very high quality epitaxial AlN layers were obtained on 6H-SiC substrate using a process temperature of 1500-1600 °C [8]. Since most conventional MOCVD reactors cannot reach such high growth temperatures, sophisticated growth schemes have been developed where the TMAI and NH_3 precursors are pulsed in alternating sequences, referred as pulsed atomic-layer deposition [44,45]. This technique has been shown to produce high quality films at a relative low growth temperature of <1200 °C [46,47].

3.3 Aspects of the gas-phase chemistry

Metal-organic precursors such as trimethylaluminum (TMAI or $(\text{CH}_3)_3\text{Al}$) and trimethylgallium (TMGa or $(\text{CH}_3)_3\text{Ga}$) together with ammonia (NH_3) are used as precursors in the MOCVD of AlGaN. The metal-organic precursors are diluted in large flows of purified hydrogen (H_2) and/or nitrogen (N_2) that act as carrier gases and deliver the metal-organic precursors to the heated growth zone as shown in Figure 3.5 (b).

The epitaxial growth of AlGaInN by MOCVD includes the transport of ammonia (NH₃) gas and the vapor from the liquid trimethylaluminum (TMAI (CH₃)₃Al)), trimethylgallium (TMGa (CH₃)₃Ga)) or solid trimethylindium (TMIn (CH₃)₃Ga)) metal-organic sources to the growth chamber and the heated substrate by carrier gas in form of nitrogen (N₂) and/or hydrogen (H₂) [48]. Other metal-organics such as triethylgallium (TEGa (C₂H₅)₃Ga)) can also be used as a Ga source. Since the ethyl radical is less reactive than the methyl radical a lower C incorporation can be expected [48].

Both nitrogen and ammonia have a high thermal stability as can be seen from the large dissociation energies of 945 kJmol⁻¹ [48] and 435 kJmol⁻¹ (H-NH₂) [49], respectively. Thus high concentrations of NH₃ are needed in order to provide enough nitrogen containing species during growth [50]. An NH₃/(TMAI+TMGa) ratios of >1000 are often used. At high process temperatures and high NH₃ flow rates, these parasitic reactions between precursors are facilitated. The overall chemical reaction in MOCVD of III-Nitrides is described in [9]:

where M is a group III metal element (Al, Ga, In). It would be expected that monomethyl radicals and atomic metal atoms form by breaking M-C bonds, which then can react with nitrogen containing species (NH₃ and/or N_{3-x}) at the surface and contribute to the growth [49]. However, in the case of MOCVD of AlN adduct formation between the TMAI and ammonia (M(CH₃)₃:NH₃) is difficult to avoid since it forms already at room temperature which strongly influences the reaction pathway [51,52]. The parasitic reactions are more severe during AlN growth as compared with GaN growth and can influence the growth rate and the compositional control of AlGaIn [51]. Kinetic models of the AlN growth process include adduct formation between TMAI and NH₃ that react in the gas phase [51,52]:

Methane (CH₄) elimination occurs according with

Finally, Al(CH₃)₂:NH₂ may climb to larger stable oligomer ring species:

Monomers (n=1) and dimers (n=2) are expected to contribute to the growth while the higher order oligomers (n>2) have a low vapor pressure and are therefore not likely to contribute to the growth but may initiate AlN particles in the gas-phase at high growth temperatures. The large AlN particles are repelled from the hot surface due to the thermophoresis effect and thus strongly reducing the growth efficiency.

It was suggested that the equilibrium of reaction (R3.2) can shift and stabilize TMAI at low V/III ratios and thus avoid severe losses by parasitic reactions [53]. Low reactor pressures [51,52] or increase the nitrogen composition in the carrier gas [54] can also improve the growth efficiency.

3.4 Aspects of the substrate selection

In this work growth was performed on both 4H-SiC and AlN substrates. Properties of the common substrates used for AlN epitaxy are summarized in Table 3.1. The SiC substrates are implemented for heteroepitaxial growth because of their large size, extremely good thermal conductivity and variety in electrical conductivity. Moreover, the lattice mismatch to AlN along the basal plane is relative small (~1%). compare to other substrates (sapphire ~ -13%) [Table 3.1]. The drawback is it the relatively low band-gap of ~3.2 eV which is not transparent for deep UV radiation.

The lattice mismatch will introduce a misfit dislocation network at the AlN/SiC interface, [55,56]. The expected critical thickness for the accumulated misfit strain to relax by creation of misfit dislocation is about ~20 nm [58]. Strain relaxation of the epitaxial layer during growth by generation of misfit dislocations is expected to occur [59]. In addition, the thermal mismatch between the substrate and the epitaxial layer can cause significant strain in the layer during the cooling [60]. If no additional relaxation occurs during cooling the thermal strain is given by [57]:

$$\varepsilon_{thermal} = \int_{T_G}^{T_{RT}} \alpha_S(T) - \alpha_L(T) dT \approx (T_{RT} - T_G)(\alpha_S - \alpha_L) \quad (3.3)$$

Since AlN has a larger thermal expansion coefficient than SiC [Table 3.1], a tensile in-plane stress is introduced during the cooling to room temperature.

Heteroepitaxial growth of AlN also leads to high threading dislocation densities. Large efforts have been made in order to reduce the threading dislocations. However, the material quality of heteroepitaxial AlN is still poor, with high densities of threading dislocations, $10^8 - 10^{10} \text{ cm}^{-2}$. On the other hand, homoepitaxial growth is expected to result in AlN layers with superior crystal quality with threading dislocation densities of the same order as the commercial substrates $10^2 - 10^4 \text{ cm}^{-2}$ and low residual strain if the growth is properly initiated. High-performance deep UV LEDs $\lambda < 280 \text{ nm}$ are obtained by MOCVD on high-quality AlN substrates.

Table 3.1 Lattice parameters and thermal properties of commonly used substrates for AlGaN growth. The lattice misfit is defined as $(a_{0\text{Substrate}} - a_{0\text{AlN}})/a_{0\text{AlN}}$ [61].

	structure	a_0 (Å)	c_0 (Å)	lattice misfit with AlN (%)	α_a ($10^{-6}/^\circ\text{C}$)	Thermal conductivity ($\text{Wcm}^{-1}\text{K}^{-1}$)
Si	diamond	3.565 ¹	-	-	3.9 ¹	1.3 ²
Al ₂ O ₃	Rhombohedral	4.759 ¹	12.991 ¹	-13	8.31 ¹	0.25 ³
4H-SiC	Hexagonal	3.080 ¹	10.083 ¹	1	4.75 ¹	4.9 ²
GaN	wurtzite	3.189 ⁴	5.186 ⁴	2.4	5.00 ¹	1.3 ²
AlN	wurtzite	3.112 ⁴	4.981 ⁴	0	5.41 ¹	2.85 ²

¹ Reference [60]

² Reference [62]

³ Reference [63]

⁴ Reference [27]

3.5 Precursors for doping

Both *n* and *p*-type conductive AlGaIn can be obtained by MOCVD by Si and Mg doping, respectively [43]. Silane (SiH_4) [64] and disilane (Si_2H_6) [65] gas diluted in H_2 have been used as efficient Si doping sources for high-Al-content AlGaIn. Si_2H_6 has been shown to decompose at significantly lower temperatures compare to SiH_4 which is of advantage due to less strong temperature dependence of the Si incorporation during GaAs growth [66]. Ge is a well-known donor in GaN [67] and has also been demonstrated as dopant for low-Al-content AlGaIn [68]. Due to the large size of the Ge atom, the incorporation efficiency is lower compared to Si. 1000 times higher flows of GeH_4 was needed to achieve similar doping concentration as with SiH_4 precursor for GaN [67].

Biscyclopentadienyl-magnesium (Cp_2Mg) is frequently used as the Mg doping source. Cp_2Mg is a solid metal-organic precursor. The Mg doping is also associated with memory effects [69,70] which make it challenging to control sharp doping profiles. In this work SiH_4 and Cp_2Mg were used as doping sources.

4 Doping

Wide band-gap semiconductors have very low *intrinsic carrier concentrations* and are therefore expected to act as true insulators at room temperature:

$$n_i = \sqrt{N_c N_v} \exp(-E_G / 2kT), \quad (4.1)$$

where N_c and N_v are the effective density of states in the conduction and valence band, respectively, k is the Boltzmann constant and E_G is the band-gap. However, unintentionally incorporated impurities and native defects, which are present also in the most pure materials, can strongly influence the conductivity of unintentionally doped semiconductors. By reducing the number of electrically active defects, it is possible to control the conductivity by intentionally introducing dopant impurities that incorporate in the crystal lattice. The impurities can form states in the band-gap, which can either be *donors* that donates electrons to the conduction band or *acceptors* that accept electrons from the valence band and thus create a hole in the valence band. The free electrons and holes can easily move and conduct current when an electric field is applied. When the conductivity is dominated by free electrons or holes the semiconductor is referred as *n*-type and *p*-type conductive, respectively. Donors (acceptors) that have an energy level close to the conduction (valence) band are denoted as *shallow* donors (acceptors). The ionization energy (E_d) of shallow dopants is typically in the order of the thermal energy at room temperature, $kT \approx 26$ meV, which results in high free electron and hole concentrations.

For wide band-gap semiconductors it is usually difficult to obtain both *n*- and *p*-type conductivity due to amphoteric defects that limit the maximum number of electrically active and uncompensated dopants [71]. There is also a tendency for intrinsic defects and impurities to form electrically active states in the band gap that affect the conductivity. If these are deep states, only a small fraction are ionized at room temperature leading to low room temperature conductivity or compensation of more shallow states. For high-Al-content AlGa_N and AlN with their remarkably wide band-gaps of up to 6.2 eV, it is truly challenging to control both the *n*-type and *p*-type conductivity. In this chapter the basic properties of doping and important results from the literature are reviewed with the purpose to put our results and work into a relevant context.

4.1 Unintentionally doped AlGa_N

The first step in order to control the doping process is to understand and control the unintentional background doping in AlGa_N. Unintentionally doped GaN is, despite its large band-gap of 3.4 eV, *n*-type conductive even in high purity materials [72]. Typically, incorporation of deep acceptors such as Fe [73] or C [74] is needed in order to render GaN insulating. The nitrogen vacancy (V_N) was originally considered as the main source of the unintentional *n*-type conductivity in GaN [75] and theoretical calculations indeed suggested that V_N acts as a shallow donor for GaN but also that its formation energy was considered too high for V_N to be abundant in high concentrations under normal growth conditions [76]. Instead the *n*-type conductivity of unintentionally doped GaN was attributed to the shallow residual O and Si impurities that were unintentionally incorporated during growth [76].

Oxygen easily reacts with Ga and especially Al and are therefore typically incorporated at high concentrations during growth of AlGa_N [77]. Typically, O is present in form of residual water incorporated during wafer loading or introduced by the carrier or precursor gases. Oxygen can also originate direct from the quartz tube (SiO₂) [48].

In contrast to GaN, unintentionally doped Al_xGa_{1-x}N is normally resistive or insulating at high Al contents [78]. The different behavior compared to GaN was attributed to the O donor that is believed to become a deep donor at Al contents above $x > 0.3$ [79,80] or by the much lower formation energy for cation vacancy related complexes (V_{III}-complexes) that act as deep acceptors and may therefore be abundant in unintentionally AlGa_N and lead to compensation of free carriers [76,81,82]. More recent publications observed that the O impurities improved the conductivity in Si doped Al_{0.6}Ga_{0.4}N [83] and in unintentionally doped Al_{0.67}Ga_{0.33}N for which a donor activation energy of $E_d \sim 90$ meV was measured [84].

Unintentionally doped Al_xGa_{1-x}N ($x > 0.6$) layers grown in this work, have a low conductivity which is not measurable (donor concentration $< 10^{15}$ - 10^{16}). Both the O and C concentrations in these layers were typical at the detection limit ($\sim 2 \times 10^{17}$ cm⁻³) as measured by secondary ion mass spectroscopy (SIMS). These are good starting conditions for intentional doping.

4.2 Si doping of AlGa_N

A simple hydrogenic model can describe the shallow substitutional donor and its properties where the ionization energy of the donor impurity (E_{d0}) can be calculated by [38]:

$$E_{d0} = 13.6 \frac{m_e^* / m_0}{\epsilon_r^2} \text{ eV}. \quad (4.2)$$

Here m_0^* is the effective mass of the free electron in the conduction band and ϵ_r is the relative dielectric constant. Thus the ionization energy of the donor reminds of the ionization energy of the hydrogen atom (~ 13.6 eV) which is then corrected by the effective mass of the electron and the reduced Coulomb interaction introduced by the dielectric medium.

At increased donor concentrations the donor impurity potential starts to overlap and donor ionization, E_d decreases. At a critical doping concentration ($N_{critical}$) the material undergoes a transition from insulator-to-metal which is also called the Mott transition [85]. This implies that the impurity binding energy vanishes ($E_d = 0$) and the electrons are free to move at any temperature. For shallow donors this transition can be expressed as,

$$N_{critical} \approx \left(\frac{0.25}{a_B^*} \right)^3 \approx \left(\frac{4.72 \times 10^7 m_e^* / m_0}{\epsilon_r} \right)^3 \text{ cm}^{-3}, \quad (4.3)$$

where a_B is the Bohr radius of the donor in the ground state given by $a_B^* = 0.53 \epsilon_r / (m_e^* / m_0)$ Å. The reduced E_d with increased donor concentration (N_D) can be expressed by:

$$E_d = E_{d0} \left(1 - (N_D / N_{critical})^{1/3} \right) \quad (4.4)$$

The $N_{critical}$ and E_{d0} for shallow substitutional donors for AlN and GaN calculated from Eq. (4.2-4.3) are given in Table 4.1.

For high doping levels the activation energy is expected to vanish due to the insulator-metal transition at doping concentrations of $[Si]=N_{critical} \approx mid 10^{18} \text{ cm}^{-3}$ for AlGaN [Table 4.1] which is in good agreement with published data for GaN and low Al-content AlGaN [86,87]. For non-degenerate ($N_D < N_{Critical}$) semiconductors the electron concentration in the conduction band can be roughly estimated using the following expression [38]:

$$n \approx \sqrt{\frac{N_D N_C}{2}} \exp\left(\frac{-E_d}{2kT}\right) \quad (4.5)$$

For GaN, n -type conductivity is easily obtained by substituting, Ga with Si (Si_{Ga}) [67], Ge (Ge_{Ga}) [67] or Se (Se_{Ga}) [92] or substituting N with O (O_N) [93]. All these donors are found to form shallow, hydrogen-like, donors with low activation energy in the range of $\sim 30 \text{ meV}$ which is in good agreement with effective mass theory. Since Si easily incorporates into AlGaN it is often used as the n -type dopant in this and other III-V alloy systems.

We note that this simple hydrogenic model described above in Eq. (4.2-4.3) gives values that are close to the values experimentally measured by electrical transport measurements (measured in low doped material) for Si doped GaN but not for AlN [Table 4.1] indicating that the Si may not be a simple substitutional shallow donor for AlN, a topic which is treated in **paper 4**. We found that for an Al content up to $x \sim 0.8$, Si behaves similar to a shallow donor and can be described to a reasonable agreement with equation (Eq. (4.3-4.5)) [87].

By using the photoluminescence spectroscopy the Si donor ionization energy in GaN and AlN was determined to $\sim 30 \text{ meV}$ [90] and $\sim 63 \text{ meV}$ [91], respectively, which is in close agreement with effective mass theory. Taking into account the reduction of the donor ionization energy due to high doping effects Eq. (3), such shallow doping levels are expected to result in efficient Si doping in the entire AlGaN compositional range.

Table 4.1 Basic electronic properties of GaN and AlN and the donor ionization energy determined from effective-mass theory (EMT) and electrical transport measurement by Hall.

	n_i (cm^{-3})	ϵ_r	m_e^* / m_0	$N_{critical}$ (cm^{-3})	$E_d \text{ Si}$ EMT (meV)	$E_d \text{ Si}$ Hall (meV)
GaN	$\sim 10^{-10 \text{ a)}$	8.9 a)	0.20 b)	$1 \times 10^{18 \text{ c)}$	$\sim 34 \text{ c)}$	30.7 d)
AlN	$\sim 10^{-33 \text{ a)}$	8.5 a)	0.32 b)	$6 \times 10^{18 \text{ c)}$	$\sim 60 \text{ c)}$	282 e)

^{a)} Reference [88]

^{b)} Reference [89]

^{c)} Reference [Eq. (4.3)]

^{d)} Reference [90]

^{e)} Reference [91]

However, electrical transport measurements of Si doped AlGa_xN layers show significantly reduced conductivity as the Al composition increases above 0.8 [64,94–96]. The resistivity in high-Al-content AlGa_xN was found to increase from 0.026 Ω cm to 2.62 Ω cm as the Al-content increased from $x \sim 0.82$ to $x \sim 0.95$ [96]. It was shown that the Si activation energy drastically increased and activation energies between 282-312 meV were determined for low Si doped AlN assuming a single shallow donor state [97]. The reason for this behavior has been controversial. Despite the large increase in Si activation energy at high Al contents it was suggested that Si acts as shallow donor in the entire compositional range and that the observed decrease in conductivity was also related to unintentional O and C doping [94,95] and formation of cation vacancies (V_{III}) [76].

Another explanation for the drastic decrease in n-type conductivity is that Si and O transform to a deep donor at high-Al-content AlGa_xN. Deep donors in other III-V semiconductor material systems, such as Al_xGa_{1-x}As doped with Si, have been extensively studied [98]. Deep metastable donor states are observed in Al_xGa_{1-x}As:Si at alloy compositions between $0.2 < x < 0.8$, which results in properties characterized by a high degree of self-compensation and persistent photo-conductivity at low temperatures. Similar characteristics were reported for Al_xGa_{1-x}N with an alloy composition above $x > 0.52$ [78,99]. Based on theoretical calculations a widely accepted model that explains the experimental observations has been proposed for AlGaAs [100], where the shallow substitutional donor configuration coexist with a distorted donor configuration. The distorted donor, referred as a *DX-center*, is formed by breaking one of the tetrahedral bonds and trapping of one additional electron whereby it undergoes a large lattice relaxation. The name “DX” was chosen since it was postulated that the defect was related to the donor D together with another unknown constituent X as the DX-center was described for the first time [101].

The formation of the DX-center can be described by [103]:

where d_0 is shallow donor state and U is the correlation energy that mainly contain contribution from the Coulombic repulsion between the captured electrons and the lattice distortion energy.

Figure 4.1 Schematic view of (a) the substitutional Si donor, (b) Si DX₁ configuration ($U = -0.27$ eV) and (c) Si DX₂ ($U = -0.06$ eV) [102].

If U is negative (thus when the Coulombic repulsion energy is lower than the lattice relaxation) the DX-center becomes stable and the center is therefore often referred as a *negative- U center* [Figure 4.1]. The properties of a shallow to DX-center transition via a large lattice relaxation can be illustrated by a configuration coordinate diagram shown in Figure 4.2 [78].

Figure 4.2 Configuration coordinate diagram describing the behavior of a DX center for Si doped AlN [78]. E_d is the shallow donor ionization energy, E_A is the thermal activation energy of the Si donor and E_{photon} is the photoionization energy.

Recent *ab initio* calculations suggest that Si, O, and Ge form stable DX-centers in AlGaIn [102,104]. It was found that Si was the most efficient donor forming a DX-center first at Al-contents above $x \approx 0.94$ [104]. In **paper 4** a drastic increase in the activation energy of the Si donor was observed for AlGaIn with high aluminum contents ($x > 0.8$). It was suggested that the DX^- center becomes drastically deeper at this alloy compositions. Below this alloy composition efficient Si doping was obtained.

4.3 Mg doping of AlGaIn

Mg is the most widely used dopant for *p*-type doping and so far the only acceptor that was proven to produce controlled *p*-type conductive AlGaIn. Recent theoretical calculations suggest that Mg is the shallowest acceptor of the group II elements [105]. However, Mg has a rather high activation energy, about 200 meV for GaN [106] and $\sim 500\text{--}630$ meV for AlN [10,107], which results in a low doping efficiency. In order to obtain appropriate *p*-type conductivity a very high Mg doping concentration is needed. In AlGaIn there are about $\sim 5 \times 10^{22} \text{ cm}^{-3}$ group III lattice sites available, giving a fundamental doping limit in the order

Table 4.2 Results obtain for Mg doping of high-Al-content $\text{Al}_x\text{Ga}_{1-x}\text{N}$ in this work compared to the reported results.

Al _x Ga _{1-x} N:Mg x	[Mg] (cm ⁻³)	Resistivity (Ω cm)		Reference
		As-grown	Annealed	
This work:				
0.60	3×10 ¹⁹	>10 ⁷	60	[paper5]
0.70	2×10 ¹⁹	>10 ⁷	2 000	
0.85	2×10 ¹⁹	>10 ⁷	7 000	
Literature:				
0	2×10 ²⁰		1	[106]
0.45	2×10 ¹⁹		8	[69]
0.70	3×10 ¹⁹		47	[114]
0.70	1×10 ²⁰		100 000	[112]
1.00	2×10 ¹⁹		~10 ⁷	[10,115]

of $\sim 10^{20} 10^{21} \text{ cm}^{-3}$ before alloying. It was suggested that the doping is limited by the solubility and the formation of Mg_3N_2 [76]. A drastic decrease in carrier concentration and morphological degradation was observed at high Mg concentrations ($[\text{Mg}] \sim 2 \times 10^{20} \text{ cm}^{-3}$) for GaN a and $\text{Al}_{0.69}\text{Ga}_{0.31}\text{N}$ ($[\text{Mg}] > 1 \times 10^{19} \text{ cm}^{-3}$) [106,108].

As-grown Mg doped AlGa_N is highly resistive since H forms a neutral complex together with Mg causing passivation of the Mg acceptors [34,109,110]. H is always present in MOCVD growth as it is used as the H_2 carrier gas and in the precursors (TMA, TMG, NH_3). Annealing in N_2 or O_2 ambient was found to be an effective method to reduce the H by out-diffusion and to activate the Mg acceptors and achieve p-type conductive GaN and AlN [97,111].

High Al-content p-type conductive $\text{Al}_x\text{Ga}_{1-x}\text{N}$ and AlN using Mg have been reported [10,108,69,112–114]. At Al contents of $x \sim 0.45$ a low resistivity of $8 \Omega\text{ cm}$ was obtained [69] at room temperature whereas at higher Al-content $x \sim 0.7$ the resistivity increased to $100\,000 \Omega\text{ cm}$ [112]. Recently a low resistivity of $47 \Omega\text{ cm}$ was reported for $\text{Al}_{0.7}\text{Ga}_{0.3}\text{N}$ [114] indicating that there is a very narrow growth window for p-type doping at this Al contents. The narrow growth window may be explained either by the formation energy of V_N which is expected to be reduced in p-type materials [110], by unintentionally incorporated Si and O donors or by over doping [108].

In Table 4.2 our results from the p-type doping are shown in comparison to the reported values. We obtained a resistivity of $\sim 7 \text{ k}\Omega\text{ cm}$ after *in-situ* annealing in nitrogen at 900°C and a pressure of 700 mbar. In Figure 4.3 the H concentration in the sample before and after annealing, as measured by SIMS is shown. After annealing the hydrogen decreased by a factor of 5 to $[\text{H}] \sim 5 \times 10^{17} \text{ cm}^{-3}$ which is sufficient to obtain measureable conductivity. The growth and measurement details are reported in **paper 5**.

Figure 4.3 SIMS depth profile of Mg doped $\text{Al}_{0.85}\text{Ga}_{0.15}\text{N}$ before and after annealing. The Mg concentration was unchanged after the annealing step while the H concentration reduced by a factor of ~ 5 . The annealing was performed inside the MOCVD reactor at a temperature of 900°C and in N_2 ambient with a pressure of 700 mbar.

5 Characterization

5.1 X-ray diffraction

X-ray diffraction (XRD) is a powerful tool to access structural information such as thickness, alloy composition, residual strain, and defect structure, of epitaxial films and device structures [28]. In addition, XRD is a non-destructive characterization technique that does not require any special sample preparation, which makes it convenient to use for fast feedback characterization to control the growth process. These factors have made this technique very popular and widely used for structural characterization of epitaxial III-nitrides.

X-ray radiation (f.e. $\lambda_{\text{Cu}\alpha 1} \approx 1.5406 \text{ \AA}$ in our setup) has a wavelength that is similar to the periodic lattice spacing in crystals of a few Ångström which make it possible to measure the crystallographic structure in crystals. Elastic scattering of the X-rays by the strongly bond core electrons gives rise to diffraction effects. Constructive interference for a set of lattice planes (hkl) occurs when Bragg's law is fulfilled:

$$n\lambda = 2d_{hkl} \sin(\theta) \quad (5.1)$$

where n is a integer, λ wavelength of the incident X-ray, d_{hkl} is the interplanar spacing between two adjacent planes (hkl) in the crystal lattice and θ is the angle between the incident X-ray and the measured plane. The AlGaN and AlN layers were studied by a high resolution (HR) triple-axis diffractometer using either a hybrid mirror or a 4-bounce monochromator as primary optics and a three-bounce analyzer crystal giving a resolution in the order of $\sim 0.003^\circ$. In HRXRD the sample can be rotated around the 2θ , ω , ϕ , and χ angles [Figure 5.1] to access certain planes.

Figure 5.1 Schematic of the rotational geometry of the sample where ω is the angle formed between the sample surface and the incident X-ray and 2θ is the angle between the incident and scattered X-ray. For symmetric measurements $\theta = \omega$.

In this work XRD was used to determine the residual strain (**paper 2** and **3**), alloy composition (**paper 2**) and the lattice parameters and structural quality (**paper 7**).

Lattice parameters and strain

In wurtzite crystal structures the lattice spacing d_{hkl} between two adjacent planes (hkl), is given by [116,117]:

$$d_{hkl} = \sqrt{\frac{1}{(h^2 + k^2 + hk)\frac{4}{3a^2} + \frac{l^2}{c^2}}}, \quad (5.2)$$

The lattice parameters, a and c , can be determined by measuring $2\theta/\omega$ scans of at least one symmetric ($\theta = \omega$) and one asymmetric ($\theta \neq \omega$) reflection. From the symmetric lattice spacing d_{hkl} determined from Eq. (5.1) the c lattice parameter can be found using Eq. (5.2). Then by using the determined c lattice parameter and the lattice spacing of the asymmetric reflection one can determine the a lattice parameter. Since the error in the c lattice parameter propagates to the determined a lattice parameter, the precision of the determined a lattice parameter is worse than for the c lattice parameter.

For high quality crystals with sharp peaks the precision of the measurements is in the order of ~ 0.0001 Å for the lattice parameters. Using more sophisticated methods this precision can be further improved by about one order [116,117]. With such high precision, it is possible to study the effect of doping and stoichiometry on the lattice parameters. However, for heteroepitaxial layers the lattice parameters slightly vary over the layer thickness, which makes it not possible to obtain lattice parameters to that precision. After extraction of the lattice parameter values, the in-plane and out-of-plane strain can then be determined directly from these:

$$\varepsilon_{xx} \equiv \frac{a - a_0}{a_0}, \quad \varepsilon_{zz} \equiv \frac{c - c_0}{c_0}, \quad (5.3)$$

where a_0 and c_0 is the relaxed lattice parameters. The data for the lattice parameters varies in the literature which causes an error in the determined strain as discussed in **paper 7**.

The composition of AlGa_N can also be estimated from the measured lattice parameters. Since large strains are present due to heteroepitaxial growth and thermal lattice mismatches it is necessary to take the strain into account when the composition is determined. As a first approximation it is assuming that the layers are biaxial strained (see chapter 2),

$$\frac{c - c_0(x)}{c_0(x)} = R_B(x) \frac{a - a_0(x)}{a_0(x)} \quad (5.4)$$

where $a_0(x)$, $c_0(x)$, and $R_B(x)$ are the relaxed lattice parameters and biaxial relaxation coefficient ($= -2C_{13}(x)/C_{33}(x)$) for Al_xGa_{1-x}N. It is further assumed that the relaxed lattice parameters and the biaxial relaxation coefficient, R_B , linearly vary between GaN and AlN:

$$a_0(x) = x a_0^{AlN} + (1 - x) a_0^{GaN} \quad (5.5)$$

$$c_0(x) = xc_0^{AlN} + (1-x)c_0^{GaN} \quad (5.6)$$

$$R_B(x) = xR_B^{AlN} + (1-x)R_B^{GaN} \quad (5.7)$$

Since the Eq. (5.4) is cubic, solving it gives three different solutions, where one of them gives a value between $0 \leq x \leq 1$ which is the alloy composition, x . The relaxed lattice parameters for $Al_xGa_{1-x}N$, can then be calculated from in Eq. (5.5) and (5.6) to determine the relaxed lattice parameters of $Al_xGa_{1-x}N$ and thereby the strain Eq. (5.3).

Structural properties

To study the structural properties the broadening of the diffraction peaks can be analyzed [118,119]. The mosaic block model is used where the thin film is assume to be made of crystal blocks that are slightly misoriented relative to each other and are characterized by a vertical and horizontal coherence length and a tilt and twist angle [119].

The broadening of the ω rocking curve is mainly caused by a finite crystallite size as well as the tilt and twist of the crystallites and can be used as a figure of merit for the crystal quality [120]. Twist will cause distortion of the (h00) lattice planes that are perpendicular to the c -axis. Due to the geometry of these planes, they are not easily accessible and the twist must be extracted by extrapolation using several asymmetric reflections at lower angle values down to $\chi=90^\circ$. For layers with randomly distributed dislocations the screw (N_s) and (N_E) edge dislocation density can then be estimated by [28]:

$$N_s = \frac{\beta_s^2}{4.35b_s^2} \quad (5.8)$$

$$N_E = \frac{\beta_E^2}{4.35b_E^2} \quad (5.9)$$

where $|b_s|$ and $|b_E|$ are the length of the Burgers vectors for screw ($|b_s|=c$) and edge ($|b_E|=a$) dislocations, respectively.

(4)

5.2 Atomic force microscopy

Scanning probe microscopy (SPM) is a surface sensitive technique that generates images with details in the nanometer scale by scanning the specimen with a probe and measuring the surface-probe interaction. Common types of SPM measure magnetic, electrical and mechanical probe-surface interactions.

In this work, atomic force microscopy (AFM) was used to study the surface topography of substrates and epitaxial films by measuring the force interaction between the tip and the surface. AFM works for both conductive and insulating samples, in contrast to many other technics, which is an advantage when insulating wide band-gap semiconductors, such as AlN, are studied.

AFM can operate in three different modes: (i) contact mode, where the tip is in physical contact with the surface and a strong force acts on the tip, (ii) non-contact mode, where the tip is not in contact with the surface but where the cantilever, vibrating above the surface,

interacts with long range forces, and (iii) tapping mode where the tip is oscillating above the surface and only lightly touches the surface at the lowest point of its oscillation. All measurements in this work were performed in tapping mode.

In tapping mode, the oscillation amplitude of the cantilever is kept at a constant setpoint value (20-100 nm) by an electronic feedback loop that adjusts and records the vertical position of the cantilever as it is moved over the surface. The small amplitude changes are detected by a laser beam that is reflected on the cantilever. Then the height of the scanner is recorded as the tip scans the surface and forms the image.

The AFM measurements were performed using a Dimension 3100 scanning probe microscope from Veeco. The vertical resolution is generally very high for AFM measurements and with the equipment used in this work the vertical resolution was limited to about 0.3 to 1 Å due to the background noise of the system. Thus, it is no problem to measure step height of one bilayer of AlN (~2.5 Å). The lateral resolution is in general worse and is strongly dependent by the shape of the tip. In this work tips with a nominal tip radius of curvature of 5-10 nm have been used, which limit the resolution to an order of ~1-5 nm.

5.3 Scanning electron microscopy and cathodoluminescence

Scanning electron microscopy (SEM) is a common technique for studies of the surface topography of a variety of conductive metals or semiconductors. Electrons are accelerated to energies between ~1-30 keV and bombard the sample surface under high vacuum conditions. The electron beam is scanned over the sample surface and the electron interaction with the specimen at different points of the surface is detected. As the beam of primary electrons hits the surface, the incident electrons lose their energy by different processes that generate a number of different signals, such as secondary electrons, X-rays and cathodoluminescence (CL), which can be studied by different detectors that are attached to the SEM chamber. The secondary electrons have a rather low energy (<50 eV) and thus it is only the secondary electrons generated very close to the surface that can escape and be detected. Since the secondary electrons are generated at the subsurface region they can be used to create an image of the surface topography. The CL signal on the other hand is generated as the primary electrons penetrate the material and generate electron-hole pairs that can recombine and generate photons which are detected.

CL imaging and spectroscopy can provide valuable information about the luminescence properties from semiconductor samples. Since the secondary electrons are recorded simultaneously, complementary information about the surface morphology can be obtained. The CL images can be recorded either at a certain emission wavelength selected by a grating, which is referred to as monochromatic imaging or by letting all light from the sample pass straight through to the detector and form a panchromatic image of the sample. An excellent example of the strength of CL imaging in combination with topographic imaging was demonstrated by Elsner et al. [121], where a strong correlation between quenched luminescence and surface terminated threading dislocations was shown.

By varying the acceleration voltage, the spatial resolution of the CL image changes drastically as calculated using Monte Carlo simulation software [122] as can be seen in Figure 5.2. A large acceleration voltage will spread the electrons over a large volume in the material, while low accelerating voltages give good spatial resolution. The change in acceleration voltage also

makes it possible to study depth resolved CL by changing the acceleration voltage. If a small acceleration voltage of 5 kV is applied the CL measurements become very surface sensitive and with a good spatial resolution compare to an acceleration voltage of 10 kV. In this work CL-SEM was used to study the luminescence properties by panchromatic imaging or by CL spectroscopy (paper 2, 6 and 7).

Figure 5.2 Monte Carlo simulation [122] of the electron propagation in AlN thin films using an electron acceleration voltage of 5 and 10 kV. The excitation volume becomes significantly larger at higher acceleration voltages, which results in a high CL intensity but a reduced lateral resolution in the CL image.

5.4 Electrical characterization

Capacitance-Voltage profiling

Capacitance-Voltage (C-V) profiling can be used to determine the net donor ($N_D - N_A$) or net acceptor ($N_A - N_D$) concentration as a function of the layer depth. A metal is put in contact with a semiconductor surface in order to form a Schottky barrier in the underlying epilayer where the free charge is depleted. The net donor concentration is determine by applying a reverse dc voltage and a small ac voltage test signal (~ 100 mV), which operates at frequency between 100 Hz up to 1Mhz, in order to change the width of the depleted barrier. In order to use the technique for fast growth feedback, a liquid mercury probe was used to form the Schottky barrier while solid metallic contacts were used for temperature dependent measurements. The net donor concentration and the depth profile are given by [123]:

$$N_D - N_A = \frac{-2}{q\epsilon_0\epsilon_r A^2 d(C^{-2}) / dV} \quad (5.10)$$

$$x_d = \frac{\epsilon_0\epsilon_r A}{C} \quad (5.11)$$

where $\epsilon_0\epsilon_r$ is the dielectric permittivity of the layer, A is the area of the Schottky contact, C is the capacitance, q is the elementary charge and x_d is the depth of the depletion region. To determine the $N_A - N_D$ concentration the sign in Eq. (5.10) is changed.

The local slope of the $C^{-2} - V$ curve gives the net doping concentration [Eq. (5.10)]. If the donors or acceptors are deep they may not be able to respond to the test signal at low

temperatures. The emission time, τ , for the electrons to be emitted to the conduction band is given by [124]:

$$\tau_e = \frac{\exp(E_C - E_T)}{\sigma v_{th} N_C} \quad (5.12)$$

where $E_C - E_T$ is the energy between the conduction band and the trap level, σ is the capture cross section and v_{th} it the thermal velocity. By reducing the frequency of the test signal the electrons have more time to be emitted to the conduction band. It is also possible to enhance the electron emission by increasing the temperature.

Transport measurements

Measurements of the Hall effect can be used in order to determine the transport properties in semiconductors i.e. the carrier concentration (n or p), mobility (μ_e or μ_h) and type of carriers (n - or p -type). The carrier concentration is determined by measuring the Hall voltage formed when an external magnetic field $\mathbf{B}$ is applied perpendicular to the current flux. The carriers are deflected due to the Lorentz force induced by the magnetic field. The carrier concentration, resistivity, and mobility are determined by:

$$n \approx \frac{-IB}{qV_H t}, p \approx \frac{IB}{qV_H t} \quad (5.13)$$

$$\rho = \frac{1}{q(n\mu_e + p\mu_h)} \quad (5.14)$$

$$\mu_e \approx \frac{1}{qn\rho}, \mu_h \approx \frac{1}{qp\rho} \quad (5.15)$$

Typically, metal contacts are deposited onto diced test pieces from the wafer to measure the Hall effect in semiconductors, a process that destroys the sample for other measurements and is time consuming. It also becomes increasingly more difficult to obtain ohmic contacts on AlGaIn layers with increasing Al contents [125]. Contactless measurements not only solve many of the described problems but also allow fast process feedback. In this work a microwave based Hall-probe technique was used to determine the carrier concentration, resistivity and mobility of the carriers. A circular waveguide directs microwaves (10 GHz) perpendicular to the sample surface. The system measures interaction between the microwave and sample by recording the reflected power and polarization of the microwave at different magnetic field strength to determine the transport properties of the sample [126,127]. This technique requires that the layers are grown on semi-insulating substrates to determine electrical properties of the film and avoid disturbances from carriers present in the wafer. Reproducible results were obtained that were in good agreement with the other techniques used in this work such as C-V and eddy current resistivity measurements.

5.5 Electron paramagnetic resonance

Electron paramagnetic resonance (EPR) is known to be a powerful technique for defect characterization in semiconductors. EPR provides information on the spin multiplicity, symmetry and hyperfine interaction, allowing a conclusive identification of defects. For impurities with nuclear spin $I \neq 0$, chemical identification is possible based on the observed self-hyperfine structure. In many cases, energy levels of the studied defect can be revealed by using photoexcitation, often called photo-induced EPR or photo-EPR [128], or by monitoring the temperature dependence of the EPR signal [129,130]

EPR can be applied for defects that have an unpaired electron spin $S \neq 0$. Under an external magnetic field, the interaction between the electron spin S and external magnetic field splits the energy levels by the electronic Zeeman interaction into $2S+1$ levels. These levels can be further split by hyperfine interaction between the electron spin S and a nuclear spin I (if the nuclear spins of the impurity and/or neighbouring atoms are different from zero). In the case of a single shallow donor impurity, one unpaired electron gives rise to $S=1/2$ and two electronic Zeeman levels corresponding to the magnetic quantum numbers $M_S = \pm 1/2$ will be observed. The splitting between these two levels is proportional to the external magnetic field strength and the Landé factor g , which can be isotropic or a tensor depending on the symmetry of the defect. Transitions between the levels can be conveniently induced by microwave radiation. The resonance condition occurs when the photon energy of microwave $h\nu$ equal to the splitting between the levels.

$$h\nu = \mu_B g B \quad (5.16)$$

here μ_B is the Bohr magneton (5.79×10^{-5} eV/T) and B the magnetic field strength. In a hexagonal lattice such as AlN, g is usually a tensor. For a single shallow donor in GaN, AlN or their alloys AlGaIn, the highest symmetry is axial (C_{3v}). The g -factor is characteristic for each impurity or defect and can be used for defect characterization. The intensity of the EPR signal is proportional to the number of spins on the neutral donor state and can be used to estimate the donor concentration.

Silicon is predicted to undergo a transition from a shallow donor in GaN to a DX center in high-Al-content AlGaIn. Such transition occurs when the Coulombic interaction between the Si donor and its surrounding environment causes a large lattice relaxation that breaks a Si-N bond, putting Si slightly off the substitutional site. In such a case, the neutral Si donor prefers capturing another electron to relax to a lower-lying negatively charged state or the DX^- state, following the process: $2d^0 \rightarrow DX^- + d^+$ (d^+ is the ionized state) [103,131]. In this work, EPR was used to estimate the Si donor concentration and to study the electronic structure of the Si donor/DX center in AlGaIn.

EPR measurements were performed using an X-band ($\nu \sim 9.4$ GHz) E500 Bruker EPR spectrometer that is equipped with a continuous Helium-flow cryostat, allowing a regulation of the sample temperature from 4 to 295 K. In the photo-EPR experiments, a halogen or xenon lamp and appropriate optical filters are used as excitation source.

5.6 SIMS

Residual impurities that are unintentionally incorporated in the layers during the growth can significantly affect the electronic properties. Therefore it is important to know the amount of trace impurities that incorporate under different growth conditions in order to control the incorporation. Secondary ion mass spectrometry (SIMS) depth profiling is a powerful technique that can be used to detect very small concentrations of residual impurities as well as intentional doping profiles. SIMS uses ions to sputter the material and the resulting charged secondary ions from the material are detected and analyzed by a mass spectrometer.

SIMS measurements were performed by Evans Analytical Group in order to measure the doping and residual impurity concentrations as well as the alloy composition. The detection limit for oxygen and carbon was typically in the order of $\sim 2 \times 10^{17} \text{ cm}^{-3}$.

6 References

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Part II – Papers

Part II

Papers

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