Homo- and Hetero-epitaxial Growth of Gallium Nitride by Metalorganic Chemical Vapour Deposition

Andy Zauner

Born in Mönchengladbach, Germany, September 1970, Andy Zauner received his diploma in senior general secondary education (HAVO) at the Scholenleenheem Jezuolen in Venray, the Netherlands, in June 1988. He obtained his pre-university (VWO) degree at the same institute in 1990.

In the same year he started studying chemistry at the University of Nijmegen, the Netherlands. In 1996, he received his university degree equivalent to a Master of Science abroad. For his M.Sc. thesis, his main research subject was Solid State Chemistry in Nijmegen and his additional subject was Inorganic Chemistry and Catalysis at the Eindhoven Technical University.

His enthusiasm in science encouraged him to pursue in research as a Ph.D. student at the Physics Department of Experimental Solid State Physics III in January 1997. There he investigated the metalorganic chemical vapour deposition (MOCVD) growth of gallium nitride, which is presented in this thesis.

Currently he works as a researcher on Ferro-electric materials grown by MOCVD.
Homo- and Hetero-epitaxial Growth of Gallium Nitride by Metalorganic Chemical Vapour Deposition
Homo- and Hetero-epitaxial Growth of Gallium Nitride by Metalorganic Chemical Vapour Deposition

een wetenschappelijke proeve op het gebied van de Natuurwetenschappen

Proefschrift

ter verkrijging van de graad van doctor aan de Katholieke Universiteit Nijmegen, volgens besluit van het College van Decanen in het openbaar te verdedigen op woensdag 21 maart 2001 des namiddags om 3.30 uur precies

door

Andreas Rudolf Antonius Zauner

geboren op 15 september 1970 te Mönchengladbach
Promotor: Prof. Dr. P.K. Larsen
Co-promotor: Dr. P.R. Hageman

Manuscriptcommissie: Prof. Dr. J.J. ter Meulen
Prof. Dr. E. Vlieg
Dr. M.R. Leys, Technische Universiteit Eindhoven

The work described in this thesis was financially supported by the Dutch Technology Foundation (STW).
to my parents
## Contents

1 Introduction

1.1 Historical background of GaN ............................................. 1
1.2 Material properties of GaN .................................................. 2
1.3 MOCVD ................................................................. 6
1.4 This thesis ............................................................. 8
References ................................................................. 11

2 Temperature dependent morphology transition of GaN films

2.1 Introduction ............................................................. 14
2.2 Experimental ............................................................ 14
2.3 Results and discussion ................................................... 15
2.4 Conclusions ............................................................. 22
References ................................................................. 22

3 The effect of Si doping on the properties of GaN films

3.1 Introduction ............................................................. 26
3.2 Experimental procedure .................................................. 26
3.3 Results and discussion ................................................... 27
3.4 Conclusions ............................................................. 36
References ................................................................. 36

4 Inversion Domain Nucleation in homo-epitaxial GaN

4.1 Introduction ............................................................. 40
4.2 Experimental ............................................................ 40
4.3 Results and discussion ................................................... 41
4.4 Conclusions ............................................................. 49
References ................................................................. 49

vii
5 Determination of polarity of GaN cross-section TEM specimens using quantitative electron diffraction 53
5.1 Introduction .............................................. 54
5.2 Experimental procedure ............................... 55
5.3 Simulations .............................................. 56
5.4 Results and discussion ............................... 57
5.5 Conclusions .............................................. 59
References .............................................. 59

6 Homo-epitaxial GaN growth on exact and misoriented single crystals: suppression of hillock formation 63
6.1 Introduction .............................................. 64
6.2 Experimental .............................................. 64
6.3 Results and discussion ............................... 65
   6.3.1 Surface morphology as a function of substrate misorientation .............................................. 65
   6.3.2 Mechanism for hillock development and overgrowth ......................................................... 71
   6.3.3 Photoluminescence properties versus misorientation ......................................................... 77
6.4 Conclusions .............................................. 79
References .............................................. 79

7 Homo-epitaxial growth on the N-face of GaN single crystals: the influence of the misorientation on the surface morphology 83
7.1 Introduction .............................................. 84
7.2 Experimental procedure ............................... 84
7.3 Results and discussion ............................... 85
   7.3.1 Exact orientation .............................................. 85
   7.3.2 Misoriented substrates .............................................. 88
7.4 Conclusions .............................................. 94
References .............................................. 95

8 Photoluminescence study of homo-epitaxial films grown on exact and misoriented single crystal substrates 97
8.1 Introduction .............................................. 98
8.2 Experimental .............................................. 98
8.3 Results and discussion ............................... 99
8.4 Conclusions .............................................. 105
References .............................................. 106
9 Spectroscopic Ellipsometry on GaN: Comparison Between Hetero-epitaxial Layers and Bulk Crystals 109
  9.1 Introduction .................................................. 110
  9.2 Experimental .................................................. 111
  9.3 Results and discussion .................................... 112
  9.4 Conclusions .................................................. 116
  References ....................................................... 116

Summary 119

Samenvatting 123

List of Publications 127

Dankwoord 131

Curriculum Vitae Inside cover
Chapter 1

Introduction

1.1 Historical background of GaN

In 1932 Gallic Nitride, as gallium nitride was called when it was firstly synthesised by W.C. Johnson et al. [1], was prepared by the action of ammonia gas on metallic gallium at high temperatures. Already at that time, the gallium nitride (GaN) powder was found to be stable at high temperatures (800°C) and resistant to dilute and concentrated solutions of HCl, HF, and HNO₃. The material prepared according to this method, a white-grey powder, was the basis for the first optical and electrical measurements on GaN and showed band-edge and yellow luminescence (≈ 2.2-2.3 eV) behaviour [2, 3]. Most of the early work on GaN describes the preparation and properties of polycrystalline deposits, prepared by the reaction of NH₃ with Ga, Li₃GaN₂, Ga₂O₃, or GaP [1, 4-7].

In 1960 single crystalline GaN material was obtained with a quit similar technique as was used by Johnson et al. in 1932, and resulted in small hexagonal needle shaped crystals with a length of 1-5 mm and a thickness of 10-30 μm [3]. Epitaxial growth of large area GaN layers on sapphire was realised in 1969 by Maruska and Tietjen, using hydride vapour phase epitaxy (HVPE) [8]. In all the early samples the concentration of electrons due to background doping was very large. Residual impurities like oxygen, silicon, and intrinsic defects were presumed to give rise to the background n-type conductivity [9]. The availability of large area films gave an impulse to GaN research. A first blue GaN LED (m-i-n) was fabricated by Pankove et al. in 1972 [10]. Stimulated emission from small GaN crystals was first observed at 2K by Dingle et al. in 1971 [11]. However, the large
n-type background concentration, the inability to dope GaN p-type, the difficulties in making good ohmic contacts, and the lack of good substrate material hampered the progress on research in III-nitrides.

The beginning of the growth of good quality epilayers was made by Yoshida et al. [12] in 1983, more than a decade later. It was shown that the use of a two-step growth process, an AlN layer was deposited between the GaN film and the sapphire substrate, improves the quality of the film. The two-step method was investigated and perfected by Akasaki, Amano and co-workers in 1988/1989 [13,14]. Amano et al. were the first to obtain p-type conductivity in GaN [15], on the basis of these results the first p-n junction GaN LED was fabricated in 1989. By the mid 1990s so much knowledge and experience in technology was achieved that there was a remarkable rapid progress in the realisation of devices. Nakamura and his colleagues from Nichia Chemical Industries brought blue and green LEDs to a level of commercialisation [16]. Injection lasers were first demonstrated in 1995 by Akasaki et al. [17]. Nakamura and collaborators reported pulsed laser diode activity in 1996 [18], followed by improvements which resulted in a room temperature CW laser with more than 10000 h lifetime in 1999 [19,20].

At the same time GaN-based FETs were fabricated on both sapphire and SiC substrates. A lot of progress is achieved within this electronic device area. The electronic side of GaN applications, microwave power and ultra-high power switches, enjoys an increasing interest of the GaN research community.

The large number of publications that appeared about III-nitrides, over ten thousand articles in the last five years, indicates the enormous interest in this field.

### 1.2 Material properties of GaN

Group III-nitrides have been considered a promising system for semiconductor device applications since 1969. The III-nitrides, gallium nitride (GaN), aluminium nitride (AlN), and indium nitride (InN) are candidate materials for opto-electronic applications in the blue-UV region of the optical spectrum and for high temperature and high power transistors. The band gaps of the hexagonal wurtzite phase III-nitrides are large and direct and range from 1.9 eV for InN and 3.4 eV for GaN to 6.2 eV for AlN. InN, GaN, and AlN form a continuous alloy system which, in principal, allows
Figure 1.1: Band gap of hexagonal InN, GaN, and AlN and their alloys versus lattice constant $a_0$. The bowing parameters to calculate the band gap of alloys were obtained from references [21–23]. Additionally the lattice constant of sapphire, with a corundum structure, is plotted as a dotted line.

The tuning of the band gaps and emission wavelengths (Fig. 1.1), however experimentally it is more complicated.

In contrast with classic III-V semiconductors like GaAs and InP, the thermodynamically stable phase of III-nitrides is the wurtzite structure (space group: P6$_3$mc). The wurtzite structure (Fig. 1.2) consists of two interpenetrating hexagonal close packed (HCP) sublattices (each with one type of atom) which have an offset of 5/8 of the cell height along the c-axis. There are two slightly different nitrogen bonds in the wurtzite structure, one nitrogen bond differs from the other three bonds. For an ideal wurtzite structure the c/a ratio equals to $\sqrt{8/3}$ and the anion-cation bond length along the (0001) direction, defined as parameter $u$, equals 8/3. The c/a ratio and $u$ of GaN, AlN, and InN differ from the ideal case, which has its influences on devices.

The wurtzite material system has both a strain independent spontaneous and a strain-induced piezoelectric component. The direction of the
piezoelectric and spontaneous polarisation is determined by the polarity of the material. Because of the sensitive dependence of the spontaneous polarisation on the structural parameters, there are some quantitative differences in polarisation between the III-nitrides.

Due to the polarisation induced bound interface charges it is possible to realise 2DEGs (two-dimensional electron gas) with high mobility and sheet carrier densities of $10^{13}$ cm$^{-2}$ or higher at the interface of nominally undoped AlGaN/GaN heterostructures.

An important property of GaN (and its related compounds) is the energy band structure with a lowest direct band gap at the $\Gamma$ point of the Brillouin zone [24]. The lowest conduction band is nondegenerate, but the valence band in wurtzite GaN is split by the combined action of the crystal field and the spin-orbit interaction (Fig. 1.3). The three upper valence bands occur within an energy range of about 30 meV, leading to three corresponding intrinsic exciton states commonly denoted A, B, and C.

$P$-type GaN is realised using magnesium (Mg) doping. Mg is the shallowest acceptor that has been found with the acceptor level at approx-
Figure 1.3: Schematic picture of the near band gap electronic structure of wurtzite GaN.

imately 170 meV above the valence band [25], which is still very deep. Approximately only 1-5% of the Mg atoms will be ionized at room temperature. $N$-type doping of GaN is easily accomplished by silicon, a shallow donor with an activation energy in a range of 12-17 meV [26].

Since epitaxial growth of the III-nitrides is commonly performed along the c-axis of the material there are two possible directions of growth, [0001] or [000 $\bar{1}$]. For homo-epitaxial growth on GaN single crystal substrates, which are plate-like crystals with \{0001\} facets, the growth direction can be selected by choosing either the Ga-face (0001) or N-face (000 $\bar{1}$) of the crystal. In the case of hetero-epitaxial growth, the polar direction of growth is selected by appropriate deposition conditions for GaN growth.

The most common techniques for the deposition of III-nitrides are metalorganic chemical vapour deposition (MOCVD)$^1$, molecular beam epi-

$^1$Also referred to as organometallic vapour-phase epitaxy (OMVPE) and other permutations of these same letters (OMCVD and MOVPE). Although the terminology organometallic, to describe the precursor molecules, agrees with the general chemical nomenclature MOCVD and MOVPE are commonly used. CVD is the most general term describing the growth process, since it implies nothing about whether the resultant layer is single crystalline, polycrystalline, or amorphous [27]
taxy (MBE), and hydride vapour phase epitaxy (HVPE). This thesis is dedicated to MOCVD growth of GaN and will describe the characterisation of GaN films grown by this technique.

1.3 MOCVD

MOCVD is a non-equilibrium growth technique which depends on the transport of gas phase organometallic precursors, hydrides (like ammonia, NH₃, as nitrogen source), and carrier gases to a heated substrate on which the precursors are pyrolysed and the film is deposited. The underlying chemical mechanisms are complex, involving a combination of gas phase and surface reactions. Composition and growth rate are regulated by precisely controlling mass flow rate and dilution of various components in the gas stream. The organometallic precursors are either liquids, such as trimethylgallium (TMG) and trimethylaluminum (TMA), or solids like trimethylindium (TMI). The organometallic sources are stored in bubblers through which a carrier gas (typically hydrogen) flows. The bubbler temperature determines the vapour pressure over the source material. Carrier gas will saturate with vapour from the source and transport the precursor to the heated substrate. NH₃ is used as nitrogen source in nitride growth. The high thermal stability of NH₃ is the reason for the high substrates temperatures², typically more than 1000°C. Dopant materials can be organometallic precursors, like bis(cyclopentadienyl)magnesium for p-type doping, or hydrides (like silane and disilane for n-type doping).

Due to the lack of GaN substrate material alternative substrates are needed for GaN growth. As a consequence of the high decomposition temperature of NH₃, and therefore the high growth temperatures needed for GaN deposition, the substrates do need the necessary thermal stability. Sapphire fulfils the condition of thermal stability and it is available in the form of large high-quality wafers. It has the hexagonal corundum structure that allows the deposition of material with a wurtzite structure. However, there is a large lattice mismatch between sapphire and the III-nitrides, which complicates the growth process.

²To reduce the required substrate temperature for nitride deposition, alternative nitrogen precursors which are thermally less stable than NH₃, like hydrazine (N₂H₂) have been used. Hydrazine, however, is extremely toxic and unstable, which restricts its large-scale application in MOCVD.
The MOCVD equipment may take various forms, and growth can take place at atmospheric pressure or moderately low pressure (of order 50 mbar). The common reactor design has a vertical or horizontal configuration. The heating is accomplished by radio frequency (RF) induction, resistance, or infrared lamp heating, with temperature monitoring by an infrared pyrometer or a thermocouple. Whether the growth tube is made of quartz or stainless-steel, the reactor walls are substantially colder than the heated susceptor, on which the substrate is placed, to minimise pre-deposition on the walls.

For the growth of GaN described in this thesis an Aixtron 200 RF reactor is used (Fig. 1.4), the gas system necessary for an MOCVD system is home-built (Fig. 1.5). The reactor has a horizontal design and is made of quartz. It is heated with a RF coil and the reactor walls are actively cooled with water. The susceptor is a flat silicon carbide (SiC) coated graphite block that is placed parallel to the gas flow direction. The susceptor is equipped with a rotating disc, on which the substrate is placed, to obtain uniform growth. The rotation is realised by a small gas flow. Since the temperature is regulated by a thermocouple placed below the centre of the susceptor disc, there is a temperature offset with the actual substrate temperature. This offset was determined with a pyrometer and
with gold melting experiments, all the growth temperatures in this thesis are corrected for this offset.

1.4 This thesis

In January 1997 I started on the project "GaN blue-light emitting diodes on GaN substrates". A very ambiguous project which aimed for the realisation of a diode structure and on the development of GaN substrates. Since epitaxial growth of GaN is carried out at around 1050°C, a new RF heated MOCVD system had to be installed which also required
the complete replacement of the existing gas system. After completion of the equipment the first GaN films were successfully deposited in June 1997 on small, 1 cm², sapphire substrates.

Due to the large lattice mismatch and large difference in thermal expansion coefficient between GaN and sapphire, the right growth regime for depositing smooth and transparent films had to be found (chapter 2) which demands an optimisation of both the low-temperature buffer layer and the high-temperature GaN layer. This search was hampered by the technical limitations of the advanced MOCVD system, which were finally adapted at the end of 1997.

Although the goal of the project was not achieved within the PhD research period, several elements necessary for device structures as well as improvements for the development of substrate material were started and realised within the "GaN-project". Growth of AlGaN, InGaN, n-doped GaN (chapter 3), HVPE, and epitaxial lateral overgrowth (see Fig. 1.6) are examples of this work. Chapters 4 and 5 deal with a very essential aspect in GaN growth, the polarity of GaN films.

The collaboration with the Polish group of Unipress enabled us to use GaN single crystal substrates for growth of GaN films that do not suffer from lattice mismatch with the substrate. The plate-like substrates have a Ga-face and a N-face which behave differently. The N-face can be mechano-chemically polished to obtain epi-ready substrates, while the Ga-face can only be polished mechanically, so that reactive ion etching is needed for further preparation of proper substrate crystals. GaN films grown on the N-face of GaN crystal substrates suffer from the formation of hexagonal hillocks (chapter 4). In chapter 6 and 7 of this thesis it is shown that the use of misoriented substrates leads to a reduction of the hillock density. In addition to the improvement in surface morphology a remarkable reduction of the unintentional/intrinsic donor concentration for films deposited on misoriented substrates is realised (chapter 8). In the last chapter of this thesis hetero-epitaxial GaN films are compared with GaN single crystal substrates using ellipsometry.

The following chapters of this thesis are based on published articles, with exception of chapter 7, the complete references of these articles can be found in the list of publications (p.127).
Figure 1.6: SEM images of GaN grown out of mask patterns.
References


Chapter 2

Temperature dependent morphology transition of GaN films\(^1\)

Abstract

The temperature dependence of the surface morphology of GaN epilayers was studied with AFM. The layers were grown by low pressure MOCVD on (0001) sapphire substrates in the temperature range of 980°C-1085°C. In this range the (0001) and \{1101\} faces completely determine the morphology of 1.5 μm thick Ga-faced GaN films. For specimens grown at 20 mbar and temperatures below 1035°C the \{1101\} faces dominate the surface, which results in matt-white layers. At higher growth temperatures the morphology is completely determined by (0001) faces, which lead to smooth and transparent samples. For growth at 50 mbar, this transition takes place between 1000°C and 1015°C. It is shown that the morphology of the films can be described using a parameter \(\alpha_{\text{Ga}}\), which is proportional to the relative growth rates of the (0001) and the \{1101\} faces.

\(^1\)The work presented in this chapter is based on the publications in Materials Research Society Symposium proceedings Volume 572 by A.R.A. Zauner, F.K. de Theije, P.R. Hageman, W.J.P. van Enckevort, J.J. Schermer, and P.K. Larsen and in Journal of Crystal Growth by F.K. de Theije, A.R.A. Zauner, P.R. Hageman, W.J.P. van Enckevort, and P.K. Larsen
2.1 Introduction

Due to its material properties gallium nitride (GaN) has attracted enormous attention in recent years, certainly after the success of GaN-based blue light emitting diodes. The lack of lattice matched substrates for epitaxial growth of GaN films has led to the application of a variety of substrates of which sapphire is most frequently used [1].

Despite the large mismatch in lattice constants between GaN and sapphire, device quality layers can be obtained using metalorganic chemical vapour deposition (MOCVD) and a two step growth procedure. On top of an initial buffer layer [2] a GaN film is deposited at relatively high temperatures. In this paper the influence of the deposition temperature on the surface morphology of the layers is investigated using atomic force microscopy (AFM) and scanning electron microscopy (SEM).

2.2 Experimental

The GaN layers were grown in a horizontal MOCVD reactor equipped with a SiC-coated graphite susceptor with a hydrogen gas driven rotating disc, for a single 2" wafer, to obtain optimum uniformity during the growth process. The growth temperatures calibrated for the centre of the disc are determined by a thermocouple. The discharge of the hydrogen flow causes a small temperature decrease towards the periphery of the disc.

Immediately before growth, the two-inch sapphire (0 0 0 1) substrates were cleaned in organic solvents, etched in a solution of HCl:HNO₃ = 3:1, and finally rinsed in de-ionised water. All deposition runs started with a 5 minutes pretreatment step in a hydrogen (H₂) gas flow at 900°C and 20 mbar followed by the nitridation of the substrate surface, carried out in a nitrogen/ammonia (N₂/NH₃) gas atmosphere during cooling down from 1020°C till 870°C (which corresponds with about 30 seconds). A 20 nm thick GaN buffer layer is deposited in a N₂ gas stream at 500 mbar when the buffer deposition temperature of 500°C is reached. The trimethylgallium (TMG) and NH₃ partial pressure during the buffer growth were 3 x 10⁻⁵ bar and 2.4 x 10⁻¹ bar respectively. On this buffer layer, the GaN films were grown.

Using TMG and NH₃ as precursors, and Pd-diffused H₂ as carrier gas, two series of GaN layers, one at 20 mbar and the other at 50 mbar total
reactor pressure, were grown at temperatures between 980°C and 1085°C. Growth was performed with a TMG flow of 63 μmol/min and a NH₃ flow of 2.5 standard litre per minute (slm), diluted with H₂ to a total flow of about 5 slm. These growth conditions correspond with TMG and NH₃ partial pressures of 1.4 x 10⁻⁵ bar and 2.4 x 10⁻² bar respectively at a reactor pressure of 50 mbar. All samples were grown for 1 hour which resulted in a GaN layer thickness of about 1.5 μm. AFM and SEM were applied to study the surface morphology of the samples.

2.3 Results and discussion

For the naked eye, lower deposition temperatures result in matt-white samples, whereas at higher deposition temperatures the layers look colourless and mirror-like. In Fig. 2.1 the specimen appearance is given as function of growth temperature and pressure. It shows that the transition from matt-white to mirror-smooth appearance occurs between 1000°C and 1015°C for samples grown at 50 mbar, and at 1035°C for those grown at 20 mbar. To ensure that changes in polarity are not the cause for the observed morphology transition, the polarity of the deposited GaN layers is determined by anisotropic etching [3]. For all samples it is found that growth occurred in the [0001] direction (Ga-face).

One sample, grown at 20 mbar and 1035°C, forms an excellent specimen to study the morphology transition, since it exhibits a mixture of both appearances. This sample, which will be referred to as sample ‘B’, has a matt-white appearance at the edges, where the deposition temperature has been slightly lower than at the central region, and is mirror-like and transparent at the centre. To determine the temperature difference during growth along sample B, the centre of a complete matt-white sample grown at 1030°C and 20 mbar and slightly thicker than sample B is used as a reference. AFM examination of this sample shows a morphology comparable to that on sample B at a position halfway between the periphery and centre. This indicates, taking the thickness difference into account, that the growth temperature near the edges of sample B has been 1027 ± 3°C. From which it can be concluded that a temperature gradient of only about 8°C can cause a dramatic change in morphology.

In Fig. 2.2 an AFM image from the periphery of sample B is shown. The main characteristic of the surface is formed by large and irregularly shaped pits of about 300-600 nm wide, with crystallographically oriented
side faces and with a density of about $1.2 \times 10^9 \text{ cm}^{-2}$. The depth of the pits is at least 250 nm, however, the sides are too steep to give reliable depth measurements using AFM. SEM observations showed that the angle between the pit walls and the (0001) face is about 60°.

From the crystal structure of wurtzite-GaN and its lattice constants [4] the theoretical crystal morphology of GaN can be determined using the ‘connected net’ theory [5, 6]. It states that \{hklm\} faces parallel to a network of atoms interconnected by strong bonds, within a slice thickness $d_{hklm}$, determine the morphology of a crystal. Three faces, \{0001\}, \{1\overline{1}01\} and \{1\overline{1}00\}, are found to be parallel with such a connected net. The occurrence of these faces was indeed reported in literature [7, 8].

The intersection lines and the inclination of the previously mentioned pit walls with the (0001) surface indicate that these side walls are in fact \{1\overline{1}01\} faces, for which an angle of $61.9^\circ$ with respect to the (0001) face can be calculated. Since growth is performed on (0001) sapphire substrates and no etching of the GaN surface is expected to occur, it can be concluded that the pits are induced by the coalescence of islands bounded by \{1\overline{1}01\} facets. The same conclusion was drawn in references [9, 10].
on the basis of surface topographs showing the nucleation, lateral expansion, and coalescence of islands for GaN grown on c-plane sapphire by MOCVD.

For the surface region located in the intermediate zone between the edge and centre of sample B, an AFM image is given in Fig. 2.3. It shows the transition stage between the lateral expansion of the islands and the dislocation induced step flow growth of the planar (0001) surface. The density of pits is still about $1.2 \times 10^9$ cm$^{-2}$, but most of them are partially closed to form about 7 nm wide grooves.

At the centre of sample B (Fig. 2.4) the same kind of cavities is found as shown in Figs. 2.2 and 2.3. However, their average sizes and density are considerably less, and are found to be, respectively, 100 to 300 nm and about $4.0 \times 10^8$ cm$^{-2}$, indicating that the coalescence of the islands is almost complete.

From the results discussed above, it is clear that the deposition temperature largely influences the surface morphology of the GaN layers. It can be argued that a lower density of nucleation islands at the periphery induces the larger size of pits near the edge of the sample. However, it is known that a lower temperature is expected to result in higher chemical
**Figure 2.3:** Height and deflection (inset) AFM image of a surface area between the periphery and the centre of sample B. Pits and grooves can be recognised.

**Figure 2.4:** Deflection AFM image of the surface at the centre of sample B.
driving force for GaN growth, therefore, the nucleation rate will certainly not decrease [9]. To determine the nucleation density along the samples, a specimen is grown for 20 minutes to a thickness of 0.46 μm (instead of ≈ 1.5 μm) under similar conditions.

On this thinner sample, indicated as sample T, the separate islands can be distinguished. The island density proved to be constant along the entire sample, therefore the different morphologies cannot be explained by a different nucleation density.

At lower temperatures, the growth velocity in the <1 1 0 1> directions is low compared to that in the [0 0 0 1] direction, causing slow lateral growth of the islands, and the morphology of the 1.5 μm thick layers is dominated by {1 1 0 1} faces. For increasing temperatures, growth velocity in the <1 1 0 1> direction increases compared to the growth velocity in the [0 0 0 1] direction and therefore, the slow growth in the [0 0 0 1] direction dominates the surface morphology.

Analogous to the CVD growth of diamond crystallites [11,12], a growth rate factor is defined to describe the morphology of the Ga faced GaN films. The growth rate factor $\alpha_{\text{GaN}}$ equals

$$\frac{v_{[0001]}}{v_{[1\bar{1}01]}} \cos \varphi,$$  \hspace{1cm} (2.1)

where $v_{[0001]}$ and $v_{[1\bar{1}01]}$ are the growth rates in the [0001] and [1 1 0 1] direction, respectively, and $\varphi(=61.9^\circ)$ is the angle between the (0 0 0 1) and {1 1 0 1} faces. For $\alpha_{\text{GaN}} = 0$ no {1 1 0 1} faces develop and a completely closed (0 0 0 1) layer is formed, for $\alpha_{\text{GaN}} \geq 1$ only {1 1 0 1} facets are present on the surface. The present work shows that besides a strong dependence on the deposition temperature, $\alpha_{\text{GaN}}$ is also pressure dependent.

Assuming that pits and islands are hexagonal in shape and (0 0 0 1) faces top the islands, the values of $\alpha_{\text{GaN}}$ can be determined (Fig. 2.5). From the average (0 0 0 1) surface area and the nucleation density of the islands, the smallest centre-edge distance $x$ of the hexagonal island can be calculated. Using this value of $x$ and the layer thickness $t$, $\alpha_{\text{GaN}}$ is given by

$$\alpha_{\text{GaN}} = \frac{t}{(t + x \tan \varphi)}.$$  \hspace{1cm} (2.2)

The minimum layer thickness $t_{\text{min}}$ necessary to obtain a smooth film
depends on $\alpha_{\text{GaN}}$ and the distance $d$ between the nuclei, and is given by

$$t_{\text{min}} = \frac{d \alpha_{\text{GaN}} \tan \varphi}{2 - 2\alpha_{\text{GaN}}}.$$

The surface area covered by the (0001) faces is estimated from AFM images along the surface of sample B. The nucleation density of the islands could be directly determined from sample T and was found to be $2.1 \times 10^9$ cm$^{-2}$. As already stated, the island density proved to be constant along sample T, it does not change as function of temperature and is assumed to be the same for sample B. SEM cross section observations on sample B showed that the growth rate in the [0001] direction was also constant, resulting in a uniform layer thickness, $t$, of $1.48 \pm 0.03 \mu$m. For sample B a film with completely coalesced islands, i.e. the islands just touching each other with their (0001) faces, is obtained for $\alpha_{\text{GaN}}$ values $\leq 0.87$. In table 2.1 it can be seen that the small temperature gradient across the substrate causes an increase of $\alpha_{\text{GaN}}$ values from 0.87 to 0.94. Since the layer thickness of sample B is constant, the change in $\alpha_{\text{GaN}}$ values is only caused by a difference in $v_{[110]}$.

More detailed AFM measurements on the centre of sample B (see Fig. 2.6) show a high density of interacting growth spirals, which emerge from dislocations with a screw component. Theoretical calculations [13] revealed that the GaN surface during growth has a surface energy comparable with a surface free of adsorbates. This implies high step and kink energies, which predict strongly polygonized growth spirals [14]. However, all spirals are found to be circular. This can be explained by assuming that crystal growth is limited by surface diffusion rather than by the inte-
Table 2.1: Growth rate factor $\alpha_{GaN}$ across sample B.

<table>
<thead>
<tr>
<th>distance from centre ($10^{-2}$ m)</th>
<th>$\alpha_{GaN}$ values</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.00</td>
<td>0.87</td>
</tr>
<tr>
<td>0.25</td>
<td>0.88</td>
</tr>
<tr>
<td>0.50</td>
<td>0.89</td>
</tr>
<tr>
<td>0.75</td>
<td>0.91</td>
</tr>
<tr>
<td>1.00</td>
<td>0.93</td>
</tr>
<tr>
<td>1.25</td>
<td>0.94</td>
</tr>
</tbody>
</table>

Figure 2.6: Deflection AFM image of the surface in the centre of sample B at high magnification. Monoatomic (ss) and double (ds) steps are shown emerging from hollow cores (hc) at dislocations with a screw component. Hollow cores related to edge dislocations (ed) can be recognised.

Integration of growth units at the step sites. Contrary, growth on the N-face is dominated by integration of growth units at the step positions (chapter 6). The spirals consist of monoatomic (2.5 ± 0.3 Å) or double steps (5.0 ± 0.4 Å), favourably comparing with the $d_{002}$ distance of 2.59 Å. Steps emerging from dislocations have in general a height of 2$d_{002}$, indicating a screw component [0001].

On these GaN layers also a number of small holes is observed with a density of $1.5 \times 10^9$ cm$^{-2}$. The holes often coincide with dislocations containing a screw component and have a narrow diameter distribution; 48 ± 9 nm. The diameter of these hollow cores is much wider than can
be expected from standard stress theory of dislocations [15]. The large diameter might be due to the precipitation of vacancies to form voids along the dislocation lines [16].

### 2.4 Conclusions

The morphology of $\approx 1.5 \mu m$ thick Ga-faced GaN epilayers, grown by MOCVD on (0001) sapphire substrates, is strongly temperature dependent. For the investigated temperature range of 980-1085°C the growth morphology is determined by (0001) and \{110\} faces. At higher growth temperatures the morphology is governed by growth in [0001] direction, whereas at lower growth temperatures, a slower lateral growth in the \langle1101\rangle directions determines the morphology for a longer time. To describe the observed morphology a growth rate factor $a_{GaN}$ is introduced. On the mirror-like surfaces single and double steps can be seen emerging from the hollow cores of dislocations with a screw component.

### References


Chapter 3

The effect of Si doping on the properties of GaN films

Abstract

The effect of Si doping on the electrical, optical, and structural properties of GaN films grown on sapphire substrates was investigated. The Si incorporation appeared to be virtually independent of the growth temperature. Furthermore it was found that there is a linear relationship between the silane input mol fraction and the free-carrier concentration in GaN layers. The relationship between the free carrier concentration and the ellipsometric data made it possible to use ellipsometry as an alternative, quick, contactless, and non-destructive technique to determine the free electron concentration in GaN layers doped with silicon. Increasing doping concentrations led to a continuous shift of the exciton related PL to lower energies, while the intensity of the UV emission was found to increase up to a carrier concentration of \( n = 2.5 \times 10^{18} \text{ cm}^{-3} \). The morphology of the samples drastically changed at high silicon concentrations, showing an enlarged roughness and crack formation.

\(^{1}\)The work presented in this chapter is based on the publications in Phys. Stat. Sol. (b) by P.R. Hageman, M.A.C. Devillers, A.R.A. Zauner, V. Kirilyuk, W.S. Bouwens, R.C.M. Crane, and P.K. Larsen and in Materials Research Society Symposium proceedings Volume 595 by P.R. Hageman, V. Kirilyuk, A.R.A. Zauner, G.J. Bauhuis, and P.K. Larsen
3.1 Introduction

Apart from being an excellent material for opto-electronic applications, group III nitrides are thought to be very attractive for electronic devices capable of operating at high power levels and high temperatures. These electronic devices rely in majority on the use of heterojunctions between GaN and Al$_x$Ga$_{1-x}$N where fortunately only $n$-type doping is necessary. In order to minimise the resistance of the layers and thereby reducing thermal losses in the devices, precise control of $n$-type doping in combination with as high as possible mobilities is necessary. These demands require an optimisation of the growth of the $n$-type GaN layers. The most commonly used $n$-type dopant in GaN is silicon, using silane (SiH$_4$) or disilane (Si$_2$H$_6$) as precursor. In this chapter a comprehensive study on the influence of SiH$_4$ doping on the electrical, optical, and structural properties in hetero-epitaxial GaN films grown by metal-organic chemical vapour deposition (MOCVD) is presented.

3.2 Experimental procedure

The GaN layers were grown in a MOCVD reactor at 1045°C and 50 mbar on two-inch sapphire (0001) substrates using trimethylgallium (TMG) and ammonia (NH$_3$) as precursors and hydrogen (H$_2$) as carrier gas. Silane (SiH$_4$), diluted to 51.9 ppm with H$_2$, was introduced in the gas stream with a silane input mol fraction ([SiH$_4$]$_{in\,mol}$) between $8 \times 10^{-10}$ and $2 \times 10^{-8}$ (corresponding with a silane partial pressure between $4 \times 10^{-11}$ and $1 \times 10^{-9}$ bar). Temperature dependent growth experiments were performed in the temperature range from 1005 to 1085°C at 50 mbar. The lower temperature boundary was determined by the transition in growth morphology as described in chapter 2; below this temperature the layers become opaque due to incomplete coalescence of the growth nuclei. The grown layers had thicknesses between 1.4 and 1.8 μm. Optical microscopy and scanning electron microscopy were used to examine the morphology of the films. Hall measurements, employing the Van der Pauw configuration, were used to characterise the samples electrically. The optical properties of the GaN films were investigated with photoluminescence (PL) measurements carried out at 4K. A HeCd laser (325 nm) was used as excitation source with a power density of about 15 Wcm$^{-2}$. The PL emission was dispersed by a 0.6 m monochromator and detected by a cooled GaAs
photomultiplier. A Gaertner L117C ellipsometer was used to measure the ellipsometric angles $\Delta$ and $\Psi$ at the HeNe-laser wavelength of 632.8 nm. The spot size of the laser beam is 1 mm in diameter. The measurements were carried out at room temperature at angles of incidence of 60°, 65°, and 70°. The values of $\Delta$ and $\Psi$ are measured with a typical precision of ± 0.02°. The structural properties were studied with HR-XRD measurements performed on a Bruker D8.

### 3.3 Results and discussion

All deposited layers up to a temperature of 1045°C resulted in colourless and mirrorlike layers (Fig. 3.1a). For higher temperatures an enlarged roughness was observed (Figs 3.1b and c). The optical microscopy images show hillock formation on the layers grown at the two highest temperatures (1065 and 1085°C). The density of the hillocks increased when the growth temperature increased from 1065 to 1085°C as can be seen in Figs 3.1b and c. The lateral size of these hillocks is typically 30 to 40 µm with a height of about 1.25 µm. Layers with a high incorporated silicon concentration, i.e. grown at the two highest temperatures with a silicon input mol fraction of $1.92 \times 10^{-8}$, suffer from crack formation as can be observed in Figs. 3.1b and c. In contrast, no crack formation was found in the layers grown at 1045°C with a high silicon concentration. Incorporation of silicon in the GaN lattice influences, to a certain extent, the crystal properties of GaN. In general, when grown on sapphire, GaN is under tensile strain at growth temperatures [1,2]. During cooling down the tensile strain goes into compressive strain due to the larger thermal expansion coefficient of sapphire.

Incorporation of Si enhances this effect because the ionic radius of Si$^+$ (0.41 Å) ions is smaller than the radius of Ga$^+$ (0.62 Å) ions. The silicon substitution compresses the GaN layer in the $c$-axis direction thereby putting the basal GaN plane in tension. The incorporation of Si in GaN can lead to crack formation when a critical doping concentration (for a given thickness) is exceeded [6] due to a large tensile strain during growth. Additionally, the formation of dislocations due to the silicon incorporation may be another factor in the crack formation process.

To check whether an increased density of dislocations may be the cause for the crack formation, X-ray diffraction rocking curve measurements were performed on the silicon doped GaN layers. The FWHM of
Figure 3.1: Optical microscopy images of silicon doped hetero-epitaxial GaN layers grown at a) 1045°C and $[\text{SiH}_4]_{\text{input}} = 7.68 \times 10^{-8}$, b) 1065°C and $[\text{SiH}_4]_{\text{input}} = 1.92 \times 10^{-8}$, and c) 1085°C and $[\text{SiH}_4]_{\text{input}} = 1.92 \times 10^{-8}$. Clearly visible is the enlarged roughness when growing GaN at higher temperatures. Also, crack formation can be observed in pictures b) and c) for an input mol fraction silane of $1.92 \times 10^{-8}$. 
The effect of Si doping on the properties of GaN films

Figure 3.2: FWHM of the (0002) (circles) and the (1015) (triangles) reflections versus the input mol fraction of SiH₄ for layers grown at identical conditions.

The (0002) and (1015) reflections increase with increasing silane input concentration, as given in Fig. 3.2, indicating that the crystal quality decreases as the amount of incorporated silicon increases which could indicate an increase in the density of all types of threading dislocations. From Fig. 3.2, it can be concluded that there is a linear relationship between the incorporated Si concentration and the FWHM for both reflections for $[\text{SiH}_4]_{\text{in}}$ up to $7.8 \times 10^{-8}$. However, this does not apply for a sample with a silane input mol fraction as large as $8.2 \times 10^{-7}$ which shows a FWHM of 356 arcsec, a value comparable to the undoped samples. In contrast to the layers with less incorporated Si, this layer is very inhomogeneous and the morphology is dominated by separate islands deposited in a rough matrix, see Fig. 3.3. This can be caused by either the relaxation of the lattice due to island formation or because of deposition of Si₁₋ₓNₓ during GaN growth, which is formed by the presence of large concentrations of SiH₄ and NH₃ [4].

The precise control and uniformity of the doping level are the two major prerequisites for any doping element to be used in MOCVD. To evaluate these criteria for SiH₄ as precursor for $n$-type doping of GaN, the dependence of the free electron concentration on the input mol fraction
Figure 3.3: SEM photograph of the morphology of the GaN sample grown with a silane input mol fraction of $8.2 \times 10^{-7}$.

SiH$_4$ and on the growth temperature was studied. Fig. 3.4a shows the free electron concentration n for GaN:Si versus the input mol fraction SiH$_4$ as determined by room temperature Hall-van der Pauw measurements. In this series of experiments the growth temperature (1045°C), the TMG and NH$_3$ partial pressures were kept constant. In this log-log plot the free electron concentration increases linearly with the silane input mol fraction with a slope of 0.95. Concentrations up to $1 \times 10^{19}$ cm$^{-3}$ have been reached easily without observation of any saturation of the free carrier concentration. This indicates that still higher concentrations can be reached by just increasing the input mol fraction of silane. The background doping level of our undoped GaN reference samples, being in the order of $1 \times 10^{17}$ cm$^{-3}$, determines the lower limit of free electron concentration.

To reveal the temperature behaviour of the silicon doping of GaN the free electron concentration n versus the inverse growth temperature for two input mol fractions of silane ($8 \times 10^{-10}$ and $1.92 \times 10^{-8}$) have been plotted in Fig. 3.4b. From Fig. 3.4b it is obvious that the n-doping of GaN is hardly temperature dependent. Apparent activation energies cannot be obtained accurately from this data because of the narrow temperature range used, which is forced upon by the morphology. This relatively tem-
Figure 3.4: a) Free electron concentration, obtained by Hall-van der Pauw measurements, versus the input mol fraction SiH₄ for GaN layers grown at 1045°C with constant NH₃ and TMG partial pressures. The slope of the linear relationship is 0.95. b) Free electron concentration versus the reciprocal growth temperature for two different input mol fractions SiH₄ (8 x 10⁻¹⁰ and 1.92 x 10⁻⁸).
temperature independent behaviour points to a diffusion limited incorporation process, i.e. the decomposition of silane at high temperatures is not the limiting step in the incorporation process. This view is supported by the 1:1 relationship between the carrier concentration and input mol fraction from Fig. 3.4a. The observed behaviour of SiH₄ as dopant in MOCVD grown GaN is very profitable because small temperature gradients, which are always present over the susceptor, have now only little influence on the resulting free electron concentration. The linear behaviour of the silicon incorporation from silane into GaN, as plotted in Fig. 3.4a, enables a very precise dosimetry of the incorporated amount of silicon and thus the resulting free electron concentration. The electron mobility, as observed by Hall measurements, gives an indication of the electrical quality of the material. For our samples values ranging from 320 cm²V⁻¹s⁻¹ for \( n = 5.3 \times 10^{17} \) to 192 cm²V⁻¹s⁻¹ for \( n = 9.2 \times 10^{18} \) cm⁻³ are obtained. These values are higher than values published in Ref. [5] indicating that the layers have a compensation degree of about 0.4 [6].

Hall measurements are often used for the electrical characterisation. The necessity for electrical contacts, which have to be evaporated or sputtered, and the demand to define the sample into a cloverleaf configuration (Van der Pauw) or into a Hall-bar makes this technique destructive and time consuming. Based on ellipsometry, a far less time consuming and non-destructive method is developed to obtain the free electron concentration. For this purpose the imaginary part of the refractive index \( n_2 \) of the doped GaN layer was calibrated with the free electron concentration as determined by Hall-van der Pauw measurements. The value of \( n_2 \) was determined by a multilayer fit on the ellipsometric parameters (\( \Delta \) and \( \Psi \)) measured at different angles (60°, 65°, and 70°). In the multilayer fit the substrate, the GaN buffer layer and the doped GaN layer are included. Examples of how \( n_2 \) can be extracted from the ellipsometric data are given in [7,8]. In Fig. 3.5 the free electron concentration obtained by Hall measurements is plotted versus \( n_2 \). For free electron concentrations in the range of \( 5 \times 10^{17} \) to \( 1 \times 10^{19} \) cm⁻³ an almost perfect linear relationship has been found between the free electron concentration and \( n_2 \) with a slope of 2.09. However, care has to be taken because non-ideal morphology, i.e. a roughness of an extra oxide layer, can disturb this relationship. How the roughness of a sample can influence the ellipsometric data is also illustrated in Fig. 3.5. Samples b and c, their morphology is given in Figs. 3.1b and c, show a large deviation from the obtained relationship. This
Figure 3.5: Free electron concentration obtained by Hall measurements versus imaginary part of the refractive index \( (n_2) \) of the Si-doped GaN layers. The linear relationship has a slope of 2.09. Samples b and c correspond with Figs. 3.1b and 3.1c.

deviation increases as a roughness of the layers enlarges. This can be corrected by introducing an additional top layer in the multi-layer fit that incorporates the roughness.

PL measurements performed at 4K were used to investigate spontaneous emission properties of Si-doped hetero-epitaxial GaN. As in the case of unintentionally doped layers the excitons bound to the neutral donors (D\(^0\)BE) dominate the PL spectra of the moderately Si-doped samples at low temperatures. Donor-acceptor pair recombination (DAP) with its LO-phonon replicas is present in all doped GaN layers. With increase of the doping concentration up to \( n = 2.5 \times 10^{18} \text{ cm}^{-3} \) the band edge PL shifts to lower energies (Fig. 3.6), probably caused by band gap narrowing. Another reason for the red shift of the exciton related PL could be a strain release caused by substitution of Ga by Si. The total UV emission first increases as the doping concentration increases, but starting from \( n = 4.6 \times 10^{18} \text{ cm}^{-3} \) the band edge PL gets broadened and diminishes, which indicates the increasing role of the non-radiative Auger recombination. No considerable changes in "yellow" luminescence were found for different doping levels.
Figure 3.6: Evolution of the band edge PL (T = 4K) as function of increasing free electron concentration \( n \).

The yellow luminescence in the samples with the lowest UV emission was however somewhat stronger. The PL signal of the sample with the highest free electron concentration (\( n = 3.2 \times 10^{19} \) cm\(^{-3} \)) is dominated by two broad lines that can reflect the structural inhomogeneity of the sample, since this layer reveals very rough and even mosaic-like morphology structure (see Fig. 3.3). Splitting of the D\(^{9}\)BE peak was also observed in the Si doped GaN layer grown directly on sapphire without a buffer layer, i.e. N-face orientation (Fig. 3.7). Both D\(^{9}\)BE and DAP peaks in the N-face layer are blue shifted as compared with the Ga-face film, although both layers were grown using the same growth conditions.

Unfortunately, the quantitative study of the band gap narrowing and
Figure 3.7: Low temperature PL (4K) of hetero-epitaxial GaN of Ga- and N-face polarity. Although both layers were grown with the same SiH₄ input mol fraction the free carrier concentration in these layers are different: \(n_{N\text{-face}} = 5.4 \times 10^{18} \text{ cm}^{-3}\) and \(n_{Ga\text{-face}} = 1.7 \times 10^{18} \text{ cm}^{-3}\).

correlation of the band gap with the lattice constants of the hetero-epitaxial layers is very difficult. A reason for this is the non-uniform depth distribution of the charge in these layers. In contrast to Hall measurements, which give an integrated value of the free carrier concentration, the PL signal comes only from the upper part of the layer (\(\approx 100 \text{ nm}\)). Although the non-uniform depth distribution in carrier concentration is in an absolute sense not large, its impact on the PL measurements is significant. As the penetration depth of the excitation light is comparable with the thickness differences in the studied GaN layers (\(d \approx 1.4-1.8 \mu\text{m}\)), the PL emission is strongly dependent on the layer thickness and some discrepancies of the PL data with the Hall measurements appear.

The qualitative comparison of the PL emission in the differently doped GaN samples shows that the silicon impurities of moderate concentrations
(up to \( n = 2.5 \times 10^{18} \, \text{cm}^{-3} \)) either eliminate non-radiative recombination centres or promote new ways for the radiative recombination in the heteroepitaxial GaN making the UV emission more efficient. From both PL and Hall data it follows that the free electron concentration is always higher in the N-face layers (see Figs. 3.4 and 3.7) in comparison with the Ga-face ones, although the same growth conditions are applied. The same phenomenon was found for the homo-epitaxial growth of GaN as well. Either the incorporation of the donor in the N-face layers is higher or the compensation ratio is smaller. The latter possibility is supported by recent suggestions about easier acceptor incorporation in Ga-face GaN [9].

### 3.4 Conclusions

The effect of Si doping on the electrical, optical, and structural properties in GaN films grown on sapphire substrates was investigated. A 1:1 relationship between the silane input concentration and the resulting carrier concentration is found. Furthermore, the silicon incorporation appeared to be hardly temperature dependent. Ellipsometry was used to determine the imaginary part of the refractive index of the doped GaN layers. For smooth films it showed an almost perfect relationship with the carrier concentration as determined by Hall measurements. For high silane concentrations a strong influence on the morphology of the GaN layer is found. Increasing silane input concentrations broadened the FWHM of the X-ray rocking curves, indicating that the structural quality of the GaN film decreases. The intensity of the UV PL signal is found to increase with increasing carrier concentrations up to \( n = 2.5 \times 10^{18} \, \text{cm}^{-3} \). For those carrier concentrations, photoluminescence studies revealed a shift of the conduction band towards lower energy positions.

### References


Chapter 4

Inversion Domain Nucleation in homo-epitaxial GaN

Abstract
Homo-epitaxial GaN grown on the N-face of GaN single-crystal substrates exhibits a large number of hexagonal growth hillocks, typically 10-50 μm in size depending on layer thickness. The evolution of these defects is dominated by the growth rate of an emergent core of an inversion domain. The inversion domains nucleate at a thin band of oxygen containing amorphous material, 2 to 5 nm in thickness, being remnant contamination from the mechano-chemical polishing technique used to prepare the substrates prior to growth.

4.1 Introduction

Despite the remarkable progress which has been made in the last decade in growing good hetero-epitaxial GaN layers, this material shows still a very high density of diverse defects, in particular dislocations. Although the high dislocation density does not seem to hamper the performance of LED’s at first sight, it has been shown that dislocations in GaN layers act as nonradiative recombination sites [1–4]. For high-power optoelectronic and elevated-temperature device applications, the present structural characteristics of hetero-epitaxial GaN seem to be insufficient.

In order to obtain low defect density device structures a variety of substrate preparation techniques are being considered including the technique of epitaxial lateral overgrowth (ELOG) [5–8], the use of hydride vapour-phase epitaxy (HVPE) for the growth of thick GaN or AlN layers followed by the lift-off technique to provide large area substrates [9–11] and the growth of single crystal GaN under high hydrostatic pressure of nitrogen [12,13]. In the latter case it has been reported that the plate-like GaN single crystals have a dislocation density of about $10^5 \text{ cm}^{-2}$ [13]. From attempts to grow GaN on the plate-like crystal substrates it was found that the homo-epitaxial GaN layers retained the polarity of the substrates. Furthermore it was reported that defects emanate from the epilayer/substrate interface due to the existence of processing induced surface inhomogeneities [14,15]. Application of a mechano-chemical polishing method led to the preparation of smooth surfaces (RMS = 0.1 nm) of bulk GaN, as measured by Atomic Force Microscopy [16].

In this work a systematic study on the morphological and structural characteristics of N-face GaN layers grown by metalorganic chemical vapour deposition (MOCVD) on mechano-chemically polished GaN single crystals is presented.

4.2 Experimental

The GaN crystals used as substrates for epitaxy were grown under a high-hydrostatic pressure of nitrogen (15-20 kbar) from liquid gallium at a temperature of 1400-1600°C [12]. Both sides of the $\{0001\}$ oriented plate-like crystals were mechanically polished using 0.1 µm grade diamond paste, while the N-faces ($000\bar{1}$) were subsequently mechano-chemically polished in an aqueous solution of KOH following the procedure described
in Ref. [16]. Undoped epitaxial GaN layers were grown in a horizontal MOCVD reactor. The crystals were heated up to the growth temperature of 1050°C in a nitrogen/ammonia (N₂/NH₃) atmosphere, which took about 20 minutes. Epitaxial growth was performed using trimethylgallium (TMG) and NH₃ as precursors with hydrogen (H₂) as carrier gas, at a total pressure of 50 mbar. The TMG flow rate was about 60 μmol/min and the NH₃ flow was 2.5 standard litre per minute (slm), diluted with H₂ to a total flow of 5 slm. The time of epitaxial growth was 1 hour, unless denoted otherwise. Using this procedure high-quality GaN epilayers have been previously grown reproducibly on sapphire substrates (see chapter 2).

A range of complementary techniques were used for the morphological and structural characterisation of the epitaxial layers including differential interference contrast microscopy (DICM), scanning electron microscopy (SEM), atomic force microscopy (AFM), and transmission electron microscopy (TEM). The techniques of conventional and high-resolution electron microscopy (HREM) were complemented by convergent beam electron diffraction (CBED), high angle annular dark field (HAADF) imaging and electron energy loss spectroscopy (EELS). Plane view TEM specimens were prepared using conventional sequential mechanical polishing and conventional Ar ion beam milling, while site specific cross-sectional foils were prepared by the focused ion beam (FIB) technique. The site selectivity of the FIB technique enabled cross-sections through chosen growth features, e.g. the emergent cores of the hillocks, to be obtained.

4.3 Results and discussion

Optical examination of the N-face homo-epitaxial GaN layers revealed numerous growth hillocks covering almost the entire substrate surface (Fig. 4.1). The size of the hexagonal base of the hillocks was in the range of 10-50 μm after 1 hour of growth, with a density in the range of 0.5-2 x 10⁵ cm⁻². This result is based on an examination of ten separate growth runs performed under nominally the same growth conditions. The majority of the hillocks possess the shape of point-topped pyramids (denoted by pt in Fig. 4.1), although some of them are macroscopically flattened or disrupted (denoted as ft and dr in Fig. 4.1b).

Inspection of the point-topped hexagonal hillocks by AFM reveals morphological details of the core on nanometer scale. The highest and most well-defined pyramids, as indicated in Fig. 4.1a, are terminated by submi-
Figure 4.1: (a) DICM images of a homo-epitaxial GaN layer grown on the N-face (0001) of a single crystal showing point-topped (pt) pyramids. (b) SEM image of point-topped, flat-topped (ft) and disrupted (dr) hexagonal hillocks.

cron sized flat hexagonal cores, as shown in Fig. 4.2. The AFM analysis shows that the flat core regions is atomically smooth, with a roughness in the range of 0.1-0.15 nm. Some of these flat cores were surrounded by material with a noticeably rougher surface morphology, edging the flat core areas, as demonstrated in Fig. 4.2b.

The macroscopically flat-topped hillocks are also flat on the nm scale. The AFM data indicate height fluctuations of 0.5-1 nm, which is on the order of the atomic layer thickness. There is also the suggestion of the emergence of dislocations in the centre of such hillocks, as evidenced by the atomic-size steps shown in Figs. 4.3a and b, while some macroscopically flat-topped hillocks exhibit a needle-shaped tip at the centre, as shown in Fig. 4.4. The tip seems to serve as a source of atomic layer steps, by which step flow growth is mediated.

Besides the tip, which is the bright central part in the AFM height image, two triangular-shaped patterns can be recognised in Fig. 4.4a. The step height of each triangular terrace is one atomic layer. The shape of this one atomic layer high terrace is triangular since the two-dimensional point group symmetry of a GaN growth layer with thickness d_{002} in the wurtzite point group P6_3mc is 3. This means that each monolayer has a three-fold symmetry and therefore only three directions will be crystallographic equivalent (i.e. every 120°). In the case of a hexagonal terrace only three from the six possible step edges will have one dangling bond
Figure 4.2: (a) AFM image and (b) line profile across the top of an hexagonal pyramidal hillock (as indicated by the arrow in Fig. 4.1a) terminated by a 100 nm sized flat-topped region.

Figure 4.3: (a) AFM image and (b) line profile taken at the centre of a macroscopically flat hillock.
per edge atom, while the other three step edges (alternating with the first kind of step edge) will have two dangling bonds per edge atom. Following the terminology of Xie et al. [20] these step edges are named type B edge and type A edge, respectively. It is reasonable to assume that the step edge containing two dangling bonds per edge atom, the type A edge, will grow faster than the type B edge. This assumption was found to be correct [20, 21]. The faster growth speed of the type A edge will ultimately result in a triangularly shaped terrace, which explains the observation in Fig. 4.4a. The fact that only two terraces are seen in this 5 x 5 μm AFM scan demonstrates that the tip is not an efficient source for the nucleation of surface steps.

The material between the hillocks also exhibit characteristics step flow growth, with approximately 1 nm step heights, as revealed by AFM (Fig. 4.5).

In order to reveal the nature and origin of the defects responsible for the formation of the hexagonal hillocks, both plan-view and cross-sectional TEM specimens were prepared from an epitaxial layer grown for 15 minutes instead of 60 minutes. This thinner layer increased the chances of hitting the nucleation source, since any small deviation in orientation of the layer when sectioned using FIB can result in missing a sub-surface target (approximately 100 nm in this instance). By inspection of the large tilt plan view TEM images, it appeared that the point-topped pyramidal
growth hillocks exhibit faceted core structures, without any other threading defects. Using the FIB technique, cross-sectional TEM specimens were prepared precisely through the cores of these hexagonal growth hillocks for more detailed structural analysis. TEM examination revealed columnar defects located just below the apex of each hillock, as illustrated in Fig. 4.6a. The column emanates from a platelet of approximately 100 nm in size, which is presumed to delineate the original epilayer/substrate interface (Fig. 4.6b). No other sign of the interface plane was evident from these diffraction contrast images.

The striped nature of the columnar defect (Figs. 4.6a and b) is simply related to the fact that these are projected images of an irregular hexagonal column of material. Precise analysis of this columnar defect and the clarification of its nucleation site required further sequential thinning of the sample and the application of a range of complementary TEM procedures. In particular, asymmetries within CBED {0002} diffraction discs allowed the polar nature of the material to unambiguously identified [15, 17, 18]. CBED patterns taken across the boundary of the central core immediately reveal a reversal in contrast within the {0002} diffraction discs and as such suggest the defect core to be an inversion domain. However, since the contrast in these patterns is strongly thickness-dependent,
Figure 4.6: TEM cross-sectional images of the columnar defect delineating the core of the hexagonal growth hillock (denoted pt in Fig. 4.1). (a) Defect imaged with g in the growth direction close to the <1100> zone, (b) weak beam image of the same defect revealing a thin planar nucleating site at the base of the column.

it is necessary to check the foil thickness separately [18,19].

Correcting for image rotation introduced by the electron microscope, the CBED patterns of Fig. 4.7 demonstrate unequivocally that the matrix, surrounding the inversion domain, retained the N-polarity of the substrate, while the columnar defects have a Ga-polarity, thereby confirming them to be inversion domains. Similar growth defects have been observed in hetero-epitaxial N-face GaN layers [22-25]. Hillock formation
on N-face surfaces apparently results from the the higher growth rate of the inversion domain located in the centre of a hillock [22]. Romano et al. [23] suggested that the resultant strain at the boundary may also enhance the growth rate of the opposite phase and dictate the final surface morphology. However, Cherns and co-workers [18] found no evidence of strain associated with inversion domains. Our AFM results indicate that the inversion domains can be a very effective nucleation site during homoepitaxy (see Fig. 4.2b), the nucleation apparently occurs at the inversion domain boundary. However, the diverse efficiency of inversion domains in the nucleation of surface steps is not understood. Some inversion domains act as an active step source (Fig. 4.2) while others emanate only singular steps (Fig. 4.4).

HAADF (or Z-contrast) imaging using a dedicated STEM showed a dark contrast as compared with the GaN matrix at the position of the inversion domain nucleation site, and therefore confirms the presence of a low atomic number material associated to the nucleation event. Prepar-

Figure 4.7: CBED patterns recorded (a) from the epitaxial matrix and (b) from the columnar defect shown in Fig. 4.6 confirms the presence of an inversion domain.
Figure 4.8: (a) HREM image of a narrow band of amorphous material at the nucleation site of an inversion domain. (b) EELS spectra from the amorphous band and the matrix showing the association of oxygen with the nucleation site.
ing samples thin enough for HREM observation confirmed the nature of such nucleation events to be narrow bands of amorphous material, 2-5 nm in thickness (Fig. 4.8a). EELS analysis shows an increase in the oxygen concentration and a drop in the nitrogen concentration at the thin planar nucleating site at the base of the inversion domain as compared with the nearby regions of the GaN matrix (Fig. 4.8b). This feature is attributed to remnant contamination from the mechano-chemically polishing technique used to prepare the substrates prior to growth. The oxygen-containing residue is presumed to be gallium hydroxide, a likely reaction product of the KOH etchant with GaN.

### 4.4 Conclusions

Homo-epitaxial MOCVD growth of GaN on the N-face of GaN substrate crystals exhibits a hexagonal growth hillock density of $10^5$ cm$^{-2}$. These defects are attributed to the nucleation of inversion domains at distributed amorphous bands of oxygen containing material, typically 2-5 nm thick, being remnant contamination from the mechano-chemical polishing technique used to prepare the substrates prior to growth.

### References


Chapter 5

Determination of polarity of GaN cross-section TEM specimens using quantitative electron diffraction\(^1\)

Abstract

In this chapter it is shown that electron diffraction patterns taken from small areas (typically 4-20 nm) of GaN cross-section TEM specimens allow unequivocal determination of the local polarity. As experimental data a set of diffraction patterns from an area with the same polarity but with increasing thickness due to the wedge-shaped morphology of the TEM specimen is used. The polarity is determined using a least-squares refinement procedure in which the local misorientation and specimen thickness is refined for the two possible polarities. The refinements show that one polarity has much better agreement between calculated and experimental intensities of reflections for all diffraction patterns in the set, allowing straightforward identification of the polarity.

\(^1\)The work presented in this chapter is based on the publication in Journal of Crystal Growth by H.W. Zandbergen, J. Jansen, A.R.A. Zauner, and J.L. Weyher
5.1 Introduction

In contrast to traditional III-V semiconductors, having a cubic structure, GaN has usually the hexagonal wurtzite structure. GaN grows on atomic scale by horizontal step movement in the direction perpendicular to the c-axis, which results on a macroscopic scale in \{0001\} oriented epitaxial layers and plate-like crystals. An important consequence is that in epitaxial growth either Ga- or N-face \{0001\} surfaces are formed. For basic research and for device structure patterning it is important to determine the polarity of the surface. Until now the determination of the polarity of the \{0001\} surface layer of GaN plate-like crystals and epitaxial layers have been realised by convergent beam electron diffraction (CBED) [1–3], X-ray photoelectron spectroscopy [4, 5], X-ray standing wave [6], X-ray anomalous dispersion [7], coaxial impact-collision ion scattering spectroscopy [8], reflection high-energy electron diffraction (RHEED) [9] and etching methods [3, 4, 9]. Alternatively, HREM investigations of inversion domains (IDs) defects, which are typical of epitaxial GaN films, can be used to determine the polarity.

In this chapter, quantitative electron diffraction on the TEM cross-section GaN specimens is used to distinguish the [0001] Ga-face from the [000\bar{1}] N-face. The main difference between electron diffraction and other diffraction techniques like X-ray and neutron diffraction is that the latter two can be described by kinematic diffraction theory, whereas electron diffraction requires a dynamic scattering theory. With kinematic diffraction the intensities of the reflections increase linearly with thickness. Dynamic scattering, which occurs in particular in electron diffraction, will change the intensities of all reflections with respect to each other as a function of specimen thickness. Therefore, kinematic refinement software [10–12] can only be used for electrons in the regime where dynamic scattering is negligible, which is for specimen thicknesses less than 3 nm for structures containing very heavy atoms, and less than 15 nm for hydrocarbons. For a noncentrosymmetric structure like GaN, the differences between the intensities of Friedel pair reflections (e.g. \( g \) and \(-g\)) will be very small for kinematic diffraction, allowing no easy distinction between the two polarities of GaN specimens. With dynamic scattering, however, the intensities of Friedel pairs can be very different, as shown in this chapter.

In structure refinements using electron diffraction data, mostly kine-
matic diffraction is assumed [10–12], because this allows a standard refinement procedure. On the other hand, in CBED, as used for the determination of the polarity [1, 2], dynamic diffraction is fully taken into account. But, structure refinement by CBED is limited because computing time increases exponentially with the number of variables to be refined and with the complexity of the convergent beam patterns (discs in the diffraction pattern, with structure-dependent intensity variations in the discs). Spence [13] gives an overview of CBED work in which the structure factors of a few reflections of simple structures (e.g. MgO and GaAs) are calculated.

Another approach was developed [14, 15] in which dynamic diffraction is also fully taken into account. An incident electron beam with only a small convergence is used (yielding rather sharp dots instead of discs) whereby only the integrated intensities of each reflection are determined. The convergence does not have to be known; the convergence should only be small enough to prevent overlap of reflections and to approximate the parallel electron beam used in the calculations. When using a field emission gun source one can make the electron beam as small as $\approx 1 \text{ nm}$, so one can take diffraction data from areas as small as necessary. Apart from the parameters related to the crystal structure, parameters like crystal thickness, crystal orientation and absorption factor can be refined simultaneously.

### 5.2 Experimental procedure

GaN epitaxial layers were grown on sapphire substrates by the MOCVD technique. The parameters of the growth process were the same as described in Ref. [16].

Electron transparent areas were obtained by conventional ion milling. Electron microscopy was carried out using a Philips CM30UT electron microscope equipped with a field emission gun operated at 300 kV. A 15 nm condenser aperture was used to obtain an electron beam with a small convergence. The electron diffraction patterns were recorded using a 1024 x 1024 pixel CCD camera with a dynamic range of 12 bits. Electron diffraction was performed with spot sizes of about 8 nm. Exposure times ranged from 0.4 to 2 s. A small spot size for electron diffraction is used to have a relatively small variation of thickness, since most crystal areas are wedge shaped. Calculations have shown [14] that a variation in thickness of the illuminated areas leads to an increase in the R-value and a less reliable
Table 5.1: Data of a set of electron diffraction, taken from a wedge-shaped area that is used for the determination of the polarity. The listed refined crystal orientation is that of the Ga-face surface. The accuracy in the determination of the crystal misorientation is ± 0.1°.

<table>
<thead>
<tr>
<th>Zone</th>
<th># Observed reflections</th>
<th>Thickness (nm)</th>
<th>Crystal misorientation (°)</th>
<th>R-value (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>About c</td>
<td>About b</td>
</tr>
<tr>
<td>[1 0 0 0]</td>
<td>74</td>
<td>3.6 (±0.4)</td>
<td>0.2</td>
<td>0.1</td>
</tr>
<tr>
<td>[1 0 0 0]</td>
<td>70</td>
<td>5.3 (±0.4)</td>
<td>0.2</td>
<td>-0.1</td>
</tr>
<tr>
<td>[1 0 0 0]</td>
<td>78</td>
<td>9.2 (±0.7)</td>
<td>0.4</td>
<td>0.9</td>
</tr>
<tr>
<td>[1 0 0 0]</td>
<td>69</td>
<td>13.8 (±0.4)</td>
<td>0.2</td>
<td>0.8</td>
</tr>
<tr>
<td>[1 0 0 0]</td>
<td>90</td>
<td>15.4 (±0.8)</td>
<td>0.2</td>
<td>0.8</td>
</tr>
<tr>
<td>[1 0 0 0]</td>
<td>75</td>
<td>18.3 (±0.6)</td>
<td>0.0</td>
<td>0.7</td>
</tr>
<tr>
<td>[1 0 0 0]</td>
<td>81</td>
<td>20.9 (±0.4)</td>
<td>0.3</td>
<td>0.2</td>
</tr>
<tr>
<td>[1 0 0 0]</td>
<td>56</td>
<td>23.1 (±0.3)</td>
<td>0.0</td>
<td>-0.1</td>
</tr>
</tbody>
</table>

structure determination. Refinements were performed using the recently developed software package MSLS [14,15], in which multislice calculation software is combined with least-squares refinement software used in X-ray crystallography. With multislice calculations, which are routinely used for image calculations of HREM images, dynamic diffraction is taken into account explicitly. The agreement between the intensities of the model and the experimental data is expressed with $R = \sum (I_{obs} - I_{calc})^2 / \sum I_{obs}^2$. In the least-squares MSLS refinement this R is minimised. Standard deviations, given in Table 5.1 between brackets, are based on the statistics in the refinement and consequently experimental errors are not included.

5.3 Simulations

[000 1] diffraction patterns for the two polarities in the absence of crystal misorientation were calculated for thicknesses in the range from 1 to 20 nm and perfect [1 0 0 0] orientation using standard multi-slice software. The correlation between the diffraction patterns of the two polarities for equal thicknesses is given in Fig. 5.1. Whereas the correlation is relatively high for thicknesses around 1 and 20 nm, it is poor in the thickness range from 4 to 15 nm so that it should be relatively easy to distinguish between the two polarities.
Figure 5.1: Correlation as a function of thickness of the intensities of the reflections of [1 0 0] diffraction patterns for the two polarities in the absence of crystal misorientation. The intensities were calculated for 300 keV electrons using standard multi-slice software.

5.4 Results and discussion

Fig. 5.2a shows a [1 0 0] HREM image of a GaN film near the film surface with an inversion domain. This inversion domain is relatively broad. It originated in the buffer layer and is stretching throughout the whole epitaxial layer. The inversion domain boundaries are parallel to the c-axis of GaN. The total volume of the inversion domains in the film is less than 2%. The HREM image shown in this figure is a section from of a larger image negative, which also contained a hole and close to that an extreme thin area, which shows the same image contrast as the area used for Fig. 5.2a. Using an amorphous part the focus of the HREM can be estimated. Given the small thickness of the specimen (< 10nm) and the used focusing condition, the white dots in the HREM image are located at the positions of the Ga atoms. Thus the shift in position of the white dots across the inversion domain boundary allows determination of the local polarity as is illustrated in Figs. 5.2b and c. Fig. 5.2b shows an enlargement of the right inversion domain boundary in Fig. 5.2a. The atomic arrangement is depicted in Fig. 5.2c. Using the GaN lattice conversion from Ref. [3] it is clear that the matrix has Ga-polarity and the inversion domain has N-polarity.
Figure 5.2: [1 0 0 0] HREM image of a GaN film near the surface (towards the top) of the film. (a) shows and inversion domain, the two inversion domain boundaries (IDB) and the surrounding matrix. (b) shows a magnification of the right IDB. The white dots are approximately located on the Ga atoms because these atoms scatter much more than the N atoms. From the change in position of the white dots across the IDB it is clear that the matrix must have a Ga-polar orientation, as schematically illustrated in (c).

For the recording of the electron diffraction patterns, an area well away from inversion domains was taken. Diffraction patterns were recorded starting from the edge of the specimen along a line approximately parallel to the c-axis of the GaN film. This gives a series of electron diffraction patterns with increasing thickness because of the wedge shape of the specimen.

After indexing the reflections (except for the polarity) in the diffraction patterns, the integrated intensities of the diffraction spots were determined. This was done by including the position of a reflection in a box or circle, the size of which is determined by the background level: if by enlarging the box or circle no extra intensity above the background is found, the optimal size is reached. A larger box would contain the same
net intensity with larger calculation errors.

The refinements were done with the software package MSLS [14]. The results of the refinements using eight data sets from an area, of which it was certain that it did not contain an inversion domain, are presented in Table 5.1. Evidently, the refinements with the Ga-polar orientation give much lower R values for all data sets. Table 5.1 also gives the refined crystal misorientation in degrees about the b- and c-axis. A gradual change can be observed whereby the tilt is largest about the b-axis, which is quite logical given the morphology of the specimen (wedge shaped along the c-axis).

Since inelastic scattering hampers CBED analysis, we have analysed [17] the effect of inelastic scattering on our method. Using energy-filtered imaging we compared nonfiltered, zero- and plasmon-loss diffraction patterns from the same areas of YBa$_2$Cu$_3$O$_7$. No significant differences in our diffraction patterns (accept for scaling) did occur. This can be understood considering that most inelastic scattering is still present in the diffraction spots. For CBED this leads to a loss of contrast in the diffraction discs, but in our method where only the integrated intensity of the the diffraction spot is taken this is not a problem. This is confirmed by the clear differences in R values for the two polarities for the thin areas, where the inelastic scattering is very small.

5.5 Conclusions

In conclusion, a method based on a set of diffraction patterns is shown to be a useful tool in determining the absolute polarity of GaN on a very local scale. The recording of the diffraction patterns is easy and takes 1 min for a series of ten diffraction patterns. The most time-consuming part is the refinement, which takes 10-60 min for a single data set depending on the computer power.

References


Chapter 6

Homo-epitaxial GaN growth on exact and misoriented single crystals: suppression of hillock formation

Abstract

GaN single crystals were used as substrates for MOCVD growth. The (000\text{\bar{I}}) plane of the substrate crystals was polished to obtain off-angle orientations of 0°, 2°, and 4° towards the [10\text{\bar{1}}0] direction. The highest misorientation resulted in a reduction of the hexagonal hillock density by nearly two orders of magnitude as compared with homo-epitaxial films grown on the exact (000\text{\bar{I}}) surface. The features that are still found on the 4° off-angle sample after growth can be explained by a model involving the interaction of steps, introduced by the misorientation, and the hexagonal hillocks during the growth process. Following from this explanation it could be concluded that surface diffusion is not important during growth on the N-face. The material quality of the N-face was examined by photoluminescence (PL) measurements. The PL spectrum measured at 5K shows dominant donor bound excitons with a FWHM of 1.4 meV as well as free excitonic transitions.

\footnote{The work presented in this chapter is based on the publication in Journal of Crystal Growth by A.R.A. Zauner, J.L. Weyher, M. Plomp, V. Kirilyuk, I. Grzegory, W.J.P. van Enckevort, J.J. Schermer, P.R. Hageman, and P.K. Larsen and preliminary TEM results obtained in the cooperation with H.W. Zandbergen and F. Morissey.}
6.1 Introduction

Gallium nitride (GaN) and related III-nitride semiconductors have attracted an enormous attention during the last decade, since these nitrides have many practical applications in the optoelectronics field. Heteroepitaxial as well as homo-epitaxial growth of III-nitrides is commonly performed along the c-axis of the wurtzite material, which is either in the [0001] direction (Ga-face) or in the [000\bar{1}] direction (N-face). For films obtained by metalorganic chemical vapour deposition (MOCVD) it was found that the surface morphology depends significantly on whether growth occurs in the [0001] or [000\bar{1}] direction [1–3].

For GaN growth in the [000\bar{1}] direction, hexagonal pyramids tend to be formed on the layer. The inversion domain, outcropping at the centre of the point-topped pyramids, apparently causes hillock formation as a result of the higher growth rate of this defect compared with the growth rate of the surrounding matrix [3]. Also for homo-epitaxial growth on the N-face, formation of hexagonal pyramids is observed [4,5].

Homo-epitaxial growth in the [000\bar{1}] direction has the advantage that the N-face of GaN single crystals can be mechano-chemically polished to obtain epi-ready substrates [6], while the Ga-face (for growth in the [0001] direction) can only be mechanically polished, so that reactive ion etching is needed for the preparation of epi-ready substrates [7].

For device applications smooth surfaces are required, therefore the formation of hexagons on top of the surface should be avoided. A common way to avoid growth features on top of the surface is the use of substrates with a slight misorientation with respect to the exact crystallographic plane [8]. In the present work, the surface morphology of homo-epitaxial GaN layers is studied for different off-angle orientations from the [000\bar{1}] direction. It is found that the formation of hexagonal pyramids can be suppressed by using sufficiently large misorientations, resulting in much smoother layers.

6.2 Experimental

Unintentionally n-doped GaN single crystals were used as substrates for MOCVD growth. These crystals were grown from nitrogen and liquid gallium under nitrogen pressures close to 15 kbar and at temperatures exceeding 1500°C [11]. The (0001) planes of the substrate crystals were
Mechano-chemically polished to obtain off-angle orientations of 0°, 2°, and 4° towards the [1 0 1 0] direction. The misorientation was confirmed by X-ray diffraction analysis. Mechano-chemical polishing was carried out using aqueous solutions of NaOH and KOH combined with diamond paste (0.1 μm), following the procedure described in Ref. [6].

Immediately before growth, the single crystals were cleaned in organic solvents, rinsed with de-ionised water, and blown dry with filtered nitrogen gas. Then the crystals were heated under a nitrogen/ammonia (N₂/NH₃) gas flow to the growth temperature in a horizontal, RF heated, MOCVD reactor. The homo-epitaxial GaN layers were grown at a temperature of 1040°C and a pressure of 50 mbar using trimethylgallium (TMG) and NH₃ as precursors, and hydrogen (H₂) as carrier gas. Growth was performed with a TMG flow of 63 μmol/min and a NH₃ flow of 2.5 standard litre per minute (slm), diluted with H₂ to a total flow of about 5 slm. The time of epitaxial growth was about 1 hour.

The surfaces of the homo-epitaxial GaN layers were investigated by optical differential interference contrast microscopy (DICM), a technique very sensitive for local differences in surface slope which are visualised by different shades of grey in the figures. Furthermore, atomic force microscopy (AFM), transmission electron microscopy (TEM), and photoluminescence (PL) were applied for characterisation of the samples. The TEM specimens were prepared by using a Ga-source focused ion beam workstation. For the PL measurements a HeCd laser (λ = 325 nm) with an excitation density of about 150 W cm⁻² was used as an excitation source.

6.3 Results and discussion

6.3.1 Surface morphology as a function of substrate misorientation

Optical examination with DICM of layers grown on (0 0 0 1) substrates without misorientation reveals a large number of hexagonal growth hillocks covering almost the entire surface. A typical example of such a morphology is given in Fig. 6.1a. Near the edges of the samples, the formation of hexagonal hillocks is reduced due to the effect of polishing-induced beveling (Fig. 6.1b).

The hexagonal base of the hillocks shown in Fig. 6.1a is 10-50 μm in size. The majority of the hillocks are regular, point-topped pyramids, al-
Figure 6.1: DICM images of a homo-epitaxial GaN layer grown on the N-face (0001) of a single crystal without misorientation. (a) Typical morphology encountered over almost the entire surface. (b) Near the edges of the sample the formation of hexagonal hillocks is reduced due to the effect of polishing-induced bevelling.
though some of them are macroscopically flat-topped or disrupted. A similar morphology has been observed for hetero-epitaxial GaN layers grown in the <0001> direction [3, 10]. Rouvière et al. [3] found that the occurrence of inversion domains in GaN films grown on sapphire, without a buffer layer, leads to the three-dimensional pyramidal growth as a result of the polarity dependence of the growth rate. The inversion domain of Ga-polarity, acting as a velocity source [11], grows faster than the surrounding matrix of N-polarity and a hillock develops.

In a detailed transmission electron microscopy (TEM) study on the origin of the formation of the hexagonal hillocks in homo-epitaxial films, it was found that the inversion domains nucleate at thin platelets of oxygen containing amorphous material [4, 5]. These platelets are possibly a remaining contamination from the mechano-chemical polishing process used to prepare the substrate prior to growth. The virtual (0001) plane of macroscopically flat-topped pyramids is faceted due to steps generated by a step source located at the centre of the hexagon. These steps originate from dislocations at the centre of such hillocks, as was concluded from the occurrence of interlaced spirals with atomic height steps [12].

For the sample with a 2° off-angle orientation towards the [1 0 1 0] direction the density of hillocks at the surface is significantly lower compared to the exactly oriented sample. The surface features, still present, have lost their symmetric hexagonal shape, i.e. the facets of many hillocks are not equally sized (Fig. 6.2a).

The misorientation induced step flow starts to overgrow part of the hexagons. For the majority of the features on the surface, however, the source of growth, originally located at the centre of the hillock for exactly oriented samples, is still present. The fact that the step flow resulting from the 2° misorientation appeared to be insufficient to overgrow the centres of the steeper hexagons indicates that these centres remain to be a dominant source of steps.

For the sample with a 4° off-angle orientation towards the [1 0 1 0] direction the hexagonal features are largely absent from the surface, resulting in areas which are much smoother than samples grown without misorientation (see Fig. 6.2b). Obviously the step flow resulting from the misorientation, which is doubled compared to the 2° off-angle sample discussed above, is sufficient to overgrow the centres of the majority of the hexagons. In an estimation of the hexagonal hillock density it is found that the density for the 4° misorientated specimen is two orders of magnitude lower as
Figure 6.2: DICM pictures of a homo-epitaxial GaN layers grown on the N-face of single crystals with a misorientation of (a) 2° and (b) 4° towards the [1010] direction.
**Figure 6.3:** The dependence of the hexagonal hillock density on the misorientation of the GaN substrates; the line represents the best exponential fit through the data points.

compared with that of specimens with exact orientation (see Fig. 6.3).

Although, for 4° misorientation most hexagonal features disappeared from the surface, there is still a number of partial and complete hexagonal hillocks that can be recognised, as shown in Fig. 6.4. Fig. 6.4a shows a kind of plateau with a hexagonal hillock near its centre, dividing the plateau in two parts. The two regions, which border on the edges of the hillock, are not equally sized. From the difference in size of those two areas it can be concluded that the misorientation is not exactly in the [10\(\bar{1}0\)] direction but must be slightly different from it. The plateau ends abruptly in a steep step bunch perpendicular to the [10\(\bar{1}0\)] direction.

Partly overgrown hexagonal hillocks were also found on the sample, as is presented in Fig. 6.4b. Like the hillock shown in Fig. 6.4a, the two side areas that border on the hexagon are not equal in size and again the plateau terminates in the [10\(\bar{1}0\)] direction resulting in a sharp, steep edge. Fig. 6.4c shows two plateaus that again terminate in a sharp edge, as is already seen in Figs. 6.4a-b. For the feature shown at the top of Fig. 6.4c (indicated by the letter A) a discontinuity in slope of the plateau itself can be recognised at the place where the plateau starts to narrow.
Figure 6.4: DICM photos of different surface features found after growth on the 4° misoriented single crystal. The arrows in c) indicate the discontinuity line on the plateaus.
For the feature shown at the bottom of Fig. 6.4c (indicated by the letter B) a part of the central hexagon can still be recognised. For B the arrow indicates a first beginning of a discontinuity line on the plateau, which is parallel to the direction of the discontinuity line of feature A. Finally, a sharp line shaped edge on the otherwise quite smooth surface area is imaged at the centre of Fig. 6.4d. On the plateaus of the surface features of Figs. 6.4a-c steps sloping towards the \( <1\ 1\ 2\ 0 > \) directions can be seen. The AFM image of the feature presented in Fig. 6.4b shows these steps even more clearly (Fig. 6.5).

### 6.3.2 Mechanism for hillock development and overgrowth

A plausible explanation for the occurrence of the surface features shown in Fig. 6.4 can be given. The sample was mechano-chemically polished to a 4° misorientation, thereby introducing steps approximately parallel to [\( 1\ 1\ 2\ 0 \)], over the sample. At the beginning of growth shallow as well as steep hexagonal hillocks tend to be formed. However, only steep hexagonal hillocks, which are formed by a more active step source, survive the propagation of the misorientation step train and will be present after a certain period of growth (see Fig. 6.4c). Less steep hillocks are overgrown in an early stage of the process or cannot be formed at all. In Fig. 6.1a

![Figure 6.5](image)

**Figure 6.5:** (a) AFM image of a hillock on the homo-epitaxial film deposited on the 4° misoriented substrate. (b) Cross-section along the line indicated in (a).
it can be seen that the height of the hillocks varies over the sample. As mentioned before, the highest hillocks, with steeper side facets, show an increased contrast. About 3% of the hillocks presented in Fig. 6.1 show this increased contrast, which is in agreement with the previous observation of the reduced hillock density by almost two orders of magnitude for the 4° misoriented sample as compared with the samples without misorientation. In addition, the activity of many individual hillocks decreases or fluctuates (see Fig. 6.6) during growth.

If the activity of the step source at the hillock centre decreases and height growth slows down, the base of the hillock still expands. The time dependent development of a steep hillock of which the height growth is suddenly almost stopped is represented schematically in Fig. 6.9. The reason for the differences and often sudden changes of the activity of step generation is not known. To investigate the reason of the activity fluctuation, site-specific cross-sectional foils through the original centre of the hillock of Fig. 6.6 were prepared by using the Focused Ion Beam technique. Preliminary transmission electron microscopy measurements show a similar nucleation event for the defective central region of the hillock as seen in chapter 4. In Fig. 6.7 it is seen that the core of the hillock emanates from a small nucleus near the epilayer/substrate interface. Energy-dispersive

![AFM image of a hexagonal hillock found on the homo-epitaxial film deposited on the 4° misoriented substrate, indicating a fluctuation in activity of the growth centre during growth.](image)

**Figure 6.6:** AFM image of a hexagonal hillock found on the homo-epitaxial film deposited on the 4° misoriented substrate, indicating a fluctuation in activity of the growth centre during growth.
**Figure 6.7:** TEM cross-sectional image through the centre of the hillock of Fig. 6.6.

X-ray (EDX) measurements on this nucleus showed the presence of oxygen. The diffraction pattern measured at the defective core region of the hillock show a tilting of the lattice by about $2^\circ$ (Fig. 6.8).

In its steep period as well as in its first time of slow height growth the slowest advancing steps, parallel to the $<11\overline{2}0>$ directions, bound the hillock (Fig. 6.9a). The steps introduced by the misorientation are more or less parallel to $[\overline{1}1\overline{2}0]$, which means that these steps also move slowly. Steps in other directions move considerably faster. Steps from the left and right hand side of the hillock form a re-entrant corner with the steps induced by the misorientation (see Fig. 6.9). Due to an increased effective supersaturation near this region the step velocity increases and the re-entrant corner becomes rounded [13]. Now a whole range of step orientations is created, and steps in the fast moving $<11\overline{2}0>$ directions are selected to propagate over the plateaus.

Fig. 6.9b represents a hillock of which the step source has already been inactive for some time at the moment that the misorientation-induced steps just start to overgrow the flat top of the hillock. The steps on the plateau, left and right from the hillock, move faster than the steps intro-
duced by the misorientation. During continued growth the hexagon-centre will be overgrown (Figs. 6.9d-e).

From the time development of Fig. 6.9 it becomes also clear that as long as the hillock, or part of it, is present on the surface the plateaus next to the hillock become wider along $\langle 10\overline{1}0 \rangle$. Since the plateaus are formed from steps emerging from the re-entrant corner, the plateaus were narrower at earlier times of growth when the hillocks were smaller. This explains the triangular shape of both plateaus parts adjacent to the hillocks and the fact that the hillock is more or less located at the centre of the plateau.

From the triangular geometry of the plateau it is possible to determine the difference in the slowest and fastest step velocities, being $v_{\text{step} < 10\overline{1}0>$ and $v_{\text{step} < 11\overline{2}0>$ respectively. By the use of basic goniometric relations it can be shown the relation between these velocities is

$$\frac{v_{\text{step} < 11\overline{2}0>}}{v_{\text{step} < 10\overline{1}0>}} = \frac{\sin(\theta + \alpha)}{\sin \theta},$$

(6.1)

where $\alpha$ is the angle between both step directions ($30^\circ$) and $\theta$ is the angle of the sharp corner of the triangular plateau (see Fig. 6.9). For the $\theta$ value of $17^\circ$ as found in Fig. 6.4 the velocity ratio is 2.5. The same value was
**Figure 6.9:** Schematic representation of the time-dependent development and subsequent overgrowth of a hexagonal hillock. Image a) is two times enlarged. The arrow in f) indicates the discontinuity line on the plateau, cf. figure 6.4c.
found by directly measuring the distances between the small step bunches on both the misoriented surface and the plateau, as can clearly be seen in the AFM image of Fig. 6.5.

On feature A in Fig. 6.4c, at the place where the plateau starts to become narrower, the expanding remnants of hillock borders can be recognized. From the moment that the hillock is half overgrown, and no steps opposite to the misorientation-steps exist (Fig. 6.9d), the position of the re-entrant corner moves along the intersection line of the remaining hillock side facet and the plateau during prolonged growth (Fig. 6.9e) and will finally evanesce (Fig. 6.9f). As argued before, only steps in the fastest moving direction are selected at the re-entrant corner. The boundary between the stepped plateau areas and the central region of the plateau, which is more or less parallel to the (0001) plane, is given by the discontinuity in slope as indicated by arrows in Fig. 6.4c. The boundary corresponds with the last fast \(<11\bar{2}0>\) step emitted from the vanishing hillock. During continued growth and assuming that the steps at the steep edge of the plateau propagate as fast as the misorientation steps, the plateau expands in the left and right directions, only due to expansion of the flat central area. Apart from translation the stepped triangular plateau regions do not change in time (Fig. 6.9).

It should be noted that the images of Fig. 6.4 do not necessarily represent a development in time, since all of the features were found on the sample after 75 minutes of growth. Namely the moment at which the situation represented in Fig. 6.9b occurs during the growth process depends on the time-dependent activity of the growth source of the hillock during the earlier stage of the growth run, which is different for the individual hillocks. Therefore, different stages of feature development appear side by side on the same grown layer. A hillock of which the step source has become inactive at a very early stage of growth will be overgrown much faster, i.e. the time between the different stages of the overgrowth process presented in Fig. 6.9 will be much shorter. Overgrowth of the hillock will also be faster for higher misorientations towards the \([10\bar{1}0]\) direction and same step source activity of the hillock. However, still some very narrow plateaus will remain on the surface as shown in Fig. 6.4d. Overgrowth of the remaining part of the hillock can only be realised if steps introduced by the misorientation move faster than the steps of the remainder of the hillock. Since steps in the \(<11\bar{2}0>\) directions move 2.5 times as fast as steps in the \(<10\bar{1}0>\) directions, a misorientation towards the \([11\bar{2}0]\)
direction should be chosen in order to overgrow the surface feature completely.

The two-dimensional point group symmetry of a GaN growth layer with thickness $d_{0002}$ in the wurtzite point group $P6_3mc$ is 3. From this it follows that the surface diffusion tensor must be isotropic [14]. In other words, if surface diffusion is the rate-determining step of growth, then the step velocity is independent of step orientation. However, in the present work it is found that steps in the $<11\bar{2}0>$ directions move 2.5 times as fast as steps in the $<10\bar{1}0>$ directions. Therefore it can be concluded that at least for the slowly propagating steps, the growth rate is mainly determined by the integration of growth units at the step positions. If surface diffusion is rate limiting, closely spaced steps are expected to move slower than widely spaced steps [15]. Fig. 6.5b displays a 2D height profile, measured by AFM, which shows a sharp transition in slope at the front of the growth hillock. If the widely spaced steps in region A move faster than the closely spaced ones in region B, then according to the kinematic wave theory of step propagation [16,17] the transition in slope will be gradual. A discontinuity will only develop if the step velocity in B is equal or larger than in A. This once more confirms that for the slow moving steps the growth rate is determined by step integration. Since the fast propagating steps are straight rather than curved, it is suggested that also for these steps integration of growth units at step positions is the rate-determining factor. In fact, step integration rather than surface diffusion is rate limiting in the MOCVD growth of N-face $(00\bar{1}1)$ GaN, under the applied growth conditions.

### 6.3.3 Photoluminescence properties versus misorientation

Low temperature (5K) photoluminescence measurements were performed to investigate the optical properties of the homo-epitaxial films. As shown in Fig. 6.10 the $(00\bar{1}1)$ sides of the single crystal substrates, before growth, show a broad PL emission pointing out a high free carrier concentration. Homo-epitaxial films grown on the N-face of exactly oriented substrates reveal PL spectra with bands that are much narrower and show a higher intensity. The high free electron concentration of these exactly oriented $(00\bar{1}1)$ samples is a clear signature of easy donor incorporation into the N-face epilayers during growth [18].

Strong improvement of the material quality of the homo-epitaxial N-
face layers was achieved by introducing a misorientation to the substrate. The PL signal of the 4° misoriented sample is dominated by donor bound excitons (DBE), with a FWHM of the DBE (at 3.4708 eV) of 1.4 meV. Even free excitonic transitions (FEA) can be seen, as shown in Fig. 6.10. By comparison of data found in Refs. [18,19] and considering the very narrow photoluminescence peaks shown in Fig. 6.10, the residual donor concentration is expected to be in the range of $10^{17} \text{ cm}^{-3}$ for the sample 4° misoriented towards $[1 0 \bar{1} 0]$. For films grown on GaN substrates with a 4° misorientation towards the $[1 \bar{1} 2 0]$ direction, the FWHM of the DBE is found to be 0.9 meV, which to our knowledge is the narrowest peak reported for homo-epitaxial GaN grown on the N-face of the single crystals. Detailed PL results are presented in chapter 8.
6.4 Conclusions

During MOCVD growth of GaN films on the N-face of exactly oriented GaN single-crystal substrates, hexagonal pyramids are formed. In this study it is found that the formation of these pyramids can be suppressed by the use of substrates with a slight misorientation towards the [1 0 1 0] direction. For a substrate misorientation of 4° the density of the elevations on the homo-epitaxial film is reduced by almost two orders of magnitude as compared with exactly oriented GaN substrates. The morphologies of those features that persist on the 4° off-angle sample during growth can be explained by a model involving the interaction of steps introduced by the misorientation with steps originating from the hillocks.

It is found that the step velocity is dependent on the step orientation: steps in the <1 1 2 0> directions move 2.5 times as fast as steps in the <1 0 1 0> directions. If surface diffusion had been the rate-determining step during growth, step velocity would have been isotropic. Therefore it can be concluded that step integration of growth units rather than surface diffusion is rate limiting in the MOCVD growth of N-face GaN.

Besides the improvement in surface morphology the higher misorientation also resulted in a strong improvement of the material quality of the N-face. A FWHM of the DBE luminescence peak of 1.4 meV was found for the homo-epitaxial layer grown on the 4° off-angle single crystal.

Considerations following from the model indicate that for a further improvement of the surface morphology by reduction of the hillock density either substrates with larger misorientations or, since the step velocity is highly anisotropic, with misorientation towards the [1 1 2 0] direction are needed.

References


Chapter 7

Homo-epitaxial growth on the N-face of GaN single crystals: the influence of the misorientation on the surface morphology

Abstract

GaN single crystals are used as substrates for homo-epitaxial growth by MOCVD. Prior to growth the N-face, or (0001) plane, of the substrate crystals is polished to obtain off-angle orientations of 0, 2, and 4° towards the [1120] direction. The hillock density of the homo-epitaxial films grown on the misoriented substrates is decreased as compared with the layers grown on the exact N-face. However, in addition to the hillocks, triangular-shaped pits are formed on the films grown on the misoriented substrates. The formation of the triangular-shaped pits is described by the blockade of the anisotropic step-flow growth.

\(^1\)The work in this chapter is based on the manuscript submitted to Journal of Crystal Growth by A.R.A. Zauner, E. Aret, W.J.P. van Enckevort, J.L. Weyher, S. Porowski, and J.J. Schermer.
7.1 Introduction

Hetero-epitaxial as well as homo-epitaxial growth of GaN is commonly performed along the c-axis of the wurtzite material, which is either in the [0001] direction (Ga-face) or in the [000\bar{1}] direction (N-face). It was found that the surface morphology depends significantly on whether growth occurs in the [0001] or [000\bar{1}] direction [1–3]. Hexagonal hillocks tend to be formed on GaN layers grown in the [000\bar{1}] direction for both hetero-epitaxial [3] and homo-epitaxial [4,5,6] deposition.

A technical advantage of homo-epitaxial growth in the [000\bar{1}] direction is that the N-face of GaN single crystals can be mechnano-chemically polished to obtain epi-ready substrates [7], while the Ga-face can only be polished mechanically, so that reactive ion etching is needed for further preparation of proper substrate crystals [8].

For device applications smooth surfaces are required, therefore the formation of hexagons on top of the epi-layers should be avoided. In previous work [6] it was demonstrated that the use of N-face GaN substrates mis-oriented towards the [1\overline{1}0\overline{0}] direction leads to a suppression of hillock formation. For a substrate misorientation of 4°, the density of hillocks on the homo-epitaxial films was reduced by almost two orders of magnitude as compared with films grown on the exactly oriented GaN substrates. Additionally, the results indicated that a further reduction of the hillock density might be achieved by the use of substrates with a misorientation towards the [1\overline{1}20] direction. In order to verify this suggestion, growth in the present work was performed on N-face GaN substrates with a 0, 2, and 4° off-angle orientations towards [1\overline{1}20].

7.2 Experimental procedure

The homo-epitaxial layers were grown on top of unintentionally n-doped GaN single crystals using low-pressure metal-organic chemical vapour deposition (MOCVD). The single crystal substrates were grown from liquid gallium under nitrogen pressures close to 15 kbar and at temperatures exceeding 1500\degree C [9]. The (00\overline{1}) planes of seven substrate crystals were mechnano-chemically polished [7] to obtain substrates with exact (two samples) and off-angle orientations of 2° (two samples) and 4° (three samples) towards the [1\overline{1}20] direction.

Immediately before growth, the single crystal substrates were cleaned
in organic solvents, rinsed with de-ionised water, blown dry with filtered nitrogen gas, and loaded into the reactor. The crystals were heated under a nitrogen/ammonia (N$_2$/NH$_3$) gas flow to growth temperature. The homo-epitaxial GaN layers were grown at a temperature of 1040°C and a pressure of 50 mbar using trimethylgallium (TMG) and NH$_3$ as precursors, and hydrogen (H$_2$) as carrier gas. Growth was performed with a TMG flow of 63 µmol/min and a NH$_3$ flow of 2.5 standard litre per minute (slm), diluted with H$_2$ to a total flow of about 5 slm. The time of growth was 1 hour. The growth conditions for the experiments discussed in this paper are identical to the growth conditions applied for the N-face substrates misoriented towards the [1 0 1 0] described in ref. [6].

The surfaces of the homo-epitaxial GaN layers were investigated by differential interference contrast microscopy (DICM), two-beam interferometry (TBI) and atomic force microscopy (AFM).

### 7.3 Results and discussion

#### 7.3.1 Exact orientation

For a (0 0 0 1) substrate with exact orientation, DICM reveals a large number of hexagonal hillocks covering almost the entire surface of the homo-epitaxial layer (Fig. 7.1). For hetero-epitaxially grown GaN films on sapphire, without buffer layer, Rouvière et al. [3] found that the occurrence of inversion domains leads to three-dimensional pyramidal growth. The inversion domain of Ga-polarity, acting as a step source, grows faster than the surrounding matrix of N-polarity and a hillock develops. In a detailed transmission electron microscopy (TEM) study on the origin of the formation of the hexagonal hillocks in homo-epitaxial films, it was found that the inversion domains nucleate at thin platelets of oxygen containing amorphous material [4, 5]. These platelets are possibly a remaining contamination from the mechano-chemical polishing process used to prepare the substrates prior to growth.

In Fig. 6.1 it can be seen that there are different types of hexagons, some of them are point-topped while others have a flat-topped surface. On one of the macroscopically flat-topped hillocks a sharp submicron sized tip, which seems to serve as a source of atomic steps, is observed. Besides the tip, which is brighter in the AFM height image, two successive triangular-shaped terraces can be recognised in Fig. 7.2a. The triangular-terraces
Figure 7.1: DICM image of a homo-epitaxial GaN layer grown on the N-face (000$\bar{1}$) of a single crystal substrate without misorientation.

are 60° rotated with respect to each other and have a step height of one atomic layer as is expected from the fact that each wurtzite GaN monolayer with thickness $d_{0002}$ has a three-fold symmetry and its succeeding monolayer is 60° rotated to it. This alternating-effect of succeeding steps has been demonstrated earlier by STM analysis carried out by several research groups [10–12].

In the case of a hexagonal terrace only three from six step edges will have one dangling bond per edge atom, while the other three step edges (alternating with the first kind of step edge) will have two dangling bonds per edge atom. Following the terminology of Xie et al. [10], these step edges are named type B edge and type A edge respectively. Consequently, the type A edge containing two dangling bonds per edge atom will grow faster than the type B edge [10, 11]. Due to their faster propagation velocity the type A edges will grow out and a triangular shaped terrace bounded by B edges develops.

Since the slowest growth directions for the succeeding growth layer are rotated by 60° the triangular-shaped terrace will also be rotated by 60° with respect to the previous terrace as is shown in Fig. 7.2a. The fast
Figure 7.2: (a) AFM height image of a macroscopically flat-topped hillock found on a sample with exact orientation. In the centre of the triangular-shaped terraces a sharp submicron sized tip is located, which seems to serve as a source of atomic steps. (b) Schematic presentation of terraces, steps of two subsequent monolayers pile-up to form bilayer height steps.
growing steps of the upper layer will catch up with the slowly moving steps in the underlying layer and a bilayer height step equal to one unit cell forms as is schematically outlined in Fig. 7.2b.

Due to the anisotropic step-flow growth of the succeeding atomic layers, steps will be interlaced at the edges of the terraces. The concept of interlaced step patterns goes back to an early paper of Frank [13] and its occurrence in this case is a direct consequence of the \( \overline{6}_3 \) axis in the GaN space group \( \text{P}6_3\text{mc} \) [14].

The interlacing of steps can also be identified for the spirals observed on the nearly flat-topped hexagonal hillocks on samples examined in this work. Besides a growth spiral, forming a small point-topped hill (Fig. 7.3a), a second step source can be recognised on the large flat-topped hexagonal hillock as shown in Fig. 7.3b. The core of this second step source, which is placed near the original centre of the partly overgrown exact plateau of the large hillock, sticks out of the (000\( \overline{1} \)) surface (7.3b). This source might be related to an inversion domain, although its dimension (0.7 x 0.5 \( \mu \)m\(^2\)) is unusually large for an inversion domain. As can be seen from the step density of the two step sources, the spiral was the more active step source at the end of the growth process (larger number of closely spaced steps). In the early growth stages, however, the inversion domain must have been the most active step source since it is located at the centre of the hillock.

### 7.3.2 Misoriented substrates

For the homo-epitaxial layers grown on the misoriented substrates, 2° and 4° towards the [1 1 \( \overline{2} \) 0] direction, the surface morphology clearly differs from the morphology observed for the exact orientation. While for the exact orientation the entire surface is covered by hexagonal hillocks, the films grown on the misoriented substrates have relatively large areas that are free of disturbances in the morphology. Compared to the exactly oriented substrates, the density of hillocks is reduced by two orders of magnitude. In comparison with previously obtained results on substrates misoriented towards the [1 0 \( \overline{1} \) 0] direction [6], the samples with a 4° misorientation towards the [1 1 \( \overline{2} \) 0] direction show a density of hillock-shaped disturbances of the same order of magnitude (Fig. 7.4). However, in addition to the hillocks pits are formed in the homo-epitaxial layers with a
misorientation in the [1 1 2 0] direction (Fig. 7.5). The density of pits, for the 2° as well as the 4° misoriented samples, is between 2 - 4 x 10^4 cm^-2. For both degrees of misorientation the shape of the pits is equivalent. The pits have a triangular shape with the blunt corner of 120° pointing in the [1 1 2 0] direction. The intersection lines of the two steep walls of the pits and the (0 0 0 1) plane are parallel with the <1 0 1 0> directions. The depth of the pits is about 500 nm for the films grown on substrates with 4° misorientation. This is less than the film thickness which is of a typical value of 1.5 μm. The same kind of pits was incidentally observed near the edges of the samples with a misorientation towards the [1 0 1 0] direction, probably due to the effect of polishing induced beveling. Since the triangular pits shown in Fig. 7.5 do not have the shape of isosceles triangles, it can be concluded that the misorientation-induced step flow is not exactly oriented towards the [1 1 2 0] direction. Because this particular crystal was only polished partly, this left a clear intersection line between the misoriented and exactly oriented part of the crystal as indicated by arrows in Fig. 7.6. From the orientation of this line relative to the {1 0 1 0} side facets of the substrate the rotation of the misorientation away from the [1 1 2 0] direction could be accurately determined to be 9°.
Two of the three films grown on substrates with a $4^\circ$ misorientation towards [1 1 2 0] showed triangular pits that were homogeneously distributed over the surface. For the third film (Fig. 7.6), however, the triangular pits are not spread homogeneously over the surface but are partly arranged in lines (Fig. 7.5). The lines that are large enough (>450 $\mu$m) to determine the orientation with respect to the crystal axes with sufficient accuracy have a preferred orientation. The majority of the lines are parallel to the $<$10 1 0$>$ direction, while the other lines are parallel to the $<$1 1 2 0$>$ direction within a few degrees.

Before growth, DICM revealed numerous randomly oriented scratches on the surface due to improper polishing of this particular sample. The presence of these polish-scratches prior to growth could not only explain the alignment of the triangular pits in a line but also their equal size, which indicates that their formation started at the same moment i.e. at the beginning of the growth process. An alternative explanation for the
Figure 7.5: (a) DICM and (b) 50x50 μm 3D-AFM image of a homo-epitaxial GaN layer grown on the N-face of a single crystal with a 4° misorientation towards the [1120] direction, showing triangular-shaped pits in the epitaxial film.
Figure 7.6: DICM picture of the GaN single crystal after growth. The upper part of the substrate is 4° mis-oriented. The white arrows indicate the transition line between the exact and misoriented part of the sample. The misorientation is not exactly towards the [1 1 2 0] direction but is 9° rotated.
observed arrangement of the triangular pits along specific line directions can be that the pits are ‘nucleated’ on dislocation arrays in the substrate.

The mechanism for the formation of the triangular pits with a 120° top angle is probably related to the anisotropic step-flow growth of the epi-layer. From the atomic height step structure of the hillocks discussed in the previous section it can be deduced that steps induced by the misorientation in the [1120] direction consist of stable steps partials directed towards the [0110] and [10\overline{1}0] directions, which are interlaced as is shown in Fig. 7.7. The schematic presentation of the interlaced steps shown in Fig. 7.7 represents an idealised situation of interlacing. The propagation of the type A edges is only partly limited by the slowly moving type B edges of the underlying layers. The other part of the type A edges can continue to propagate over the underlying terrace as is indicated by broad arrows in Fig. 7.7. As a result of this step growth, the type A edge of the next layer can advance freely over the newly formed terrace. Consequently, the steps induced by the misorientation in the [1120] direction will grow faster as compared with steps in the [10\overline{1}0] directions, since the propagation velocity of the [10\overline{1}0]-steps is determined by the slowly moving type B step edge.

Figure 7.7: Schematic presentation of the misorientation induced steps towards the [1120] direction. The broad arrows indicate the direction in which the fast type A edge can freely propagate over the underlying terrace.
The triangular pits in the surface of the homo-epitaxial films are very probably formed due to a blockade of the steps at a particular point. At this point the steps resulting from the misorientation cannot continue in the [11\bar{2}0] direction and break up in two larger individual \(<10\bar{1}0>\) components at both sides of the pinning point. The reduced velocity of these blocked step partitions will induce step bunching by collision of the faster interlaced steps coming from behind. This results in a triangular pit with a 120° top angle and sidewalls formed by bunched \(<10\bar{1}0>\) steps. The actual cause for the pinning of the steps is not observed with AFM and SEM, indicating that the source for the step obstruction is very small.

Incidentally a flat-topped hillock is located near a triangular pit. Since the top face of the hexagonal hillock is a \((00\bar{1}0)\) facet it can serve as a reference point to determine the misorientations of the surrounding areas. The slope of the triangular pit wall, near to the top angle of the pit, is found to be 32° ± 2° as measured with AFM. A comparable result was found with two-beam interferometry. Using this technique the slope of the pit walls near the top angle was found to be 34° ± 4° and diminishes gradually as the distance from the centre of the pit increases (Fig. 7.8). The values found with both techniques are close to the slope of a \(\{10\bar{1}3\}\) plane. The bottom of the pit has a misorientation of about 2° towards the [11\bar{2}0] direction, for the layers on the 4° misoriented substrates. The films grown on substrates misoriented towards the [11\bar{2}0] direction showed a clear improvement of the surface morphology with respect to films deposited on exactly oriented substrates. However, as compared with layers grown on substrates misoriented towards [10\bar{1}0] the morphology gets worse, due to the additional pits that appear in the surface. Photoluminescence results, presented in chapter 8, show a remarkable reduction of the unintentional/intrinsic donor concentration for films deposited on substrates misoriented towards [11\bar{2}0] with respect to layers grown on exactly oriented substrates. Also in comparison with films grown on substrates misoriented towards [10\bar{1}0] the line widths of the excitonic transitions decreases and the intensity of luminescence increases [15, 16].

### 7.4 Conclusions

MOCVD-growth on the N-face, i.e. \((00\bar{1}0)\) plane, of GaN substrate crystals with a 2° and 4° misorientation towards the [11\bar{2}0] direction resulted in a large reduction of the hillock density as compared with exactly
oriented substrates. In comparison with homo-epitaxially grown GaN films on substrates with a misorientation towards the $[10 \bar{1} 0]$, the hillock density was found to be of the same order of magnitude. However, the GaN layers grown on the miscut substrates towards $[11 \bar{2} 0]$ showed pits in the film surface after growth. The formation of these pits is described by a blockade of the anisotropic step-flow growth.

Acknowledgements

Stefan Müller is acknowledged for the AFM measurement of Fig. 6.2.

References


Chapter 8

Photoluminescence study of homo-epitaxial films grown on exact and misoriented single crystal substrates

Abstract

Homo-epitaxial GaN layers were studied by photoluminescence (PL). The GaN films were grown on exact Ga-face and N-face GaN single crystal substrates as well as on vicinal N-face substrates by metal-organic chemical vapour deposition. In contrast to broad PL emission in exact (0001) layers, narrow-bound (0.9 meV) and free- (A and B) excitonic transitions were observed for the epilayers deposited on the misoriented substrates. By following the PL spectra as function of temperature and excitation power, the main optical transitions in the Ga- and misoriented N-face layers were found to be the same. The observed differences are related to the distinct creation of donor and acceptor states in both kind of samples.

---

8.1 Introduction

In hetero-epitaxy, such as GaN on sapphire, the lattice mismatch and different expansion coefficients of the epilayer and substrate cause a high density of defects and a biaxial strain in the hetero-epitaxial layer changing the basic optical properties of the material [1−4]. In contrast, homoepitaxial GaN layers correspond to almost stress-free material [5] with a much lower dislocation density (10^4−10^6) [6]. Superior optical quality has been demonstrated for (0001) Ga-face layers, showing excitonic transitions narrower than 1 meV [6, 7]. From a technical point of view, N-face GaN epilayers, are also very attractive since, in contrast to Ga-face films, they are easily processable by mechano-chemical polishing. However, epitaxial layers grown on a N-face GaN substrate generally reveal a rough surface morphology with hexagonal hillocks and a high free-carrier concentration [8]. The lack of good homo-epitaxial N-face layers has also hampered the study of polarity-related effects in GaN. In order to improve the morphology of these layers it was recently proposed to grow N-face films on a misoriented GaN substrate [9]. The miscut introduces additional steps on the substrate surface leading to an overgrowth of hillocks and potential hillock nucleation centers.

In this chapter, results of a photoluminescence (PL) study of homoepitaxial GaN (Ga-face and N-face) is presented. PL spectroscopy is used to compare the optical properties of exact N-face (0001) films with layers deposited on misoriented substrates with off-angles of 2° and 4° towards [1 1 2 0] and 4° towards the [1 0 1 0] direction. By using a N-face misoriented substrate, an improved epilayer morphology together with a significant suppression of the donor concentration was achieved. As a result of the optical quality of the N-face film was found to be drastically improved, enabling a direct comparative study of epilayers of Ga and N polarities.

8.2 Experimental

Unintentionally n-doped GaN single crystals were used as substrates for MOCVD growth. The plate-like GaN single crystal substrates were, typically, 100-200 μm thick with a surface area of 30-50 mm² and a free-electron concentration close to 5 x 10^{19} cm^{-3}. The details of their structural properties and the growth technique have been described elsewhere [10, 11]. Prior to epitaxial growth, mechano-chemical polishing (for
the N-face) or mechanical polishing with subsequent reactive ion etching (for the Ga-face) were applied in order to obtain smooth substrate surfaces. Nominally undoped GaN epilayers were deposited on the GaN substrates at a temperature of 1040°C and a pressure of 50 mbar using trimethylgallium (TMG) and ammonia (NH₃) as precursors, and hydrogen (H₂) as carrier gas. Growth was performed with a TMG flow of 63 μmol/min and a NH₃ flow of 2.5 standard litre per minute (slm), diluted with H₂ to a total flow of about 5 slm. The time of epitaxial growth was about 1 hour, resulting in homo-epitaxial layers with a thickness of approximately 1-2 μm.

PL measurements were performed at temperatures from 4 to 110 K. A HeCd laser (325 nm) was used for excitation with power densities up to I₀ = 50 W/cm², incident at approximately 30° to the normal of the sample surface. The PL emission was dispersed by a 0.6 m monochromator and detected by a cooled GaAs photomultiplier. The spectral resolution was 0.4 meV in the region from 3.2 to 3.55 eV, unless stated otherwise.

8.3 Results and discussion

Low-temperature PL spectra of an exact (0001) Ga-face, a (0001) N-face, and a miscut (0001) N-face epilayer are presented in Fig. 8.1. The epitaxial layers grown on the exact N-face substrate result in a broad PL emission, indicating a high free-electron concentration as a consequence of either intrinsic donor generation or easy donor incorporation [14]. Different substrate preparation, either mechano-chemical polishing or mechanical polishing with subsequent reactive ion etching, did not influence the PL spectra in intensity or shape.

In contrast to the broad PL emission of the exact film, narrow excitonic lines are characteristic for the misoriented film. The main optical transitions observed in the misoriented N-face epilayers are very similar to that of Ga-face samples (Fig. 8.1), featuring narrow-bound and free-excitonic (FE) lines. Two peaks, FEₐ (3.4789 eV) and FEₜ (3.4832 eV), are associated with A and B free excitons, which dominate the PL spectra at higher temperatures for Ga-face as well as misoriented N-face films (Figs. 8.2a and 8.2b). The assignment of these peaks is also supported by reflectance measurements performed on similar (Ga-face) samples [7,15,16].

The PL line at 3.4714 eV (Fig. 8.1) was attributed to excitons bound (BE) to a neutral donor (D⁰BE) with an exciton localization energy of 7.5
meV. The full width at half maximum (FWHM) of the D\textsuperscript{0}BE peaks at 4 K goes down to 0.35 meV in the Ga-face layer, and to 0.9 meV in the misoriented N-face one (4° towards [11\overline{2}0]). The D\textsuperscript{0}BE line in the misoriented N-face sample is unusually narrow for homo-epitaxial GaN grown on the N-face of single crystal substrates. Although the narrow PL peaks of the misoriented N-face sample show a strongly reduced free-carrier concentration, the dominant character of the D\textsuperscript{0}BE peak at low temperature still indicates a considerable amount of donors.

By comparison with similar homo-epitaxial GaN results reported earlier [13,14] and considering the very narrow PL peaks, the free-carrier concentration of the top 100 nm of the layer is estimated to be in the range of low 10\textsuperscript{17} cm\textsuperscript{3} for both the Ga-face and the misoriented N-face samples.

The influence of different misorientations on the PL properties of the (000\,\overline{1}) GaN epilayers is presented in Fig. 8.3. All vicinal (000\,\overline{1}) GaN films show a distinct improvement in optical quality as compared to the exact (000\,\overline{1}) layers and reveal similar luminescence properties. From temperature-dependent PL of the GaN films 4° misoriented to [1\,1\,\overline{2}0]
Figure 8.2: Temperature-dependent PL spectra taken for (a) the Ga-face GaN epilayer at a temperature ranging from 5 to 100 K and (b) the misoriented N-face GaN epilayer (4° towards [1120]) at a temperature ranging from 4 to 110 K. The numbers on the curves denote the corresponding temperature in K.
Figure 8.3: Low-temperature PL spectra of homo-epitaxial GaN of different misorientations: 2° and 4° towards [1120], and 4° towards [1010].

and [1010], Fig. 8.2b and 8.4 respectively, it can be concluded that the PL lines in these samples are of the same origin. The misorientation in the [1120] direction seems, however, to lead to slightly better optical properties than in the [1010] one. The FWHM of the D⁰BE peak at 4 K is 0.9 meV for the 4° misorientation towards [1120] and 1.4 meV for the same degree of misorientation towards [1010]. The free excitons, FEₐ, are more pronounced in the sample with the [1120] miscut, whereas the A⁰BE are relatively stronger in the film with the [1010] miscut. The intensity of the donor-acceptor recombination peak (not shown) in the layers with the misorientation towards [1010] was found to be a few times stronger than in the [1120] direction. All these PL features emphasise that the miscut in the [1120] direction is the most profitable one since it results in an N-face epilayer with the lowest level of impurity states. It is well known that both intrinsic and incorporated impurities could behave as shallow donor/acceptor levels, however, it is unclear what kind of impurities and what kind of mechanism for the impurity reduction is involved.

Changing the angle of misorientation from 2° to 4° in the [1120] direction does not influence the PL properties significantly, although the PL
Figure 8.4: Temperature-dependent PL spectra taken for the N-face GaN epilayer with a misorientation towards the [1 0 1 0] direction at a temperature ranging from 4 to 70 K. The numbers on the curves denote the corresponding temperature in K.

peaks observed in the 2°-miscut epilayer are broader and less intense in comparison to the 4° misorientation.

It is important to note that the energy positions of almost all main PL peaks observed in the miscut N-face films are equal to those in the Ga-face layer. This also includes the peak labeled a (at 3.4752 eV), which can be associated with donor-bound excitons formed with participation of a deeper valence-band hole, and a peak originating from excitons bound to neutral acceptors (A0BE at 3.4556 eV). As a consequence, it can be concluded that the structural properties, i.e., lattice parameters of the Ga- and misoriented N-face layers, are identical.

The main difference between the high-quality Ga- and N-face layers is related to the spectral region around 3.466 eV. The origin of the emission lines BE1 (3.4654 eV) and BE2 (3.4664 eV) in this region seems to be ambiguous and has been previously indentified either as excitons bound to a neutral acceptor [16,17] or as ionized-donor-bound exitons [18,19].
Figure 8.5: Excitation-dependent PL spectra taken at 4 K for (a) the Ga-face GaN epilayer and (b) the misoriented N-face GaN epilayer (4° [1120]). The numbers on the curves denote the corresponding excitation intensities, with $I_0 = 50$ W/mm².
The BE\textsubscript{1} peak is more pronounced than BE\textsubscript{2} in the Ga-face sample but not present in the misoriented N-face one. In the Ga-face layer, the BE\textsubscript{2} peak can only be seen as a high-energy shoulder of the BE\textsubscript{1} line because it FWHM ($\approx 2$ meV) is larger than the separation between the BE\textsubscript{1} and BE\textsubscript{2} transitions ($\approx 1$ meV). The localization energies of these bound excitons are found to be 13.5 and 12.5 meV for BE\textsubscript{1} and BE\textsubscript{2}, respectively. The thermal quenching of the lines happens, however, earlier than for the D\textsuperscript{9}BE\textsubscript{1}, at 50 K for the BE\textsubscript{1} (Fig. 8.2a) and at 30 K for the BE\textsubscript{2} (Fig. 8.2b). This unusual behaviour is probably related to exciton tunneling from BE\textsubscript{1}/BE\textsubscript{2} to donor-bound or even free excitons that has been derived from the time decay of PL at temperatures above 30-40 K [16]. The excitation-dependent PL for the Ga-face layer in Fig. 8.5a shows saturation of the BE\textsubscript{1} peak intensity with increasing excitation power. On the other hand, the PL spectra for the misoriented N-face layer of Fig. 8.5b reveal no saturation of the BE\textsubscript{2} line even at higher excitations. Thus, from the temperature and excitation power-dependent PL it follows that the BE\textsubscript{1} and BE\textsubscript{2} peaks have different origins. It is supposed that the BE\textsubscript{1} peak can be assigned to excitons bound to an acceptor as this transition is not seen in the N-face samples, but dominates the spectrum of the Ga-face epilayer, in which the incorporation of acceptors is expected to be easier [14]. The origin of the BE\textsubscript{2} line can be another acceptor or donor present in both kind of epilayers. In order to identify the specific acceptor corresponding to the BE\textsubscript{1} peak and to determine the origin of the BE\textsubscript{2} peak, further investigations are needed.

### 8.4 Conclusions

It has been shown that the homo-epitaxial growth on misoriented N-face GaN single crystal substrates leads to a significant improvement of the optical properties of N-face epilayers. In comparison with the exact (000\textsubscript{1}) films a strong reduction in the donor concentration was achieved. The luminescence properties of the 2\textdegree{} and 4\textdegree{} misoriented layers towards [11\overline{2}0] and [\overline{1}0\overline{1}0] are essentially similar. Compared with the other misorientations the film with the 4\textdegree{} miscut towards the [11\overline{2}0] direction reveals slightly better optical properties. The main PL transitions, such as FE\textsubscript{A}, FE\textsubscript{B}, D\textsuperscript{9}BE, and A\textsuperscript{0}BE, were observed at the same energies for both Ga- and misoriented N-face samples. Temperature and excitation-dependent PL of the Ga-face sample reveals, however, an optical transi-
tion (BE$_1$), which is not present in the misoriented N-face film. It can be associated with excitons bound to a neutral acceptor, incorporated only in the Ga-face epilayer.

References


Chapter 9

Spectroscopic Ellipsometry on GaN: Comparison Between Hetero-epitaxial Layers and Bulk Crystals

Abstract
In the present study spectroscopic ellipsometry was used for characterising GaN bulk crystals obtained at high pressure and thin films grown on sapphire. The undoped GaN films grown by MOCVD show interference fringes below the fundamental gap. The ellipsometric data ($\Delta$ and $\Psi$), measured in the wavelength range between 500 nm and 680 nm, were analysed using a multilayer description in the transfer matrix formalism. For the thin films grown on sapphire the model includes a buffer layer, a GaN epilayer, and a hypothetical overlayer. Furthermore, both, the real and imaginary part of the complex refractive index were taken into account. The real part of the refractive index $n_1$ was found to follow a Cauchy-type of dispersion $n_1 = 2.290 + 0.06 \left( \frac{280}{\lambda - 280} \right)^2$. For bulk crystals $n_1$ was found to be $2.337 \pm 0.010$ at the wavelength of 632.8 nm. This value compares well with MOCVD grown GaN where $n_1(\lambda = 632.8 \text{ nm}) = 2.328 \pm 0.003.$

\footnote{The work presented in this chapter is based on the publication in MRS Internet J. Nitride Semicond. Res. by A.R.A. Zauner, M.A.C. Devillers, P.R. Hageman, P.K. Larsen, and S. Porowski}
9.1 Introduction

Due to its material properties gallium nitride (GaN) has attracted enormous attention in recent years, certainly after the success of GaN-based blue-light emitting diodes. The lack of lattice-matched substrates for epitaxial growth of GaN films has led to the application of a variety of substrates of which sapphire is most abundantly used [1]. Despite the large mismatch in the lattice constants between GaN and sapphire, a two-step growth process, proposed by Amano et al. [2], makes it possible to grow device quality hetero-epitaxial GaN layers. However, these layers are still highly defective thereby degrading device performance. GaN single crystals would provide perfect lattice matched substrates which can be easily cleaved. Although considerable progress has been made in increasing the size of the GaN single crystals [3], at present, their relatively small crystal-size is still a bottleneck for the application as lattice matched substrate.

Ellipsometry has been used by several authors [4-7] to study GaN. It is a non-destructive technique which can be performed on optically flat surfaces of almost any material in order to study surface as well as bulk properties. If polarised light is reflected from the sample at an angle of reflection $\varphi$, the reflected beam will be elliptically polarised. Dividing the p-polarised component by the s-polarised component one can define two ellipsometric quantities $\Delta$ and $\Psi$, given by,

$$\rho = \frac{R_p}{R_s} = \tan \Psi \exp (i\Delta). \quad (9.1)$$

The two parameters, $\Delta$ and $\Psi$, contain information on the sample as thickness and refractive index of the film. They are very sensitive to the presence of overlayers on the surface of the material such as a natural oxide layer or a rough surface layer [8,9]. In this paper ellipsometry was applied for the characterisation of GaN single crystals obtained by the high pressure technique [3] and GaN layers grown on sapphire. For the hetero-epitaxial films a multilayer model is used, in which the real and the imaginary part of the complex refractive index as well as the film thickness are fitted simultaneously from the ($\Delta,\Psi$)-spectra. The results were compared with the data obtained from the GaN single crystals.
9.2 Experimental

Undoped GaN films were grown on two-inch sapphire (0001) substrates using a horizontal metalorganic chemical vapour deposition (MOCVD) reactor. Immediately before growth, the substrates were cleaned in organic solvents, etched in a solution of HCl:HNO$_3$ = 3:1, rinsed with de-ionised water, and blown dry with filtered N$_2$ gas. After nitridation of the substrate surface, carried out in an ammonia (NH$_3$) gas stream at 1030°C, the temperature was lowered to 500°C and a 20 nm thick GaN buffer was deposited. On this buffer, a 1.5 μm thick GaN layer was grown at a temperature of 1050°C and a pressure of 50 mbar using trimethylgallium (TMG) and NH$_3$ as precursors, and H$_2$ as carrier gas. Growth was performed with a TMG flow of about 60 μmol/min and a NH$_3$ flow of 2.5 slm, diluted with H$_2$ to a total flow of about 5 slm. The GaN epilayers on sapphire have a mirror smooth surface and were found to be of Ga-polarity, according to selective etching experiments [10].

Unintentionally $n$-doped GaN single crystals were grown from nitrogen and liquid gallium under nitrogen pressures close to 15 kbar and at temperatures higher than 1500°C [3,11]. Before ellipsometry was performed the as-grown single crystals were polished with diamond paste (0.1 μm) to remove a visible surface layer resulting from the transition from growth to ambient conditions. The side of gallium polarity was found to be unaffected by chemical etchants, only the side of nitrogen polarity can be mechano-chemically polished with aqueous solutions of NaOH and KOH [10]. As a result of this anisotropic behaviour, the roughness of the $N$-polarity side is lower which makes it more suitable for ellipsometry.

Ellipsometric measurements were performed with two experimental set-ups. A Gaertner L117C ellipsometer was used to measure the ellipsometric angles $\Delta$ and $\Psi$ at the HeNe-laser wavelength of $\lambda = 632.8$ nm. The spot-size of the laser beam is 1 mm in diameter. The measurements were carried out at an angle of incidence of 70.00° ± 0.02°. Spectroscopic ellipsometry (SE) was measured by a four zone spectrometer [9,12] in the region 240 nm - 840 nm with a resolution of 0.4 nm (or 2 meV) at the bandgap. A Xenon lamp was used as light source, the spot size during measurements was 1 mm in diameter, the angle of incidence was the same as for the single wavelength ellipsometer. The values of $\Delta$ and $\Psi$ are measured with a typical precision of ± 0.02°. All measurements were performed at room temperature.
Figure 9.1: A thickness profile of the hetero-epitaxial GaN layer (GaN-C) obtained by single wavelength ellipsometry.

9.3 Results and discussion

Since several hetero-epitaxial layers grown under similar conditions gave comparable results, data from a characteristic sample, referred to as GaN-C, were chosen to be analyzed in detail.

Determination of the GaN film thickness over the wafer shows a thickness variation of about one percent, as can be seen in Fig. 9.1.

In a first approximation the maxima and minima in the s-reflection, in the transparent region 362 nm - 840 nm, were analysed using a Cauchy-type of dispersion, in which the real part of the refractive index $n_1$ is given by:

$$n_1(\lambda) = A + B \left( \frac{C}{\lambda - C} \right)^2,$$

and the imaginary part of the refractive index $n_2$ is set to zero. In the above equation $A$, $B$, and $C$ are fitting parameters and $\lambda$ is the wavelength of light in nanometers. Furthermore the buffer is not treated as separate layer but as part of the epitaxial GaN film. The best fit for the measured data was obtained for $A = 2.290$, $B = 0.05$, and $C = 280$ nm. The corresponding film thickness $d$ of $1470 \pm 20$ nm, is within the accuracy of the average-thickness determination by gravimetry, $1482 \pm 12$
Figure 9.2: The SE parameters (data points), Δ and Ψ, measured at an angle of incidence of 70.00°, were obtained at two subsequent times with an one-month interval. The lines are a guide to the eye.

nm (assuming only deposition of wurtzite GaN on top of the substrate), from which can be concluded that our first ellipsometric approximation is sufficient for accurate and non-destructive layer thickness determination.

In order to study the stability of hetero-epitaxial grown GaN film, the GaN-C sample was investigated at two subsequent times with a one-month interval. SE was performed near the centre of the samples at energies near the bandgap of GaN (Fig. 9.2).

The measurements show that no detectable change of the GaN surface occurs within this one-month period in ambient conditions, in contrast to materials like GaAs where a continuous oxidation of the surface takes place [8]. In Fig. 9.2 a small shift of the ellipsometric angles Δ and Ψ at the two subsequent times can be recognised. This shift occurs because there is a small thickness variation over the sample (Fig. 9.1) and the light beam position of the second measurement is not exactly the same as of the first measurement (thickness difference < 0.3 nm). A feature in Ψ at
Figure 9.3: The SE parameters (data points), $\Delta$ and $\Psi$, measured at an angle of incidence of 70.00°, are fitted ($\Delta$ = solid line, $\Psi$ = dotted line) using a multilayer model.

$\lambda = 363$ nm (3.42 eV) is assumed to be exciton related.

A refinement of the results of the first approximation is obtained by a full multilayer description in the transfer matrix formalism [12] of high precision recordings of $\Delta$ and $\Psi$ in the region 500 nm - 680 nm, as shown in Fig. 9.3. In this model, the deposited layer on the sapphire substrate is composed of a buffer layer, a GaN epilayer, and a hypothetical overlayer respectively. Furthermore, the dispersion of sapphire was set to data found in literature [13], the refractive index of ambient air was taken to be 1.0003, and a thickness of 20 nm for the GaN buffer layer was used, as was determined by transmission electron microscopy.

According to this model, the refractive index $n_1$ was found to follow a Cauchy-type of dispersion as given by equation 9.2. The values obtained for the fitting parameters A and C are the same as for the first approximation, while B is found to be 0.06 instead of 0.05. The hypothetical top-layer, if there is any present, is smaller than 1 nm. An overview of the results for sample GaN-C is given in table 9.1.

Fig. 9.3 shows that there is an excellent fitting of the SE measurement
Table 9.1: A summary of the results of the multilayer model used for GaN-C

<table>
<thead>
<tr>
<th>Layer</th>
<th>d</th>
<th>n_1</th>
<th>n_2</th>
</tr>
</thead>
<tbody>
<tr>
<td>GaN epilayer</td>
<td>1456</td>
<td>d = 2.290 + 0.06 \left(\frac{280}{\lambda - 280}\right)^2</td>
<td>n_2 = 0.0007 \left(\frac{500}{\lambda}\right)</td>
</tr>
<tr>
<td>Buffer layer</td>
<td>20</td>
<td>d = 20 nm</td>
<td>n_1 = n_1(GaN) - 0.035</td>
</tr>
<tr>
<td>Top layer</td>
<td>&lt; 1</td>
<td>d &lt; 1 nm</td>
<td></td>
</tr>
</tbody>
</table>

data and the multi-layer-model simulation, the small difference between model and experiment for \(\lambda > 620\) nm is thought to be due to a difference in dispersion of the ordinary and extra-ordinary refractive index near 620 nm of substrate or sample, which is not included in the model.

The square of the refractive index of both, the first approximation and the multi layer model, appear to be close to the Sellmeier-type description as given by Yu et al. [6]. However, it is off by a few percent compared with a subsequent Sellmeier description which was measured on a sample without a buffer layer [7]. Deviations between the various parametric ratios are found particularly in the region 3.5 eV - 4.0 eV, where a single term Sellmeier description appeared not to be sufficient and a next term should be added.

As mentioned before in section 9.2, GaN single crystals were polished before SE was performed. Since only the side of nitrogen-polarity could be mechano-chemically polished, resulting in a lower surface roughness, this side was investigated by ellipsometry.

Two mechano-chemically polished samples were studied with ellipsometry at \(\lambda = 632.8\) nm. It appears that there is an overlayer on top of the samples, which can be a rough surface layer and/or an additional layer of e.g. gallium oxide. Atomic force microscopy reveals that the surface of the single crystals is rough, at least a factor of three rougher than the hetero-epitaxial layers. Assuming that the overlayer is only due to a residual surface roughness, the ellipsometric data indicate that the roughness, given as top-bottom value, is 0.5-2 nm and 1.5-3 nm respectively. This values can be considered as maximum values, which are less in case the overlayer also contains gallium oxide remaining.

The real part of the refractive index at \(\lambda = 632.8\) nm, averaged over
Table 9.2: Comparison of the results obtained for GaN single crystals and GaN epilayers.

<table>
<thead>
<tr>
<th>GaN single crystals</th>
<th>GaN epilayers</th>
</tr>
</thead>
<tbody>
<tr>
<td>( n_1 (\lambda=632.8\text{nm}) = 2.337 \pm 0.010 )</td>
<td>( n_1(\lambda=632.8\text{nm}) = 2.328 \pm 0.003 )</td>
</tr>
<tr>
<td>( n_2 \approx 0.003 )</td>
<td>( n_2 = 0.0005 ) for ( \lambda = 680 \text{ nm} )</td>
</tr>
<tr>
<td>for: 400 nm &lt; ( \lambda &lt; 800 \text{ nm} )</td>
<td>( n_2 = 0.0007 ) for ( \lambda = 500 \text{ nm} )</td>
</tr>
<tr>
<td>roughness (top-bottom) of 0.5-3 nm</td>
<td>top-layer &lt; 1 nm</td>
</tr>
</tbody>
</table>

Both samples is \( n_1 = 2.337 \pm 0.010 \) which compares well with \( n_1 = 2.328 \pm 0.003 \) of the MOCVD sample. In table 9.2 the results for single crystals are compared with those of MOCVD grown GaN. On similar single crystals the absorption coefficient \( \alpha \) was measured and found to be ranging from 35 cm\(^{-1}\) - 200 cm\(^{-1}\) between 500 nm < \( \lambda < 680 \text{ nm} \) [14]. This means that \( n_2 = \frac{\alpha}{4\pi} = 0.0002 - 0.0009 \), which is in the same order as the values found for hetero-epitaxial layers which are between 0.0005 and 0.0007, as can be determined from table 9.1. Full spectroscopy on these bulk samples has to wait for an adequate model which can take into account the rough surface layer.

9.4 Conclusions

Ellipsometry is shown to be a useful technique for characterisation of GaN films and bulk material, it can be used for local film thickness determination. From precision recordings of the ellipsometric quantities (\( \Delta, \Psi \)) the dispersion of the refractive index is calculated in a full multilayer transfer matrix description. The surfaces of the as-grown hetero-epitaxial layers are smoother than surfaces of the polished single crystals examined in this paper. However, within the experimental error the resulting refractive index of the MOCVD films and high pressure samples are consistent with each other.

References


Summary

This thesis deals with the homo- and hetero-epitaxial growth of gallium nitride by metalorganic chemical vapour deposition. Gallium nitride (GaN) is together with the other III-nitrides, aluminium nitride (AlN) and indium nitride (InN), a candidate material for opto-electronic applications in the blue-UV region of the spectrum and for high-power transistors. The band gaps of the hexagonal wurtzite III-nitrides are large and direct. InN, GaN, and AlN form a continuous alloy system which, theoretically, allows band gap tuning from 1.9 to 6.2 eV. However, experimentally the III-nitride system is more complicated.

One of the challenging problems is related to the lack of lattice matched substrate material for homo-epitaxial deposition of GaN films. Therefore a variety of alternative substrates, of which sapphire is most frequently used, is applied for growth of III-nitrides. To obtain good hetero-epitaxial layers a low-temperature buffer layer is deposited before the actual film is grown. The use of the buffer layer improves not only the morphology but also the structural quality, however the density of dislocations is still very high (≈ 10⁹ cm⁻²).

Chapter 2 describes the morphology of Ga-faced (0001) GaN epilayers, deposited on sapphire substrates, which was found to be strongly temperature dependent. For the investigated temperature range of 980°C-1085°C the growth morphology is determined by (0001) and {1̅1̅01} faces. At higher growth temperatures the morphology is governed by growth in the [0001] direction, whereas at lower growth temperatures, the slower lateral growth in the <1̅1̅01> directions determines the morphology for a longer time. To describe the observed morphology a growth rate factor $\alpha_{GaN}$ is introduced. For $\alpha_{GaN}$ values smaller than one, nucleation islands can after a sufficient time of growth coalesce resulting in smooth transparent films. For $\alpha_{GaN}$ values equal to or larger than one, the nucleation islands will never coalesce.
In chapter 3 the n-type doping of GaN with silane (SiH₄) is presented. A 1:1 relationship between silane input concentration and the resulting carrier concentration is found. Furthermore, the silicon incorporation appeared to be hardly temperature dependent. Ellipsometry was used to determine the imaginary part of the refractive index of the doped GaN layers. For smooth films this part of the refractive index showed an almost perfect relationship with the carrier concentration as obtained from Hall measurements. Growth with high silane concentrations increases the surface roughness, which complicates the ellipsometry analysis. For increasing silane input concentrations the FWHM of the X-ray rocking curves is broadened, indicating that the structural quality of the GaN film decreases. The intensity of the UV PL signal is found to increase with increasing carrier concentrations up to \( n = 2.5 \times 10^{18} \text{ cm}^{-3} \). For those carrier concentrations, photoluminescence studies revealed a shift of the conduction band towards lower energy positions.

Homo-epitaxial growth of GaN on the N-face of GaN substrate crystals exhibits a hexagonal growth hillock density of \( 10^5 \text{ cm}^{-2} \). In chapter 4 it is shown that these defects are attributed to the nucleation of inversion domains at amorphous material on the surface. This amorphous material, typically 2-5 nm thick, was found to contain oxygen and is a possible remnant contamination from the mechno-chemical polishing technique used to prepare the substrates prior to growth.

The determination of the absolute polarity of GaN, based on a set of diffraction patterns, is demonstrated in chapter 5.

In chapter 6 it is shown that the formation of hexagonal hillocks can be suppressed by the use of substrates with a slight misorientation towards the [1 0 1 0] direction. For a substrate misorientation of 4° the density of the elevations on the homo-epitaxial film is reduced by almost two orders of magnitude as compared with exactly oriented GaN substrates. The different morphologies of those features that persist on the 4° off-angle sample during growth can be explained by a model involving the interaction of steps introduced by the misorientation with steps originating from the hillocks. It is found that the step velocity is dependent on the step orientation: steps in the \(<1 \overline{1} 2 0>\) directions move 2.5 times as fast as steps in the \(<1 0 \overline{1} 0>\) directions. If surface diffusion had been the rate-determining step during growth, step velocity would have been isotropic. Therefore it can be concluded that integration of growth units at the steps rather than surface diffusion is rate limiting in the MOCVD growth of N-face GaN.
Considerations following from the model indicate that for a further reduction of the hillock density, either substrates with larger misorientations or, since the step velocity is highly anisotropic, with misorientation towards the [11\overline{2}0] direction are needed.

In chapter 7 homo-epitaxial GaN growth on substrates with misorientations towards the [11\overline{2}0] direction was studied. In comparison with films grown on substrates with a misorientation towards the [10\overline{1}0], the hillock density was found to be of the same order of magnitude. However, the layers grown on the miscut substrates towards [11\overline{2}0] additionally showed pits in the film surface after growth. The formation of these pits is described by a blockage of the anisotropic step-flow growth.

Besides the improvement in surface morphology the higher misorientation also resulted in a strong improvement of the optical properties of N-face epilayers, as is shown in chapter 8. In comparison with the exact (000\overline{1}) films a strong reduction in the donor concentration was achieved. The luminescence properties of the layers with 2° and 4° misorientation towards [11\overline{2}0] and [10\overline{1}0] are essentially similar. Compared with the other misorientations the film with the 4° miscut towards the [11\overline{2}0] direction reveals slightly better optical properties. The main PL transitions, such as FE_A, FE_B, D^0BE, and A^0BE, were observed at the same energy positions for both Ga- and misoriented N-face samples. Temperature and excitation-dependent PL of the Ga-face sample reveals, however, an optical transition (BE_1), which is not present in the misoriented N-face film. It can be associated with excitons bound to a neutral acceptor, incorporated only in the Ga-face epilayer.

Chapter 9 deals with the ellipsometric comparison of GaN single crystals and hetero-epitaxial GaN films on sapphire substrates. The refractive index of the MOCVD films and the GaN single crystals are, within the experimental error, consistent with each other.
Samenvatting

In dit proefschrift wordt de homo- en hetero-epitaxiale groei van galliumnitridemet metalorganic chemical vapour deposition beschreven. Galliumnitride (GaN) heeft samen met de andere III-nitrides, aluminiumnitride (AlN) en indiumnitride (InN) toepassingsmogelijkheden in opto-electronische componenten in het blauw-UV gedeelte van het spectrum en als hoog-vermogen transistors. De bandafstand van de hexagonale wurtzite III-nitrides is groot en direct. InN, GaN en AlN vormen een continue legeringssysteem dat, theoretisch, de afstemming van de bandafstand tussen 2.9 en 6.2 eV mogelijk maakt. Experimenteel is het III-nitride systeem echter gecompliceerder.

Een van de uitdagende problemen is gerelateerd aan het gebrek aan substraten met een juiste roosterafstand voor de epitaxiale depositie van GaN lagen. Verschillende alternatieve substraten, waarvan saffier het meest gebruikt is, worden toegepast voor de groei van III-nitrides. Om goede kwaliteit hetero-epitaxiale lagen te krijgen vindt eerst depositie plaats van een lage-temperatuur buffer laag. Op deze bufferlaag wordt de eigenlijke GaN film gegroeid. Het gebruik van de bufferlaag verbetert niet alleen de morfologie van de film maar ook de structuurkwaliteit. Desondanks is de dislocatie dichtheid nog steeds erg hoog (≈ 10⁹ cm⁻²).

Hoofdstuk 2 beschrijft de morfologie van Ga-kant (0001) GaN epilagen, gegroeid op saffier substraten, die een sterke temperatuur afhankelijkheid toont. Voor het bestudeerde temperatuurgebied, tussen 980 en 1085°C wordt de morfologie van de laag bepaald door (0001) en {1 1 0 1} facetten. Bij hoge groeitemperaturen wordt de morfologie gedomineerd door de [0001] richting, terwijl bij lage groeitemperaturen de lagere latere groei in de <1 1 0 1> richting de morfologie voor een langere tijd bepaald. Om de waargenomen morfologie te beschrijven is een groei factor αGaN geïntroduceerd. Voor αGaN waarden kleiner dan één kunnen nucleatie eilanden, bij voldoende lange groeitijd, uiteindelijk vergroeien.
tot gladde transparante lagen. Voor \(\alpha_{\text{GaN}}\) waarden groter of gelijk aan één zullen de nucleatie eilanden nooit met elkaar vergroeien.

In hoofdstuk 3 wordt de n-type dotering van GaN met silaan (SiH\(_4\)) gepresenteerd. Een 1:1 relatie is gevonden tussen de silaan toevoer-concentratie en de resulterende landingsdragerconcentratie is gevonden, daarbij bleek de silaan toevoer-concentratie nauwelijks temperatuur afhankelijk te zijn. Ellipsometrie werd gebruikt om het imaginaire deel van de brekingsindex van gedoteerde GaN lagen te bepalen. Voor gladde lagen geeft dit deel van de brekingsindex een bijna perfecte relatie met de ladingsdragerconcentratie zoals bepaald met Hall-metingen. Hoge silaan concentraties tijdens de groei van GaN beïnvloeden de morfologie van de GaN lagen sterk. De toegenomen oppervlakte ruwheid maken de ellipsometrie analyse gecompliceerd. Voor toenemende silaan toevoer-concentraties neemt de FWHM-waarde van de Röntgen diffractie rocking curves toe, wat duidt op een achteruitgang in de structuurkwaliteit van de GaN film. De intensiteit van het UV deel van het fotoluminescentie (PL) signaal neemt toe tot ladingsdragerconcentraties van \(n = 2.5 \times 10^{18} \text{ cm}^{-3}\). Naast de toename in intensiteit wordt ook een verschuiving van de geleidingsband naar lager energie waarde waargenomen met PL.

Homo-epitaxiale groei van GaN op de N-kant van éénkristallijne GaN substraten resulteert in een laag met hexagonale groeiheuvels met een dichtheid van \(10^5 \text{ cm}^{-2}\). In hoofdstuk 4 wordt getoond dat deze defecten worden veroorzaakt door de nucleatie van inversiedomeinen op amorf, zuurstof bevattend, materiaal aan het oppervlakte van het substraat. Het materiaal, met een typische diepte van 2-5 nm, is mogelijk een resterende vervuiling van het mechanisch-chemisch polijstproces dat gebruikt is voor de preparatie van de substraten voor de groei.

De bepaling van de absolute polariteit van GaN, gebaseerd op een set van diffractie patronen, wordt behandeld in hoofdstuk 5.

In hoofdstuk 6 wordt getoond dat de vorming van hexagonale heuvels kan worden onderdrukt door gebruik te maken van misgeoriënteerde substraten naar de \([10\overline{1}0]\) richting. Voor substraten met een misoriëntatie van 4° is de dichtheid van de heuvels op de homo-epitaxiale laag gereduceerd met twee orde van magnitude vergeleken met exact georiënteerde GaN substraten. De morfologieën van de oppervlakte verstoringen die gevonden worden op de 4° misgeoriënteerde laag kunnen worden verklaard met een model dat de interactie van stappen geïntroduceerd door de misoriëntatie en stappen die voortkomen uit de heuvels omvat. De stapsnelheid blijkt
afhankelijk te zijn van de stap-oriëntatie: stappen in de \(<11\bar{2}0>\) richting bewegen 2.5 keer zo snel als stappen in de \(<10\bar{1}0>\) richting. Als oppervlakte-diffusie snelheidsbepalend zou zijn geweest dan zou de stapsnelheid isotroop zijn. Daarom kan worden geconcludeerd dat in plaats van de oppervlakte-diffusie de inbouw van de groeieenheden aan de stappen snelheidsbepalend is bij de MOCVD groei op de N-kant van GaN. Overwegingen die volgen uit het model duiden erop dat voor een verdere reductie van de heuveldichtheid, ofwel substraten met een grotere misoriëntatie nodig zijn of, gezien het feit dat de stapsnelheid anisotroop is, een misoriëntatie in de \([11\bar{2}0]\) richting gebruikt moet worden.

In hoofdstuk 7 wordt de groei van GaN op substraten met een misoriëntatie in de \([11\bar{2}0]\) richting beschreven. In vergelijking met lagen gegroei op substraten met een misoriëntatie in de \([1\bar{0}10]\) richting blijft de heuveldichtheid van dezelfde orde van grootte. Echter, de GaN lagen gegroei op misgeoriënteerde substraten in de \([11\bar{2}0]\) richting vertonen na groei gaten in het oppervlak. De vorming van deze gaten kan worden beschreven door een blokkade-mechanisme van de anisotrope stappen.

Naast de verbetering in de oppervlaktemorphologie resulteert de grotere misoriëntatie ook in een sterke verbetering van de optische eigenschappen van de N-kant epilagen, zoals wordt behandeld in hoofdstuk 8. In vergelijking met exact georiënteerde \((00\bar{1}1)\) films wordt een sterke reductie van de donor concentratie bereikt. De luminiscentie eigenschappen van lagen met een misoriëntatie van 2° en 4° in de \([11\bar{2}0]\) en \([1\bar{0}10]\) richting zijn in essentie gelijk aan elkaar. Vergeleken met andere misoriëntaties laat de laag met de 4° misoriëntatie in de \([11\bar{2}0]\) richting iets betere optische eigenschappen zien. De belangrijkste PL overgangen, zoals de \(FE_A\), \(FE_B\), \(D^0BE\) en \(A^0BE\), worden waargenomen bij dezelfde energieën voor zowel de Ga- als ook misgeoriënteerde N-kant samples. Temperatuur- en excitatie-afhankelijke PL aan het Ga-kant sample laat echter een optische overgang (\(BE_1\)) zien die niet aanwezig is in misgeoriënteerde N-kant lagen. Dit kan in verband worden gebracht met excitons gebonden aan een neutrale acceptor, die alleen ingebouwd wordt in de Ga-kant epilag.

Hoofdstuk 9 behandeld de ellipsometrische vergelijking van GaN éénkristallen en hetero-epitaxiale GaN lagen op saffier substraten. De brekingsindex van de MOCVD films en de GaN éénkristallen zijn, binnen de experimentele fout, consistent met elkaar.
List of Publications


Dankwoord

Dit proefschrift vormt de afronding van mijn promotieonderzoek dat ik de afgelopen jaren heb verricht op de afdeling voor Experimentele Vaste Stoffysica III. Het beschrijft een groot deel van de wetenschappelijke resultaten die bereikt zijn met de metalorganic chemical vapour deposition (MOCVD) van galliumnitride (GaN) lagen. Achter de toepassing van deze kristalgroeitechniek verschuilt zich echter ook een berg engineering. Gelukkig stond ik daar niet alleen voor en had ik o.a. hierbij de steun van ervaren en enthousiaste collega’s. Zonder anderen tekort te doen wil ik sommigen van hen langs deze weg persoonlijk bedanken.

Paul Hageman, met jaren lange MOCVD ervaring, leerde mij naast de In & Outs van de naar hem genoemde ”Hageman-tape” het groevak. Paul waardeer ik ook voor zijn doortastende aanpak in het oplossen van technische problemen. Samen met Harry van der Linden voerde we het mechanische onderhoud uit aan pompen, kleppen en mass-flow controllers. Erik Haverkamp, de grote Labview-nerd van de afdeling, zorgde onder meer voor de uitstekend werkende computerbesturing van de GaN-reactor. Wil Corbeek wil ik bedanken voor zijn bijdrage aan de bouw van o.a. het MOCVD gassysteem.

Poul Larsen dank ik voor de ondersteuning die hij me in de afgelopen jaren gegeven heeft bij het doen van mijn onderzoek en de geboden vrijheid bij de invulling hiervan. Poul waardeer ik verder voor de effectiviteit waarmee hij tijdens zijn aanvankelijk slechts eendaagse werkweek in Nijmegen veel knelpunten bij het onderzoek wist op te lossen.

Met John Schermer heb ik tal van vruchtbare discussies gehad tijdens het "fruiten" die hebben gezorgd voor een beter begrip van de groei van GaN. Naast John dank ik ook Willem van Enckevort voor zijn aandeel in de misoriëntatie verhalen.

Jan Weyher wil ik bedanken voor onze samenwerking en zijn gedrevenheid in het GaN onderzoek. Ik ben hem onder meer erkentelijk voor de

Peter Mulder wil ik bedanken als sympathieke en motiverende collega die o.a. regelmatig het opdampen van de Hall contacten voor zijn rekening nam. Gerard Bauhuis dank ik voor zijn XRD inbreng, zijn beleggingsstrategieën en niet te vergeten de succesvolle brieven. Mona Moret wil ik graag bedanken voor onze discussies, haar begrip en de tal van "dingetjes" waarbij ze me geholpen heeft gedurende de afgelopen jaren. Natuurlijk kan ik Marijn Devillers in dit dankwoord niet vergeten, ik dank Marijn voor zijn enthousiasme en samenwerking in het GaN onderzoek.

Graag wil ik ook een aantal mensen van ondersteunende afdelingen bedanken, met name Jos Haerkens, Peter van Dijk en Peter Wahraven van glasbewerking voor hun snelle en adequate ondersteuning. Gerard Dekkers en Dick van Aalst van fotografie wil ik bedanken voor hun inzet bij het verwerken van mijn vele foto’s.

Nijmegen, januari 2001

Andy Zauner
Born in Mönchengladbach, Germany, September 1970, Andy Zauner received a diploma in senior general secondary education (HAVO) at the School for Senior General Education in Venray, the Netherlands in June 1988. He obtained his pre-university (VWO) degree at the same institute in 1990.

In the same year he started studying chemistry at the University of Nijmegen, the Netherlands. In 1996, he received his university degree equivalent to a Master of Science abroad. For his M.Sc. thesis his main research subject was Solid State Chemistry in Nijmegen and his additional subject was Inorganic Chemistry and Catalysis at the Eindhoven Technical University.

His enthusiasm in science encouraged him to pursue in research as a Ph.D. student at the Physics Department of Experimental Solid State Physics III in January 1997. There he investigated the metalorganic chemical vapour deposition (MOCVD) growth of gallium nitride, which is presented in this thesis. Currently he works as a researcher on ferro-electric materials grown by MOCVD.