Strain and crystalline defects in epitaxial GaN layers studied by high-resolution X-ray diffraction

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A dissertation submitted in partial satisfaction of the requirements of the degree of Doktor der Naturwissenschaften
- Dr. rer. nat. -
am Fachbereich 1
der Universität Bremen

Bremen, 2007
## Contents

**Introduction**

1. **Introduction to GaN**
   1.1 Crystalline structure ........................................... 1
   1.2 Optical properties ............................................. 3
   1.3 Growth methods ................................................. 3
      1.3.1 HVPE ............................................... 4
      1.3.2 MBE ................................................. 4
      1.3.3 MOVPE ............................................... 4
   1.4 Substrates ...................................................... 6
      1.4.1 Sapphire ............................................. 7
      1.4.2 6H-SiC ............................................. 7
      1.4.3 Si ................................................... 8
      1.4.4 Nucleation layer ....................................... 8
      1.4.5 Mosaic model ......................................... 9
   1.5 Strain and stress ............................................... 10
      1.5.1 Biaxial stress .......................................... 11
      1.5.2 Hydrostatic strain ....................................... 12
      1.5.3 Hydrostatic + biaxial stress .......................... 12
      1.5.4 Uniaxial stress ....................................... 13
      1.5.5 Influence of strain on bandgap energy .............. 13
   1.6 Crystal Defects ................................................. 13
      1.6.1 Point defects ......................................... 13
      1.6.2 Line defects ......................................... 14
      1.6.3 Planar defects ...................................... 15
   1.7 Lateral overgrowth ........................................... 15
      1.7.1 LEO ................................................. 16
## CONTENTS

1.7.2 Pendoe epitaxy ...................................................... 16  
1.8 Alloys .......................................................................... 17  
1.8.1 AlGaN ...................................................................... 17  

2 Experimental setup ......................................................... 19  
  2.1 Basic elements of x-ray diffraction ................................ 19  
  2.1.1 Bragg’s law .......................................................... 19  
  2.2 Instrumentation ............................................................ 20  
  2.2.1 Crystal arrangement .................................................. 20  
  2.2.2 DuMond-model ....................................................... 21  
  2.3 Reciprocal space .......................................................... 23  
  2.3.1 Ewald construction .................................................... 23  
  2.3.2 Scans in reciprocal space .......................................... 24  
  2.3.3 Lattice constant measurement ..................................... 25  
  2.4 Standard and non-standard x-ray geometries .................. 26  
  2.5 Microstructures .......................................................... 28  
  2.5.1 Mosaicity .............................................................. 28  
  2.5.2 Visibility criterion for TDs in x-ray diffraction .............. 31  
  2.6 Origin of strain in MOVPE-grown GaN layers .................. 31  
  2.7 Temperature dependent measurements .......................... 33  
  2.8 High temperature chamber .......................................... 36  
  2.9 AlGaN strain determined by XRD .................................... 38  
  2.9.1 Model of the relaxation line ...................................... 38  
  2.9.2 Atomic force microscopy (AFM) ............................... 40  
  2.9.3 Transmission electron microscopy (TEM) .................... 41  

3 Growth induced strain and defects ...................................... 43  
  3.1 Introduction .............................................................. 43  
  3.2 Mosaic structure .......................................................... 46  
  3.2.1 Tilt and coherence lengths ...................................... 46  
  3.2.2 Twist ...................................................................... 54  
  3.2.3 Defect determination ............................................... 57  
  3.2.4 Dislocation densities ............................................... 58  
  3.3 Strain .......................................................................... 60  
  3.3.1 Elastic modulus ....................................................... 64
4 Strain and defects in GaN layers grown by pendeoepitaxy 67
   4.1 Dislocation density reduction in GaN 67
       4.1.1 Pendeoepitaxy (PE) 68
       4.1.2 Wing tilt 69
   4.2 GaN on SiC 72
       4.2.1 GaN layers 72
       4.2.2 GaN stripes on SiC 75
   4.3 Pendeoepitaxy 77
       4.3.1 Lateral overgrowth 78
       4.3.2 Local strain in wing and stripe 79
   4.4 Uncoalesced structures: temperature dependent measurements 80
       4.4.1 Wing tilt: thermal strain 84
       4.4.2 Wing tilt: dislocation effect 89
   4.5 Conclusions 90

5 Strain and defects in layers of inhomogeneous composition 93
   5.1 AlGaN nucleation layers on SiC 94
   5.2 X-ray reflectivity 98
       5.2.1 Theory 98
       5.2.2 Experiment: Analysis of AlGaN/GaN superlattices 100

6 Summary 107

Bibliography 111

Publications 117

Acknowledgment 121

Curriculum Vitae 123
Introduction

GaN has a large bandgap of 3.42 eV and can thus be used for optoelectronic devices operating in the short wavelength region[1]. Due to its high saturation drift velocity, it also finds application in high power, high frequency devices[2]. The various potential applications initiated extensive growth aiming to an improvement of the structural perfection. Several attempts were made to first synthesize GaN crystals during the period 1930-1960. Small needles of GaN could be synthesized in 1938 by Juza and Hahn [3] by passing ammonia over hot gallium, but good quality crystals of reasonable size could not be grown. It was only in the late 1960s that epitaxial GaN layers were reported using hydride vapor phase epitaxy (HVPE). The first blue GaN LED was fabricated by Pankove et al. [4] in 1971, it was a metal/insulating diode. Indeed the difficulty in p-doping of GaN layers and making good ohmic contacts has for long time hampered the progress in the fabrication of GaN-based devices. The growth of good quality epilayers has been made possible using the two step method, i.e. an AlN or GaN buffer layer is grown on the substrate previous to the growth of the GaN layer. Finally, in 1988, also the p-doping was obtained by Amano et al. [5]. Large improvements in the fabrication and performances of GaN-based devices have been reported in the last years [6, 7, 8, 9, 10, 11].

In spite of the progresses in GaN growth heteroepitaxial GaN epilayers are an example of highly distorted epitaxial films. So far, GaN films are often grown on sapphire or SiC substrates. The large lattice mismatch between GaN and the substrate material causes typical dislocation densities in the range of $10^8$ to $10^{10}$ cm$^{-2}$, which is by orders of magnitude larger than in other epitaxial layers commonly used for semiconductor devices[12, 13]. Since the dislocation density affects the device performance, several detailed studies on the defect structure were initiated. Using cathodoluminescence measurements it was found that threading dislocations act as non-radiative recombination centers[14], and that the yellow luminescence typically present in GaN photoluminescence spectra could be caused by extended defects such as dislocations at low-angle grain boundaries[15]. Because of the large mismatch in the lattice constants and thermal expansion coefficients of the GaN epilayers and substrates, the epilayers are typically strained.

Scope and organization of the thesis

The scope of this thesis is to study the strain state, dislocation densities and other microstructural features of GaN-based layers grown by metalorganic vapor phase epitaxy (MOVPE) on (0001) sapphire and (0001) 6H-SiC substrates using x-ray techniques. This work was done in parallel to the development of GaN-based devices made at the University
INTRODUCTION

of Bremen (MOVPE GaN and AlGaN layers on (0001) sapphire) and at North Carolina State University (MOVPE GaN and AlGaN layers on (0001) 6H-SiC) in order to improve the quality of the layers. Thus the selection of topics and the scientific depth of their treatment in this thesis was mainly determined by the requirements of epitaxial growth optimization rather than by aiming for a full comprehensiveness of problem analysis.

In the first Chapter an overview on the general properties of GaN will be given. The crystal growth methods will be shortly reviewed. Considerable attention will be given to the growth process, with respect to its impact on the formation of strain and defects. The lateral overgrowth of GaN layers will be explained as this technique reduces locally the dislocation density and alters the strain.

In the second Chapter the x-ray technique will be explored, the experimental setup shown and different methods reviewed. In particular High Resolution X-ray Diffraction (HRXRD) will be presented and discussed. This technique is useful in the determination of dislocation densities and the investigation of the mosaicity of MOVPE GaN layers. Moreover, temperature dependent HRXRD measurements are discussed.

In the third Chapter the process of island coalescence during epitaxial growth of GaN layers will be discussed. It will be shown that a reduction of the dislocation density (mainly edge type TD) can be achieved by increasing the coalescence thickness. Indeed, the GaN layer grows in crystallites which are slightly rotated with respect to each other. Edge type TDs originate at the boundaries of these crystallites whereas screw type TDs are randomly distributed. A reduction of the dislocation density is obtained for a large coalescence thickness corresponding to large grain diameters. Moreover, intrinsic and extrinsic strain components which are related to this process will be analyzed.

In the fourth Chapter a detailed study of the strain in GaN pendeo-epitaxy layers will be presented to understand the origin of the crystallographic tilt of the wings and to clarify in which way it is connected with the strain and the defect structure of the layers. It will be shown that the tensile stress due to the thermal mismatch present in the stripes is relieved in the wings, causing the wing to tilt with respect to the seed. For this purpose the strain present in plane GaN layers grown on AlN/SiC and stripes of GaN grown on AlN/SiC have been analyzed.

In the fifth Chapter the composition and the strain state of AlGaN nucleation layers on SiC and AlGaN superlattices are studied using XRD mappings and x-ray reflectivity. The potential of these techniques for the analysis of the complex strain and composition situation in inhomogeneous or heterogeneous layer systems is demonstrated.
Chapter 1

Introduction to GaN

GaN is a relatively new material in the family of heavily investigated compound semiconductors. The first studies on this material date back to the 60ties, the first LED based on a metal-isolator-GaN junction was produced in 1971 by Pankove [4]. The development of GaN-based devices has been for long time limited by the huge density of defects in the material and from the difficulty to obtain p-type conductivity. Meanwhile the quality of this material has been largely improved, and also a technique for p-doping has been determined. Still the defect density is too large mostly due to the large lattice mismatch between GaN and its substrates. The first LED with a high luminosity has been realized by Nakamura [16] in 1994 at Nichia Inc. This first success has stimulated the interest on GaN as a blue light emitter. In 1995 the first laser diode GaN-based has been realized by Nakamura [16].

GaN has a direct band, exhibits a good chemical stability and a good mechanical toughness. Furthermore its physical properties make it attractive for devices operating at high temperature and at high frequency. Its large band-gap allows its use in UV photodetectors. With the realization of InGaN alloys, GaN has become also a concurrent of GaP for yellow-green emitters. A better understanding of its properties for a larger employment in the optoelectronic has increased the study of its basic properties. Unfortunately, in comparison with other III-V materials, a complete understanding of its parameters is still far away. The objective of this chapter is to report on the general properties of GaN that are related to the studies of this thesis.

1.1 Crystalline structure

GaN, and in general the group-III nitrides, can crystallize in three different structures: wurtzite, zincblende and rocksalt. Under ambient conditions, the thermodynamically stable structure is wurtzite. The zincblende structure occurs when cubic substrates are used, in this case structural compatibility overcomes the intrinsic tendency to form the wurtzite structure. The rocksalt structure can be induced under very high pressure. The wurtzite structure has a hexagonal non-primitive unit cell and thus two lattice constants. The commonly used non-primitive unit-cell, which is shown in Fig.1.1, contains 6 atoms of each type and consists of two interpenetrating hexagonal closed packed (hcp) sublattices, each with one type of atoms. The zincblende structure has a cubic non-primitive unit cell, that
contains 4 atoms of each type and consists of two interpenetrating face centered cubic sublattices. The two structures are similar, because in both of them each group-III atom has coordination four with respect to the nitrogen atoms. The different two crystallographic structures result in different stacking sequences of closest packed diatomic planes. As can be seen from Fig. 1.1, the wurtzite structure has an \textbf{ABABAB} stacking sequence of the (0001) planes along the \langle 0001 \rangle direction. Also shown in the picture are the two lattice constants of the wurtzite structure. Instead the zincblende structure has an \textbf{ABCABC} stacking sequence of the (111) planes along the \langle 111 \rangle direction. The wurtzite phase is mostly used due to its stability. In table 1.1 the lattice parameters of the two crystalline structures and the respective thermal expansion coefficients at room temperature (RT) are listed. Experimental studies by Leszczynski \textit{et al.} [19] have revealed that the thermic expansion coefficient depends on the temperature in the range 300K-700K.

![Hexagonal structure of GaN, lateral lattice constant a and perpendicular lattice constant c[17].](image)

<table>
<thead>
<tr>
<th>crystalline structure</th>
<th>hexagonal</th>
<th>cubic</th>
</tr>
</thead>
<tbody>
<tr>
<td>lattice constant [Å]</td>
<td>(a_{300K} = 3.188 ) [18]</td>
<td>(a_{300K} = 4.511 ) [18]</td>
</tr>
<tr>
<td></td>
<td>(c_{300K} = 5.185 ) [18]</td>
<td></td>
</tr>
<tr>
<td>thermal expansion coefficient ([10^{-6}K^{-1}])</td>
<td>(\alpha_a(300K) = 3.1 - 4.4 ) [19]</td>
<td>not determined</td>
</tr>
<tr>
<td></td>
<td>(\alpha_c(300K) = 2.8 - 3.8 ) [19]</td>
<td></td>
</tr>
</tbody>
</table>

Table 1.1: Lattice constants and thermal expansion coefficients of wurtzite and cubic GaN
1.2. OPTICAL PROPERTIES

GaN has a direct bandgap of around 3.5 eV at 0 K. The degeneracy of the valence bands at \( k = 0 \) is lifted in GaN by the crystal field interaction and by the spin-orbit coupling, and, consequently, there are three bandgap excitons, which are usually labelled \( A^{-}, B^{-}, \) and \( C^{-} \)exciton (see Fig. 1.2). Furthermore, the effective mass approximation has very limited use for the GaN valence band, since the valence bands in GaN are strongly non-parabolic and anisotropic. Typical near band-edge photoluminescence (PL) spectra of GaN at different temperatures are shown in Fig. 1.3 a). At low temperature the spectra are dominated by the BX peak due to the recombination of excitons bound to residual donors[20]. As the temperature rises, the BX peak decays faster than the free exciton peaks marked by \( FX_{N=1}^{A^{-}} \) and \( FX_{N=1}^{B^{-}} \) and all peaks move to lower energies. The latter two peaks are due to the \( A \) and \( B \) excitons (i.e., due to transitions involving holes in the \( A \) and \( B \) valence bands shown (in Fig. 1.2). At 75 K the \( A \) exciton peak becomes the strongest. PL peaks are also observed on the low energy side of the near band-edge transitions as shown in Fig. 1.3 b). The main features are a yellow band at 2.2-2.3 eV and donor-acceptor pair (DAP) bands [20]. The yellow band is associated with deep levels arising from point defect such as Ga or nitrogen vacancies[18]. These defects reduce the carrier lifetime.

1.3 Growth methods

As the melting point of GaN is approximately 1700° C the growth of GaN crystals from a liquid melt is difficult. Thus GaN is mostly grown using halide vapor phase epitaxy (HVPE), metalorganic vapor phase epitaxy (MOVPE) or molecular beam epitaxy (MBE).
1.3.1 HVPE

The first GaN epitaxial films were obtained by utilizing HVPE. Usually, a mixture of 
GaCl₃ and ammonia as the Ga and nitrogen source gases, respectively, are used. The 
growth speed in HVPE is too high (μm/min) to control the layer thickness on a monolayer 
scale. Also, high crystal purity is not easily achieved due to the interaction of hydrogen 
chloride, which is used as the carrier gas for Ga, with the reaction vessel [6, 13]. HVPE 
is often used to produce thick GaN layers of low dislocation density for the subsequent 
over-growth by MBE and MOVPE, respectively.

1.3.2 MBE

The MBE system is a refined form of ultrahigh vacuum (UHV) evaporation. Elements are 
heated in furnaces and directed beams of atoms or molecules are condensed onto a heated 
single-crystal substrate where they react. Because it is a UHV-based technique, it has the 
advantage of being compatible with a wide range of surface analysis techniques. Typically, 
the growth rate employed is approximately 0.3—1μm/h, although much higher growth rates 
can be obtained. The MBE growth is usually performed at relatively low temperatures of 
650 – 800°C. The problem with this growth technique is that nitrogen is inert at these 
temperatures. Radio Frequency (RF) and Electron Cyclotron Resonance (ECR) plasma 
sources are most commonly employed to activate the nitrogen species [13, 18].

1.3.3 MOVPE

MOVPE growth of GaN films is performed at atmospheric pressure or low pressure of some 
ten Torrs. Trimethylgallium (TMG) and ammonia (NH₃) are commonly used as Ga and N 
source, respectively. They react at a substrate heated to roughly 1000°C.

![Figure 1.4: Schematic MOVPE system [21].](image-url)
1.3. GROWTH METHODS

A typical MOVPE system is presented in Fig. 1.4. GaN epilayers of reasonably crystal quality on sapphire substrates can be obtained if the growth is performed in two steps. In the first step a thin GaN or AlN nucleation layer is grown at a relatively low temperature. The main epilayer is grown in the second step at a higher temperature. The nucleation layer provides the high density of nucleation centers and promotes the lateral growth of the main epilayer. A real-time monitoring of the growth is possible in MOVPE systems by using an optical reflection setup. Due to interference of multiple reflections of a laser beam within the growing epilayer intensity oscillations are observed. These oscillations can be used to measure the thickness and roughness of the layer.

A typical MOVPE growth process can be schematized as follows:

- **Nitridation**: The nitridation is caused by ammonia and has the purpose of generating a thin layer of AlN on the sapphire surface.

- **Nucleation layer deposition**: After the pre-treatment, the substrate is cooled to a temperature ranging between 500 and 800° C, at which the deposition of the GaN or AlN nucleation layer occurs.

- **Nucleation layer heat treatment**: When the sample is ramped up to growth temperature, the nucleation layer undergoes a recrystallization process.

- **Growth of the main epitaxial layer** (see Fig.1.5 and Fig.1.6):
  1. Nucleation of GaN island (3D growth)
  2. Lateral and vertical island growth
  3. Coalescence of the islands
  4. 2D growth

---

**Figure 1.5**: Island coalescence process during MOVPE growth of GaN.

**Figure 1.6**: Reflectivity trace recorded during the MOVPE growth of GaN[21].

![Figure 1.5: Island coalescence process during MOVPE growth of GaN.](image)

![Figure 1.6: Reflectivity trace recorded during the MOVPE growth of GaN[21.](image)
Fig. 1.6 shows the reflectance measured during MOVPE GaN growth on a nucleation layer. In Fig. 1.5 the corresponding steps of growth of the layer are illustrated. A TEM picture of a typical GaN layer grown on (0001) 6H-SiC by MOVPE is shown in Fig. 1.7. The density of threading dislocations is of the order $10^8 \text{cm}^{-2}$.

![Figure 1.7: Typical TEM cross-sectional micrograph of a GaN layer grown on 6H-SiC(0001) by MOVPE using an AlN Nucleation layer[21].](image)

### 1.4 Substrates

The lattice constants of III-nitrides are shown in Fig. 1.8 as a function of the band gap. The lattice constants of sapphire and 6H-SiC, the most commonly used substrates, are also shown. There is a lattice mismatch as well as a thermal mismatch between the III-nitrides and the substrates on which they are grown.

<table>
<thead>
<tr>
<th>Material</th>
<th>6H-SiC</th>
<th>Al$_2$O$_3$</th>
<th>Si</th>
<th>AlN</th>
</tr>
</thead>
<tbody>
<tr>
<td>a lattice constant [(\AA)]</td>
<td>3.0806</td>
<td>4.758</td>
<td>5.43</td>
<td>3.111</td>
</tr>
<tr>
<td>c lattice constant [(\AA)]</td>
<td>15.1173</td>
<td>12.991</td>
<td>5.43</td>
<td>4.789</td>
</tr>
<tr>
<td>$\alpha_c \cdot 10^{-6} [\text{K}^{-1}]$</td>
<td>4.7</td>
<td>8.5</td>
<td>3.59</td>
<td>5.3</td>
</tr>
<tr>
<td>$\alpha_a \cdot 10^{-6} [\text{K}^{-1}]$</td>
<td>4.2</td>
<td>7.5</td>
<td>3.59</td>
<td>4.2</td>
</tr>
</tbody>
</table>

Table 1.2: Lattice constants and thermal expansion coefficients ($\alpha_c$ and $\alpha_a$) of the most commonly used substrates for the growth of GaN and AlN, respectively [18, 13].
Due to the mismatch epilayers with a dislocation density lower than $10^{11}\text{cm}^{-2}$ could not been obtained until the late 1980s.

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{figure1_8.png}
\caption{Lattice constants and band-gaps of III-nitrides and substrate materials}
\end{figure}

In table 1.2 are shown the lattice constants and thermal expansion coefficients of the most used substrates for GaN growth.

1.4.1 Sapphire

Sapphire is the most widely used substrate for the growth of III-nitrides. Large area crystals of high quality are easily available at low cost. They are transparent, stable at high temperature, and the technology of growth of the nitrides on sapphire is quite mature. The c-axis of sapphire and GaN (grown on c-plane [0001]sapphire) are parallel, but the unit cell of GaN is rotated by $30^\circ$ around the c-axis with respect to the sapphire unit cell. The lattice mismatch of GaN with sapphire is $\approx 15\%$. In general the quality of the films grown directly on any plane of sapphire is poor. The FWHM of the x-ray rocking curves is large, and strong deep-level yellow luminescence is observed. The surface morphology is also poor, and many hillocks are often observed. That is the result of the large mismatch in the lattice constants (see Fig. 1.8) and coefficients of thermal expansion of GaN and sapphire. Films of reasonable crystal quality can be grown by first growing a low temperature AlN or GaN nucleation layer as was described in section 1.5.

1.4.2 6H-SiC

SiC has several advantages compared to sapphire. It can be made electrically conductive in contrast to the sapphire which is an insulator. It is then possible to fabricate vertical devices.
utilizing backside contacting of the substrate area. SiC substrates up to 3” in diameter of low dislocation density are available commercially. The large thermal conductivity of SiC and the ability to cleave it more easily than sapphire are additional advantages. The high cost hampers its use. The lattice mismatch with GaN is only 3.5 %, and with AlN, the mismatch is even smaller ($\approx 0.5 \%$). Indeed the latter is used as a buffer layer of GaN layers grown on SiC. Unfortunately, the AlN is not a good conductor, therefore several groups have attempted to grow low Al content AlGaN as a conducting buffer layer. However, despite the fact that 6H-SiC is better lattice mismatched to GaN, the quality of GaN grown on 6H-SiC does not yet exceed that of GaN grown on sapphire.

1.4.3 Si

To accomplish integration of GaN LEDs or LDs with Si electronics, these devices will have to be grown locally on a processed Si chip. Therefore, considerable work has been devoted to the growth of GaN on Si substrates [22, 23]. A low temperature buffer layer of 30 nm AlN is generally grown on Si before the growth of the main epilayer. The layers grown on (111) Si are predominantly wurtzite, with localized inclusions of the cubic phase. Better quality wurtzite GaN has been obtained on (111) Si by ECR MBE where the Si surface exhibited atomically flat terraces [18]. These layers exhibited free exciton recombination in photoluminescence spectra taken at low temperature.

1.4.4 Nucleation layer

The properties of the GaN epilayer are strongly influenced by the thickness and the growth temperature of the nucleation layer [17, 24]. The experimentally determined critical thickness of GaN on c-plane sapphire with an AlN nucleation layer is about 3 nm.

For films thinner than that, the lattice constant of the film is equal to that of AlN, i.e., the films are pseudomorphic with the AlN. As the thickness increases, the in-plane lattice constant increases due to the relaxation of strain by misfit dislocations. At a certain thickness, the relaxation is nearly complete and the lattice constant becomes the same as that
1.4. SUBSTRATES

Hiramatsu et al. [25] developed a model for the MOVPE growth of GaN on a thin AlN nucleation layer (see Fig.1.9). The AlN nucleation layer was grown at 600° C on sapphire. At this temperature the nucleation layer is amorphous. It crystallizes at the growth temperature (≈1050° C) in a columnar structure [26]. The thin columnar crystallites of the nucleation layer have an extension in the growth direction of ≈10 nm and a rough morphology. This morphology is reproduced in the layer grown directly on the nucleation layer. The column growth is selective, i.e. only the columns oriented in the direction of the growth(c-axis) are reproduced. This layer has a large defect density and it extends for some tenth nm. In the following zone, the lateral growth is enforced. The layer grows in crystallites of trapezoidal shape. The final layer is relatively poor of defects. It has been shown that the same model is valid also for the growth on a GaN nucleation layer [27, 28].

1.4.5 Mosaic model

Typical cross-sectional transmission electron microscopy (TEM)images[6] of MOVPE GaN layers reveal a 50 nm region with a large concentration of dislocations immediately on the top of the nucleation layer. Above this region, there is another zone (about 150 nm) which was made up by the growth of trapezoidal crystals. In this zone the dislocation density is much lower than in the interfacial zone. The remaining region on top exhibits a rapid decline in dislocations (10^8-10^{10} cm^{-2}). The GaN layer displays features similar to those of the AlN nucleation layer[6], i.e. fine columnar crystals. Each GaN column has probably grown from a GaN nucleus formed on the top of each columnar AlN region. The columns have different crystallographic orientations. The prismatic growth then leads to a general alignment along the c-direction with some remaining twist and tilt. The relative twist and tilt (see Fig.1.10) between the columns decrease as the layer thickness increases, expressing that the film structure gets more ordered as growth proceeds.

![Figure 1.10: Model of the mosaic structure. In the picture are also shown the tilt, twist and lateral coherence length (d).](image-url)
A structure like that presented is often described by a model called mosaic block model, a schematization of which is shown in Fig.1.10. The layer is assumed to consist of crystallites which are misoriented with respect to each other and to the substrate. The average lateral and vertical dimensions of these crystallites are called lateral and vertical coherence length, respectively. This structure and its characterization will be widely treated in Chapter 2 and 3.

### 1.5 Strain and stress

A layer grown on a substrate with a different lattice constant and a different thermal expansion coefficient, as it is the general case for III-nitrides layer, is usually strained. When there is a lattice mismatch between layer and substrate, the strain depends on the layer thickness. If the thickness of the layer is lower than a critical thickness ($h_c$), the layer is pseudomorphic, meaning that the in-plane lattice constants of the substrate ($a_{0s}$) and the layer ($a_l$) are equal, see Fig.1.11 a). When the thickness of the layer exceeds the critical thickness, the layer relaxes totally (as shown in Fig.1.11 b) and c) ) or partially by forming misfit dislocations. For a partially relaxed layer two cases are possible:

1. $a_l < a_{0s}$ the layer is under tensile strain
2. $a_l > a_{0s}$ the layer is under compressive strain.

where the 0 index refers to the lattice constants of totally relaxed layers.

![Figure 1.11: Schematic for the biaxial strain resulting from the lattice mismatch between layer and substrate.](image)

The stress-strain relations for a hexagonal crystal ($C_{6w}$) is given from Hooke’s law and can be expressed by a 6x6 matrix:
1.5. STRAIN AND STRESS

\[ \sigma_i = \sum_j C_{ij} \epsilon_j \]  

where \( C_{ij} \) represent the elastic stiffness coefficients. GaN layers are, in general, under a biaxial and hydrostatic strain.

1.5.1 Biaxial stress

If the crystal is stressed in the (0001) plane and is free to relax in the [0001] direction, it is said to be under biaxial stress (see Fig.1.12).

There are only three non-vanishing strain components given by:

\[ \epsilon_{xx} = \frac{a - a_0}{a_0} = \epsilon_{yy} \] (1.2)

\[ \epsilon_{zz} = \frac{c - c_0}{c_0} = -\frac{C_{13}}{C_{33}} (\epsilon_{xx} + \epsilon_{yy}) \] (1.3)

The last can be written also as:

\[ \epsilon_{zz} = -2 \frac{C_{13}}{C_{33}} \epsilon_{xx} \] (1.4)

and using the Poisson ratio \( \nu \):

\[ \epsilon_{zz} = -\frac{2\nu}{1-\nu} \epsilon_{xx} \] (1.5)

Using equation (1.1) the stress in the (0001) plane is given by:
CHAPTER 1. INTRODUCTION TO GAN

\[ \sigma_{xx} = \left( C_{11} + C_{12} - \frac{2C_{13}^2}{C_{33}} \right) \epsilon_{xx} \quad (1.6) \]

1.5.2 Hydrostatic strain

A crystal under hydrostatic strain does not change the shape of its unit cell. It will be enlarged or reduced but will maintain the same ratio of lateral to vertical lattice constant, \( \frac{c}{a} \). In GaN the hydrostatic strain is supposed to be caused by point defects. The strain induced by point defects can be expressed by the following equation due to Vegard’s law:

\[ \epsilon = b \cdot N_{\text{defect}} \quad (1.7) \]

where:

\[ \epsilon = \frac{\Delta c}{c_0} = \frac{\Delta a}{a_0} \quad (1.8) \]

\( N_{\text{defect}} \) is the concentration of point defects and \( b \) describes the dilatation due to a certain type of point defects, and was derived to be [30]:

\[ b = \frac{1}{3} \left[ 1 - \left( \frac{r_s}{r_h} \right)^3 \right] \cdot N^{-1} \quad (1.9) \]

where \( N \) is the concentration of lattice sites of the host matrix (8.8x10^{22} \text{ cm}^{-3} \text{ Ga+N sites in GaN}), \( r_h \) is the covalent tetrahedral radius of host atoms and \( r_s \) is the radius of solute atoms.

1.5.3 Hydrostatic + biaxial stress

The coexistence of hydrostatic and biaxial stress can be most simply described assuming isotropic elastic theory. In this approximation the relation between stress and strain is:

\[ \epsilon_i = E^{-1} \left[ \sigma_i - \nu(\sigma_j - \sigma_k) \right] \quad (1.10) \]

where \( E \) is Young modulus. For the case of a biaxial stress in the basal plane, this relation gives:

\[ \epsilon_a = E^{-1}\sigma_a(1 - \nu) \quad (1.11) \]

\[ \epsilon_c = E^{-1}\sigma_a2\nu \quad (1.12) \]

The superposition of hydrostatic and biaxial stress can be written as:

\[ \epsilon_c = (1 - bN_{\text{defect}}) \left[ 1 - 2\nu\sigma_a E^{-1} \right] - 1 \quad (1.13) \]

\[ \epsilon_a = (1 - bN_{\text{defect}}) \left[ 1 + (1 - \nu)\sigma_a E^{-1} \right] - 1 \quad (1.14) \]
1.5.4 Uniaxial stress

If the stress is uniaxial, i.e., if only $\sigma_{xx} \neq 0$ and all the other stress components are zero, the non-zero strain components are:

\[
\epsilon_{yy} = \frac{C_{12}C_{33} - C_{13}^2}{C_{13}^2 - C_{11}C_{33}} \epsilon_{xx}
\]

(1.15)

\[
\epsilon_{zz} = \frac{C_{11}C_{13} - C_{12}C_{13}}{C_{13}^2 - C_{11}C_{33}} \epsilon_{xx}
\]

(1.16)

1.5.5 Influence of strain on bandgap energy

The band structure and electronic properties of semiconductors are strongly modified by the strain. To determine the band structure of the strained crystals, the components of the strain tensor are required. The strain dependence of the $\Gamma_7$ conduction band minimum and the $\Gamma_9$ valence band maximum of GaN are given from [31, 32]:

\[
E(\Gamma_7^c) = E_1 + D_1 \epsilon_{zz} + D_2(\epsilon_{xx} + \epsilon_{yy})
\]

(1.17)

\[
E(\Gamma_9^v) = E_0 + C_1 \epsilon_{zz} + C_2(\epsilon_{xx} + \epsilon_{yy}) + C_3 \epsilon_{zz} + C_4(\epsilon_{xx} + \epsilon_{yy})
\]

(1.18)

where $E_i$ are the energy of the PL peaks of a strain-free GaN layer, $D_i$ and $C_i$ are the conduction and valence band deformation potentials, respectively, whereas $\epsilon_{ij}$ are the strain components. A larger energy of the PL peak with respect to the free-strain PL peak indicates the presence of a compressive biaxial strain. A smaller energy of the PL peak indicates the presence of a tensile strain.

1.6 Crystal Defects

The commonly observed defects in (0001) oriented GaN grown on sapphire substrates can be categorized into three types: point, line and areal. The point defects are e.g. vacancies, interstitial and impurities; the line defects are mainly threading dislocations (TD) and the areal are stacking faults. These defects are thought to be electrically active in GaN and are thus of major concern for electronic and optical devices.

1.6.1 Point defects

Point defects, as native defects or intrinsic defects, are the most common defects occurring in semiconductors. They are important for the electrical and optical properties of nitrides semiconductors. For example they influence the carrier lifetime and consequently the radiative quantum efficiency and the longevity of GaN-based lasers and light-emitting diodes [?]. There are three basic types of native points defects: vacancies (atom missing from lattice sites), antisites (cations sitting on anion sites or vice versa) and interstitials (additional atoms in between the lattice sites).

GaN is commonly assumed to contain a large density of point defects ($\approx 10^{16}$ cm$^{-3}$).
CHAPTER 1. INTRODUCTION TO GAN

The n-type background conductivity of early GaN samples is associated with the presence of point defects or impurities. Originally it was attributed to N vacancies ($V_N$), but theoretical calculations suggest a low concentration of $V_N$ in n-type GaN and a much higher concentration of Ga vacancies $V_{Ga}$ [33]. Moreover, epitaxial GaN layers typically contain a considerable amount of oxygen which acts as a shallow donor in the material.

1.6.2 Line defects

GaN layers contain a high density of threading dislocations (TDs) in the range of $10^8$-$10^{10} \text{ cm}^{-2}$. There are three predominantly observed TDs:

- pure edge, with Burgers vectors $\frac{1}{3} \langle 2110 \rangle$ and [0001] line direction,
- mixed character with Burgers vector $\frac{1}{3} \langle 2 1 1 3 \rangle$ and line direction inclined $\approx 10^\circ$ from [0001] towards the Burger vector,
- pure screw TDs with Burgers vector $\langle 0 0 0 1 \rangle$ and line direction [0001].

The screw type TDs are a small fraction of the total density of TDs[6].

![Figure 1.13: Edge (a) and screw (b) type dislocation, with $\vec{g}$ direction of the Burgers vector and $\vec{s}$ line direction of the dislocation][34].

TDs act as non-radiative recombination centers[35] and affect the performance of GaN-based light emitters[36]. They act also as strong scattering centers[37].

**Edge type TDs** arise as an additional half lattice plane inserted in the crystal between two adjacent lattice planes (see Fig. 1.13 a). Its terminal edge constitutes the dislocation line.

**Screw type TDs** arise as a part of the crystal is moved with respect to the rest and no additional lattice plane is inserted (see Fig. 1.13 b). The dislocation line constitutes the edge along which the displaced and non-displaced region border.
1.7. LATERAL OVERGROWTH

1.6.3 Planar defects

All crystals whose structures can be described by layers are prone to stacking faults. A stacking fault is any defect that alters the periodic sequence of layers. These defects may be a wrong layer inserted into the sequence, a change of the layer sequence or a different translation between two subsequent layers. These defects may affect the whole crystal or a finite region if, e.g., an additional layer is present between an otherwise perfect sequence of layers. The schematic diagram of the stacking sequences of wurtzite (2H) and zincblende (3C) are exhibited in Fig. 1.14 (a) and (b), respectively. The stacking faults in GaN interrupt the ideal stacking sequence $ABABAB$ of the wurtzite lattice i.e. a $ABABCBCBC$ stacking sequence is observed. Recent theory suggests that stacking faults in GaN are not electrically active[38].

![Figure 1.14: Stacking sequences of (a) wurtzite (2H), (b) zincblende (3C)[39].](image)

1.7 Lateral overgrowth

Most GaN films contain TDs with a density of $10^8$-$10^{10}$ cm$^{-2}$. As these defects seriously impair the electrical and optical properties of the material, it is of great importance to reduce the number of dislocations. Lateral Epitaxial Overgrowth (LEO) and Pendeo-Epitaxy (PE) are two approaches towards this direction. The density of TDs can be of the order of $10^4$ cm$^{-2}$ in selected areas [40].

The reduction in the TD density down to $10^5$ cm$^{-2}$ has led to improved performance in GaN-based optoelectronic devices such as blue lasers, light emitting diodes and p-n junctions with increased lifetime, lowered leakage current and low-dark current [41, 42, 36, 43].
1.7.1 LEO

The LEO technique consists of coating a film with a patterned mask (SiO$_2$ or silicon nitride) so that dislocations under the mask are prevented from propagating into the overgrown parts of the layer during subsequent growth. Continuation of growth takes place only on the seeds (windows) left uncovered by the amorphous material (see Fig.1.15). As soon as the growth front reaches the top of the mask, the GaN layer starts to grow not only vertically, along the c-axis, but also laterally, perpendicular to the c-axis, over the mask. The lateral growth can be several times faster than the growth along the c-axis. During this growth step, dislocations close to the edge of the seed areas tend to bend over and to follow the faster growth direction, such that their line directions differ between the laterally grown parts (wings) and the seed columns. Ideally there should be no dislocations grow along the c-axis in the wing regions. However some segments extending in the c-direction will inevitably be formed in particular at the meeting front of overgrown material, as dislocation lines cannot terminate inside bulk material (unless they annihilate with dislocations with a Burger’s vector of opposite sign, i.e., forming a loop).

![Lateral epitaxial overgrowth (LEO)](image)

**Figure 1.15:** Lateral epitaxial overgrowth process of GaN on SiC

1.7.2 Pendeo epitaxy

For PE (see Fig. 1.16) stripes are etched through the film into the substrate. Again GaN is grown laterally and vertically, the growth starts from the sidewalls of the GaN stripes and the wings hang free without being in contact with the substrate. The TD density in the laterally grown wings is reduced to $\approx 10^5$ cm$^{-2}$ relative to the initial GaN stripe [44]. Comparing PE and LEO, PE does not use a mask to initiate lateral growth but employs the substrate itself as a pseudomask.
1.8 Alloys

GaN-based devices involve heterostructures of GaN and its alloys, AlGaN and InGaN.

1.8.1 AlGaN

The energy band gap of Al$_x$Ga$_{1-x}$N is expressed as a function of the Al mole fraction ($x$):

$$E_g = (1 - x)E_g(GaN) + xE_g(AlN) - bx(1 - x)$$  \hspace{1cm} (1.19)

where $b$ is the bowing parameter and expresses the deviation of the Al$_x$Ga$_{1-x}$N energy band-gap from a linear dependence on $x$.

The lattice constants of an unstrained Al$_x$Ga$_{1-x}$N layer are given by Vegard’s law:

$$c_{0,AlGaN} = xc_{0,AlN} + (1 - x)c_{0,GaN}$$  \hspace{1cm} (1.20)

$$a_{0,AlGaN} = xa_{0,AlN} + (1 - x)a_{0,GaN}$$  \hspace{1cm} (1.21)

The "0" index indicates the lattice constants of unstrained layers. The lattice constants of a strained Al$_x$Ga$_{1-x}$N layer can be derived using the elastic theory for biaxially stressed layer in the c-plane(Eq. 1.4).

The strain status and the Al concentration of AlGaN layers grown on GaN can be determined simultaneously by x-ray diffraction, as it will be described in section 2.9.
Chapter 2

Experimental setup

2.1 Basic elements of x-ray diffraction

X-ray diffraction is a powerful technique for the non-destructive quantification of the crystalline quality. Over the years, the improvements in material growth have necessitated finer and finer resolution. Using x-ray diffraction it is possible to determine the chemical composition, the layer thickness with an accuracy in the nanometer range, but also to investigate the layer structure and structural features peculiar to thin heteroepitaxial layers. X-rays are electromagnetic radiation of a wavelength around 1 Å, which is about the same size as an atom. X-ray diffraction is one of the most important characterization tools used in solid state chemistry and materials science. The size and the shape of the unit cell for any compound can be determined most easily using the diffraction of x-rays.

A basic understanding of x-ray diffraction can be obtained using the kinematic theory, which calculates the sum of the amplitude of the waves scattered from the single atoms. The amplitude is assumed to be very small, such that the probability of multiple interaction with the crystal will be small as well. That means that the intensity loss of the scattered beam due to multiple processes is neglected.

2.1.1 Bragg’s law

Bragg’s Law refers to the simple equation (2.1) and is used to explain the interference pattern of x-rays scattered by crystals:

\[ n\lambda = 2dsin\theta \]  

(2.1)

where \( d \) is the distance between atomic layers in a crystal, and the variables \( \lambda \) and \( \theta \) are the wavelength and the incident angle of the incident x-ray beam, respectively, (see Fig.2.1) and \( n \) is the diffraction order. It was derived by the English physicists Sir W.H. Bragg and his son Sir W.L. Bragg in 1913.
CHAPTER 2. EXPERIMENTAL SETUP

2.2 Instrumentation

2.2.1 Crystal arrangement

The x-ray diffraction experiment requires an x-ray source, an holder for the sample under investigation and a detector to pick up the diffracted x-rays. Fig. 2.2 is a schematic diagram of a high resolution x-ray diffractometer. The scans are allowed along all the angles in the Fig. 2.2 where $\omega$ is the angle between the incident x-ray beam and the sample and $2\theta$ is the angle between the incident x-ray beam and the detector. The notation ”high resolution” refers to a low wavelength dispersion of the used x-ray beam and a limiting of the beam divergence, therefore in front of the x-ray source is placed a monochromator. A four-crystals arrangement of the monochromator is used to obtain a monochrome parallel incident beam.

The resolution of the diffractometer can be improved reducing the polychromacy and the divergence of the beam. In the past, these effects were normally reduced using a slit in front of the detector, but the high resolution required at present can not be achieved by this arrangement, later an analyser-crystal between sample and detector was inserted. The analyser crystal will only accept scattered X-rays that fall within its intrinsic diffraction range.
width (FWHM $\sim 10''$). High resolution diffractometers are needed, which usually makes use of a five-crystal arrangements (see Fig. 2.2). X-ray diffraction scans recorded with analyser and with slit are shown in Fig. 2.3, as can be seen the measurement with analyser avoids apparatus effects, and even interference peaks can be resolved.

![Graph of intensity vs. $\omega$](image)

**Figure 2.3:** X-ray diffraction scans recorded with a slit and with an analyser crystal [17].

In a five-crystal diffractometer the resolution gradually decreases only for Bragg angles greater than 70°. This configuration, a four crystal monochromator plus analyser crystal, is also called triple-axis. In this work the x-ray measurements were performed using high resolution x-ray diffractometers (Philips MRD and X’Pert MRD) equipped with a four-crystal monochromator in Ge(220) configuration and a two or three reflection Ge(220) analyzer. The x-ray wavelength was the $CuK_{\alpha1}$ with $\lambda = 1.5406\text{Å}$.

### 2.2.2 DuMond-model

If an x-ray beam of broad bandwidth falls upon a crystal at a specific angle of incidence, the crystal will reflect only those wavelengths of the beam which satisfy Bragg’s law for one of the crystal reflections. Thus it is evident that any Bragg reflection may be used to monochromatize an x-ray beam. However, for optimum performance, the design of the monochromator should be chosen so as to pass on as many as possible of the photons that fall within the desired energy range. A model is presented by DuMond[45] for the comprehension of more than two successive x-ray crystal reflections. A crystal reflection is described by a graphical representation of the Bragg’s law solved in $\lambda$. When the angle $\theta$ and the wavelength $\lambda$ of the incident beam satisfy equation (2.1), the beam will be reflected. A graph of $\lambda$ as a function of $\theta$ can describe the diffraction geometry of the crystal reflection. An example is shown in Fig. 2.4.
A plane monochromatic wave is represented by a point on the wavelength axis and will diffract at a certain point. $\lambda(\theta)$ plot for the first crystal is drawn starting from the origin.

![Figure 2.4: DuMond diagram](image)

The reflection at the second crystal (with the same planar spacing) is indicated with $+n$ if it deflects the beam in the same sense as does the first crystal (dispersive arrangement, see Fig. 2.5 a)), and with $-n$ if the it deflects in the opposite sense (non dispersive arrangement, see Fig. 2.5 b)). If the second reflection is $-n$ then the plots of the reflections of the crystals superimpose and no rotation is necessary for diffraction at the second crystal.

![Figure 2.5: Double-crystal arrangement: a) non-dispersive and b) dispersive](image)

If the second reflection is $+n$ then the plots go in the opposite direction, diffraction at the second crystal occurs when its curve on the DuMond diagram intersect part of the curve of the first crystal that occurs at $\theta = \theta_B$. This second arrangement gives excellent monochromatization but poor intensity. The finite beam divergence is represented by the area between a pair of vertical lines marking the maximum and minimum incidence angles on the first crystal.

The DuMond diagram construction can be extended to a series of more than two Bragg reflections. A four-crystal monochromator is a $(+n -n -n +n)$ arrangement.
2.3 Reciprocal space

Bragg’s law is equivalent to the Laue equations:

\[
\vec{q} = \vec{k}_e - \vec{k}_i
\]  \hspace{1cm} (2.2)

where \(\vec{q}\) is the scattering vector and \(\vec{k}_i\) and \(\vec{k}_e\) are the incident and the scattered wave vectors, respectively, and \(|k_e| = |k_i| = 2\pi/\lambda\).

The scattering vector is inversely proportional to the spacing \(d_{hkl}\) of the \((hkl)\) lattice planes in real space:

\[
|q| = \frac{1}{d_{hkl}}
\]  \hspace{1cm} (2.3)

The spacing of the \((hkl)\) lattice planes is directly related to the lattice constants. In the case of GaN with a wurtzite structure one obtains:

\[
\frac{1}{d_{hkl}^2} = \frac{4}{3} \cdot \frac{h^2 + k^2 + h \cdot k}{a^2} + \frac{l^2}{c^2}
\]  \hspace{1cm} (2.4)

2.3.1 Ewald construction

An intuitive understanding of x-ray diffraction is given by the Ewald construction (see Fig. 2.6), which links the reciprocal space of the sample to the angle used in a diffractometer by graphical visualization.

![Ewald construction diagram](https://example.com/ewald_construction.png)

**Figure 2.6:** Illustration of the Ewald-sphere construction.

The radius of the Ewald sphere is given by \(|k_e| = |k_i| = \frac{1}{\lambda}\). One point of the Ewald sphere is fixed to the origin. A certain RLP contributes to the diffraction signal, if the sphere crosses it. Fig. 2.7 shows the region of the reciprocal space that can be reached by the Ewald sphere, at a given wavelength, when the sample is rotated. The RLPs along
the \( q_z \) axis represent symmetric reflection; all others are asymmetric reflections. The two green half circles represent the region which is only accessible in transmission or in skew diffraction geometry.

\[
\lambda = 0.15406 \text{ nm}
\]

\[\begin{align*}
q_x & = \frac{1}{\lambda} \\
q_z & = \frac{1}{\lambda}
\end{align*}\]

\((104)\) (204) (303)

\(k_i = k_e\)

\(\omega\) \(2\theta\)

\(\omega\)-scan

\(2\theta\)-\(\omega\)-scan

**Figure 2.7:** Area accessible in reciprocal space by XRD for GaN (0001) films using a wavelength of 1.5406 Å.

### 2.3.2 Scans in reciprocal space

Using the Ewald sphere construction we can now see that for these RLPs that intersect the Ewald sphere Laue equations are fulfilled. Therefore, to observe all potential reflections we will have to place each individual reflection onto the Ewald sphere.

**Figure 2.8:** Scans in reciprocal space
2.3. RECIPROCAL SPACE

This can be done by either manipulating the Ewald sphere or the reciprocal lattice. The most common method is to change the orientation of the crystal relative to the x-ray beam. This causes a corresponding rotation of the reciprocal lattice and, in this manner, all reflections can be passed through the Ewald sphere. However it is also possible to change the Ewald sphere itself by changing the wavelength. A rotation of the sample, i.e. a change of the angle $\omega$, corresponds to a scan perpendicular to the scattering vector $\vec{q}$ (see Fig. 2.8 a)) in the reciprocal space. The resulting curve is also called rocking curve. A rotation of the detector changes the angle $2\theta$, and this corresponds to a circular arc in the reciprocal space. A combination of the two rotations corresponds to a scan parallel to the scattering vector $\vec{q}$ (see Fig. 2.8 b)) in the reciprocal space and is called $2\theta$-$\omega$-scan or relative scan. Furthermore, reciprocal space maps (RSMs) of RLPs are obtained by performing $2\theta$-$\omega$-scans at different $\omega$ angles around a RLP.

2.3.3 Lattice constant measurement

The lattice constants $a$ and $c$ can be obtained utilizing Eq.s (2.1) and (2.4) for two different reflections. In order to obtain accurate numbers for the lattice constants, the Bragg angle $\theta_B$ has to be measured with high precision, first Bond [46] technique was widely used that made use of a relative measurement to obtain the Bragg angle. The technique proposed by Fewster and Andrew [47] made use of a high quality precision goniometer to obtain the direct measurement of the scattering angle. Therefore the important parameter for the determination of the lattice constants is the direction of the beam and not the position of the analyser or excentric mounting of the sample. This technique can be even used for every crystalline form and for inhomogeneous or bent samples.

Correction to $2\theta$

For an absolute determination of the lattice constant the direction of the primary beam with analyser has to be measured first. Furthermore physical corrections have to be taken into account such as the refraction correction due to the different refraction indices of the solid and the air and Lorentz and polarization corrections that refer to the angular range over which the RLP interacts with the surface of the Ewald sphere. The latter two corrections can be neglected as the intrinsic diffraction profile of the layers are very narrow. Absorption effects can also change the form of the diffracted beam and therefore displace the position of the peak. The corresponding correction is less than $\sim 0.4^\circ$ and can be then neglected. The refraction correction is given by [47]:

$$\Delta(2\theta) = \delta [\cot(\theta - \phi) + \cot(\theta + \phi) + \tan\theta]$$  \hspace{1cm} (2.5)

where $\phi$ is the inclination of the lattice plane to the surface and $\delta$ is related to the refraction index as follows:

$$\delta = 1 - n = \frac{\lambda^2 \cdot c^2}{2\pi \cdot m \cdot e^2} \sum_i (Z_i + \Delta f_i) \cdot N_i$$  \hspace{1cm} (2.6)

there $Z_i$ is the atomic number of the element i, and $f_i$ the dispersive component and $N_i$ is the number of atoms per unit cell. The amount of $\delta$ for GaN layers is $1.71175 \cdot 10^{-5}$. 

2.4 Standard and non-standard x-ray geometries

Symmetrical and asymmetrical geometry: Traditionally two kind of geometries have been developed in x-ray diffraction, which are the symmetric (Fig. 2.9) and asymmetric (Fig. 2.10) geometry. In these geometries the incident and the scattered vectors are in a plane perpendicular to the sample surface, this plane is called scattering plane. The difference between these two geometries is in the angle that the incoming and outgoing beams form with the sample surface. In symmetric geometry, the scattering angle and the incident angle are identical. In asymmetrical geometry, the angles of the incoming and of the outgoing beam are different and this is given by:

$$\omega = \frac{2\theta}{2} \pm \phi$$  \hspace{1cm} (2.7)

where \(\omega\) is the angle between the incident beam and the sample surface, \(2\theta\) is the angle between the scattered beam and the incident beam and \(\alpha\) is the lattice plane inclination relative to the surface. The lattice plane inclination for a wurtzite crystal, is given by:

$$\phi = \arctan \left( \frac{2}{\sqrt{3}} \cdot \frac{c}{a} \cdot \frac{1}{l} \cdot \sqrt{h^2 + k^2 + hl} \right)$$  \hspace{1cm} (2.8)

where \(hkl\) are the Miller indices and \(c\), and \(a\) are the lattice constants.

Skew symmetry: When the scattering plane is not perpendicular to the layer surface, but to the lattice planes under investigation which are inclined by an angle \(\phi\) with respect to the layer surface, this is called skew symmetry. In this case the incident and scattering angles of the x-ray beam are the same (see Fig. 2.11 a)).

Transmission geometry: In transmission geometry the diffracted beam penetrates through the sample and exits from the rear surface (see Fig. 2.12). This geometry is of some interest in the case of thin layers and with large attenuation length.
2.4. STANDARD AND NON-STANDARD X-RAY GEOMETRIES

![Figure 2.11: Skew symmetric diffraction geometry: real space (a) and reciprocal space (b).](image)

![Figure 2.12: Transmission geometry](image)

**Grazing incidence geometry:** In grazing incidence geometry, the x-ray beam strikes the sample surface at an incident angle close to the critical angle of total reflection (see Fig. 2.13). The sample is rotated around the surface normal until a particular lattice plane lying perpendicular to the surface fulfills the Bragg condition. This measurement is surface sensitive.

![Figure 2.13: Grazing incidence diffraction geometry in real space.](image)

**Edge geometry:** In edge geometry (Fig. 2.14), the incident and the diffracted beam are in a plane perpendicular to the edge surface of the sample. The edge surface should be flat to avoid scattering from other planes.
Examples for measurements in these geometries on GaN can be found in the literature particularly for the case of grazing incidence and edge geometry\cite{48, 49}. The twist of mosaic structures has been deduced and, in the case of grazing incidence\cite{49}, compared with XRD results. They agree but as the resolution obtained with these non-standard geometries is limited, the derived value can be considered only as an upper limit of the real twist.

### 2.5 Microstructures

While a crystal lattice of infinite size and perfect three-dimensional periodicity corresponds to delta function like RLPs, rather broad intensity distribution are obtained for real heteroepitaxial layers. Often an elliptical shape of two-dimensional images of these RLPs is observed.

#### 2.5.1 Mosaicity

Heteroepitaxial thin films with a large lattice mismatch with respect to the substrate commonly exhibit high dislocation densities\cite{50, 51, 52}. These structures are often described by the model of mosaic crystals illustrated in Fig. 2.15.

![Figure 2.15: Schematic for a mosaic crystal.](image-url)
The layer is assumed to consist of single crystallites with certain mean vertical and lateral dimensions. Since the crystallites are assumed to be free of dislocations, they can coherently scatter the x-rays, and their dimensions are called vertical and lateral coherence length. The terms vertical and lateral are related to the directions perpendicular and parallel to the growth plane, respectively, where the vertical coherence length is commonly related to the thickness of the layer. Furthermore, the mosaic blocks are assumed to be slightly misoriented with respect to each other.

![Diagram](image)

**Figure 2.16:** Influence of a limited lateral coherence length on symmetric reflections

The out-of-plane rotation of the blocks perpendicular to the surface normal is called tilt, and the in-plane rotation around the surface normal is called twist. Tilt and twist thus define the full width at half maximum (FWHM) of the corresponding distributions of crystallographic orientations.

![Diagram](image)

**Figure 2.17:** Influence of a large tilt on symmetric reflections

The four characteristic parameters of a mosaic layer structure (vertical and lateral coherence length, tilt and twist) can be determined by high resolution x-ray diffraction.
CHAPTER 2. EXPERIMENTAL SETUP

Figure 2.18: Influence of the superposition of a limited lateral coherence length and tilt on symmetric reflections

For that, the influence of the mosaicity on the broadening of RLP, i.e. the distribution of the scattered intensity in reciprocal space, has to be analyzed. Pronounced broadening of a RLP along a certain direction in reciprocal space may indicate the dominance of a particular characteristic parameter of the mosaic structure. The impact of the various mosaicity parameters on the RLP broadening is illustrated in Figs. 2.16 and Figs. 2.17.

Figure 2.19: Influence of the mosaic structure on the orientation of elliptically shaped RLPs.

A limited lateral coherence length causes a RLP broadening in the \((q_x, q_y)\) plane, while a limited vertical coherence length is correlated with a RLP broadening along the \(q_z\) direction.
Thus, these broadening effects are oriented along fixed axes in reciprocal space. They are independent of the reflection order as schematically shown in Fig. 2.16. In contrast to this, a rotational disorder of the mosaic blocks results in a RLP broadening perpendicular to the reciprocal lattice vector of the corresponding reflection. This is sketched in Fig. 2.17 for the example of tilt. Here, the broadening increases with the length of the reciprocal lattice vector. Tilt appears only for RLPs with \( q_z \neq 0 \), whereas twist results in RLP broadening in the \((q_x, q_y)\) plane. The superposition of a rotational disorder and a limited lateral coherence length is shown in Fig. 2.18 for a symmetrical reflection and in Fig. 2.19 for an asymmetrical reflection. The described impact of the mosaicity on the distribution of the diffracted x-rays is the basis of the algorithms used to determine the parameters of mosaic structures which will be discussed in detail in chapter 3.

### 2.5.2 Visibility criterion for TDs in x-ray diffraction

The traditional way to evaluate the quality of GaN layers was to measure the FWHM of the (002) reflection rocking curve, as it was assumed to be directly related to the TD density in the layer. However, cross-sectional TEM studies have revealed inconsistencies which are due to the specific defect structure of GaN\([52]\). As already mentioned, pure edge TDs with line direction along the c-axis are the predominant TDs in GaN. Particular types of TD will affect only specific crystallographic planes, e.g. edge type TDs with Burgers vector \( \mathbf{b} = \frac{1}{3}(1120) \) will affect only \((hkl)\) planes with either \( h \) or \( k \) nonzero. FWHM of rocking curves of the \((302)\) reflection were demonstrated to be a good measure for the edge type TD density. Hence the inconsistency has been explained with the sensitivity of diffraction geometries to the different type of TDs. Particularly, a rocking curve of a symmetric reflection \((00l)\) will be insensitive to the pure edge type TDs. Furthermore pure screw \((\mathbf{b} = \pm[0001])\) or mixed \((\mathbf{b} = \pm[101])\) type TD are present. They will affect \((hkl)\) planes with \( l \) nonzero, thus the \((00l)\) reflections are sensitive only to the screw-mixed type TDs. An equation for the visibility criterion is:

\[
\mathbf{b} \cdot \mathbf{g} \neq 0 \quad (2.9)
\]

with \( \mathbf{b} \) as the Burger’s vector and \( \mathbf{g} \) as the scattering vector.

### 2.6 Origin of strain in MOVPE-grown GaN layers

As already pointed out in section 1.5 two types of stresses are present in GaN epitaxial layers: biaxial and hydrostatic stress. The origin of stress in a heteroepitaxial layer can be manifold, a short review of them is given below: **Biaxial compressive stress due to the difference in thermal expansion coefficients between GaN and the substrate or external stress**: This stress is due to the different thermal expansion coefficients of the layer and the substrate, and it builds up during the cooling of the layer from growth temperature to room temperature. It depends on the temperature and it is zero at growth temperature. The magnitude of this stress depends on the difference between the growth and room temperature. Thus it is expected to be larger for MOVPE than MBE layers. In general the biaxial stress is usually reduced by increasing the thickness of the layer\([53]\). It varies also with the growth conditions of the buffer layer\([54]\). Probably the tensile stress
between buffer layer and substrate, due to lattice mismatch, decreases or increases the compressive stress depending on the buffer layer growth parameters. The data presented in the literature vary quite a bit and are sometimes confusing, as the real origins of the variation of the compressive stress with buffer layer growth parameters are often not obvious.

**Hydrostatic stress:** This stress is normally due to non-stoichiometric growth of the layer or impurity incorporation. The hydrostatic stress is independent of the temperature. Rough theoretical estimations [17] have shown that the hydrostatic strain is not negligible for point defect concentrations of the order of $10^{19} - 10^{20}$ cm$^{-3}$. However, these estimations have neither taken into account the point defect configuration, their interaction nor the relaxation of the lattice due to points defects. The importance of the hydrostatic stress for the strain state of GaN epitaxial layers has been proved by Kisielowski et al. [30]. Indeed the presence of non-stoichiometric defects or impurities make the ratio of the vertical strain to the lateral strain ($\varepsilon_{zz}/\varepsilon_{xx}$) vary largely. This ratio is supposed to be constant and equal to $-2C_{zz}/C_{xx}$ [55, 56].

**Biaxial stress due to lattice mismatch:** This stress appears when the layer and its substrate have different lattice constants. In case of pseudomorphic growth the unit cell is under a biaxial stress in the growth plane. The layer will relax totally or in part by forming misfit dislocations when the critical thickness is exceeded. The stress can be compressive or tensile, depending on the lattice constants of substrate and epilayer. For GaN grown on (0001) sapphire this is compressive.

There is experimental evidence [57] that GaN layers are under tensile stress during growth when a nucleation layer is used. This was first explained by the pseudomorphic growth of GaN on the nucleation layer. However, it is present also when the nucleation layer is made out of AlN although between GaN and AlN there should be a compressive stress.

**Figure 2.20:** Biaxial intrinsic tensile strain builds up during coalescence of the islands
2.7. TEMPERATURE DEPENDENT MEASUREMENTS

The second hypothesis is that a biaxial tensile stress originates from the coalescence process [58] (see Fig. 2.20). At the earliest stage of the growth of a GaN layers on a nucleation layer by MOVPE, crystallites nucleate and grow laterally and vertically until they begin to impinge on each other, eventually forming a coalesced film. The coalescence reduces the interfacial energy as recognized by Hoffman et al. [59], i.e. when two crystallites are brought into close proximity they spontaneously snap together to form a grain boundary and a tensile stress builds up. A schematization of the formation of the stress during the MOVPE growth of a GaN epitaxial layer is shown in Fig.2.21

Figure 2.21: Stress evolution in GaN during and after the growth process [21]

2.7 Temperature dependent measurements

The various contributions to the stress can be separated by utilizing temperature dependent measurements of the lateral and vertical lattice constants of the layer, taking advantage of the different behaviour of the three stress components with temperature. Fig. 2.22 shows the expected behaviours of the lattice constants c and a, respectively, in the case of pure hydrostatic stress or pure biaxial stress. Furthermore, the trend of a stress-free reference sample is shown (solid line in all plots). If only a hydrostatic stress is present in the epilayer then the curves will be shifted relative to the reference values for all temperatures (see Fig. 2.22 a) and d)). With the hypothesis that the sample is free of stress at the growth temperature and that the cooling to room temperature will induce a biaxial stress (compressive or tensile in dependence of the layer and substrate lattice constants), then the lattice constants will intercept the reference values at growth temperature (see Fig. 2.22 b) and e)).
Generally a superposition of different stresses is present, and the temperature dependence of the lattice constants is hard to foretell.

An example is given in Fig. 2.22 c) and Fig. 2.22 f), where the superposition of a pure thermally induced biaxial compressive stress with pure tensile or compressive hydrostatic stress is schematized. The separation of the stress components requires an iterative procedure. The component due to the hydrostatic stress does not change the ratio \( c/a \) and, therefore, only the biaxial stress is reflected in a graph of \( c/a \) over temperature (see Fig. 2.23). In the same graph are also presented the reference values of a stress-free layer [60]. At the temperature where the two lines intersect, no biaxial stress is present in the sample. The hydrostatic strain can be obtained from the lattice constants at this temperature, as shown in Fig.2.23, by:

\[
\begin{align*}
    c_{\text{ref}} \left(T_{\text{biaxial}=0}\right) &= c_{\text{meas}} \left(T_{\text{biaxial}=0}\right) - \Delta c_{\text{hyd}} \\
    a_{\text{ref}} \left(T_{\text{biaxial}=0}\right) &= a_{\text{meas}} \left(T_{\text{biaxial}=0}\right) - \Delta a_{\text{hyd}}
\end{align*}
\]
where \( c_{\text{ref}} \) and \( a_{\text{ref}} \) are the reference values, \( c_{\text{meas}} \) and \( a_{\text{meas}} \) are the measured ones, and \( \Delta c_{\text{hyd}} \) and \( \Delta a_{\text{hyd}} \) are the contributions of the hydrostatic strain to the total strain.

**Figure 2.23:** Trend of the \( c/a \) ratio with temperature

**Figure 2.24:** Schematic for the dependence of the lattice constants on the temperature
Then the tensile biaxial strain at the growth temperature is extrapolated utilizing the assumption that at the growth temperature the biaxial compressive stress vanishes (see, also, Fig. 2.24):

\[
c_{\text{ref}}(T_{\text{growth}}) = c_{\text{meas}}(T_{\text{growth}}) - \Delta c_{\text{hyd}} - \Delta c_{\text{biax-tens}} \tag{2.12}
\]

\[
a_{\text{ref}}(T_{\text{growth}}) = a_{\text{meas}}(T_{\text{growth}}) - \Delta a_{\text{hyd}} - \Delta a_{\text{biax-tens}} \tag{2.13}
\]

where \(\Delta c_{\text{biax-tens}}\) and \(\Delta a_{\text{biax-tens}}\) are the contribution of the biaxial tensile strain at the growth temperature. Once the contribution of these temperature independent components of the strain (hydrostatic and biaxial tensile) are known, the contribution of the biaxial compressive strain can be calculated for each temperature.

### 2.8 High temperature chamber

A high resolution x-ray diffractometer in combination with a high temperature chamber (HTC) (Anton Paar HTK 1200) has been used for the temperature dependent measurements of the strain. A picture of the high temperature chamber is presented in Fig.2.25.

![Figure 2.25: High temperature chamber used in this work.](image)

The chamber is mounted on a Huber-Goniometer in the center. On the right side are the monochromator and x-ray source, on the left side the detector with the analyser. The
chamber is in the x-ray path, the beam enters the chamber through a window covered by two transparent films. The chamber can move around the $\psi$ and $\phi$ angle (see Fig. 2.26) by using the Huber-Goniometer. Thus, the normal of the reflecting plane can be placed in the diffraction plane. The temperature is measured with a thermocouple and then the heating-current is adjusted. Water-cooling is used to protect the sensible parts of the chamber from heating. Furthermore, the inner part of the chamber is under vacuum ($\sim 10^{-4}$ Torr). The chamber operates at temperatures between 298 and 1500 K.

![Inclination of the high temperature chamber](image1.png)

Figure 2.26: Rotation limits of the high temperature chamber for the adjustment of the angle $\phi$

![Lattice constants of Si](image2.png)

Figure 2.27: Lattice constants of Si in dependence on the temperature[61].
CHAPTER 2. EXPERIMENTAL SETUP

If the φ angle is larger than ±2.5° a reduction of the primary beam intensity is observed as shown in fig. 2.26. Due to the small vertical width of the window the x-ray beam cannot enter in the chamber if the φ angle is larger than 4.2°.

The first temperature dependent measurements with the chamber were conducted on a Si(001) sample. The (004) and (224)-reflections of the Si and the method of Fewster et al.[47] were utilized for the determination of the lattice constants of the cubic material between 298 K and 1250 K. The values obtained were compared with reference data. The latter were deduced by using the lattice constants at room temperature and the thermic dilatation coefficient found in the literature [62]. The reference and experimental data are shown in Fig. 2.27, in the insert is plotted the difference between the measured and the real Temperatures at the different temperatures. The difference between the experimental and reference data can be only due to a different temperature of the sample and of the thermocouple. The relation between the two temperatures is collected in Table 2.1.

Table 2.1: Temperature measured by the thermocouple and corresponding real sample temperature.

<table>
<thead>
<tr>
<th>$T_{\text{measured}}$ [K]</th>
<th>298</th>
<th>400</th>
<th>500</th>
<th>600</th>
<th>700</th>
<th>800</th>
<th>900</th>
<th>1000</th>
<th>1100</th>
<th>1200</th>
<th>1250</th>
</tr>
</thead>
<tbody>
<tr>
<td>$T_{\text{real}}$ [K]</td>
<td>298</td>
<td>413</td>
<td>533</td>
<td>640</td>
<td>750</td>
<td>846</td>
<td>935</td>
<td>1022</td>
<td>1115</td>
<td>1203</td>
<td>1250</td>
</tr>
</tbody>
</table>

2.9 AlGaN strain determined by XRD

2.9.1 Model of the relaxation line

The real structure of imperfect epilayers can be examined using reciprocal space maps (RSMs) [63]. In this way information about the mosaicity, composition variations or macroscopic strain can be obtained. A layer grown on a substrate with a different lattice constant will be strained tetragonally provided that the thickness of the layer does not exceed a critical thickness $t_c$. For a layer thickness larger than $t_c$, the layer relaxes partially by forming misfit dislocations, i.e. the lattice constants of the epilayer approach the relaxed values. During the relaxation process the ratio of the vertical strain $\epsilon_\perp$ to the lateral strain $\epsilon_\parallel$ is assumed to be constant and equal to the material constant $D_i$. In the case of a hexagonal crystal this ratio is also given by Eq. 1.4. The lattice constant of an epilayer is between the lattice constants of the unstrained layer ($a_0$, $c_0$) and the lattice constants of the substrate ($a_{\text{sub}}$, $c_{\text{sub}}$), i.e., the in-plane lattice constant has a value in the interval $[a_0$, $a_{\text{sub}}]$. To describe the different strain- or relaxation-state of a layer, a strain parameter $\gamma$ is defined in this way:

$$
\frac{a - a_{\text{sub}}}{a_{\text{sub}}} = \frac{a_0 - a_{\text{sub}}}{a_{\text{sub}}}(1 - \gamma)
$$

(2.14)

$$
\frac{c - c_{\text{sub}}}{c_{\text{sub}}} = \frac{c_0 - c_{\text{sub}}}{c_{\text{sub}}}(1 + \left(\frac{\epsilon_\parallel - \epsilon_\perp}{\epsilon_\perp} - 1\right)\gamma)
$$

(2.15)
2.9. ALGAN STRAIN DETERMINED BY XRD

The parameter $\gamma$ is unity for a fully strained layer and vanishes for a fully relaxed layer. For a hexagonal structure:

$$\frac{\epsilon_\parallel - \epsilon_\perp}{\epsilon_\perp} = 1 + 2 \frac{C_{13}}{C_{33}} \gamma.$$  (2.16)

Fig.2.28 illustrates the relaxation process of an epilayer on a substrate with a smaller lattice constant in reciprocal space. The line connecting the points referring to a fully strained and a completely relaxed layer is called relaxation line. Assuming that Hooke’s law applies during the relaxation process of the epilayer this must be a straight line. It is defined by the angles $\alpha$ and $\phi$ as shown in Fig.2.28, where $\phi$ is the inclination of the lattice planes given by Eq.(2.10). The angle $\alpha$ together with the position of the RLP of the layer defines the relaxation line and is given by:

$$\alpha = \arctan \left( \frac{C_{33}}{2C_{13}} \tan \phi \right).$$  (2.17)

The relaxation line of AlGaN varies with the Al concentration, as the distance between the peaks changes with the Al concentration. For fully relaxed layers the Al concentration can be easily derived from the Vegard’s law:

$$x = \frac{c - c_{GaN}}{c_{AlN} - c_{GaN}}$$  (2.18)

where $c$ is the lattice constant of AlGaN, and $c_{GaN}$ and $c_{AlN}$ are unstrained lattice constants of GaN and AlN, respectively. The value of $c$ is determined by using x-ray diffraction by recording a $2\theta - \omega$ scan of a symmetric reflection.
For strained layer the following formula can be used:

\[ x = \frac{(c - c_{\text{GaN}}) + \zeta(a - a_{\text{GaN}})}{(c_{\text{AlN}} - c) + \zeta(a_{\text{AlN}} - a)} \]  

(2.19)

with:

\[ \zeta = 2 \frac{C_{\text{GaN}} c_{0_{\text{GaN}}}}{C_{\text{AlN}} c_{0_{\text{AlN}}}} \]  

(2.20)

the equation is derived from the elastic theory with the approximation that the stiffness constants and the \( \frac{c_0}{a_0} \) ratio of AlGaN layers differ only slightly from the corresponding parameters of the GaN layer. The Al concentrations extracted with this approximation differs only slightly from the values calculated without approximation [21].

In order to get a RSM with both the \((hkl)\) reflections of the substrate and of the layer, the difference in lattice constants must be small. This is not the case, for example, for AlGaN grown directly on sapphire or SiC. More the Al concentration of strained layers can not be evaluated from Eq.2.24 as the \( \frac{c_0}{a_0} \) ratio of AlGaN is strongly different from \( \frac{c_0}{a_0} \) ratio of sapphire or SiC. In chapter 5 the strain and Al concentration of AlGaN grown directly on SiC will be evaluated by using a RSM as it will be explained in the chapter.

2.9.2 Atomic force microscopy (AFM)

AFM provides pictures of surfaces.

The AFM works by scanning a fine ceramic or semiconductor tip over a surface. The tip is positioned at the end of a cantilever beam. As the tip is repelled by or attracted to the surface, the cantilever beam deflects. The magnitude of the deflection is captured by a laser that reflects at an oblique angle from the very end of the cantilever (Fig. 2.29). A plot of the laser deflection versus tip position on the sample surface provides the resolution of the hills and valleys that constitute the topography of the surface. The AFM can work with the tip touching the sample (contact mode), or the tip can tap across the surface (tapping mode).
2.9.3 Transmission electron microscopy (TEM)

Electron Microscopes (EMs) function exactly as their optical counterparts except that they use a focused beam of electrons instead of light to "image" the specimen and gain information as to its structure and composition. In TEM a thin specimen is illuminated with electrons, the primary electrons. Many physical techniques rely on the interaction between high energy electrons and the atoms in a solid. There are many possible interactions. An electron passing through a solid may be scattered not at all once (single scattering) several times (plural scattering), or very many times (multiple scattering). Each scattering event might be elastic or inelastic. The scattered electron is most likely to be forward scattered but there is a small chance that it will be backscattered. In crystalline samples an image of the reciprocal space is formed behind the specimen due to interference of electron waves. For more details on TEM, Williams and Carter wrote an interesting book [64].
CHAPTER 2. EXPERIMENTAL SETUP
Chapter 3

Growth induced strain and defects

3.1 Introduction

The real structure of imperfect epilayers can be extracted from high resolution x-ray diffraction measurements by including the structural imperfections as a parameter of disturbed coherence into the simulations of rocking curves. This is also the idea used to study the mosaicity of GaN layers, grown by metalorganic vapour phase epitaxy (MOVPE) on (0001) sapphire, with different grain diameters. Disturbed periodicity of the lattice results in the incoherent scattering of x-rays, and this incoherent scattering broadens the reciprocal lattice points. GaN layers have typically a so-called mosaic structure due to the use of a low-temperature nucleation layer that induces a high-temperature islanding process (see Fig. 3.1 a)). These islands can be considered as single crystallites almost free of dislocations (Fig. 3.1 b)), apart sometimes a screw dislocations in the center of a grain. The threading dislocations are assumed to originate mainly from the island coalescence[65]. Furthermore, the layers are under intrinsic tensile stress due to the coalescence process and under extrinsic compressive strain due to the cooling process to RT.

The first part of this chapter will deal with the characterization of the layers with regard to mosaic structure parameters and the density and structure of dislocations. The second part will deal with the strain of the layers utilizing temperature-dependent x-ray diffraction measurements to separate the components of the strain in the layers.

Figure 3.1: (a)Islanding process and strain and (b)formation of threading dislocations
The coalescence process has been monitored with in-situ reflectometry to determine the layer thickness at coalescence [12].

![Plan-view TEM images of samples with different coalescence thickness.](image)

**Figure 3.2:** Plan-view TEM images of samples with different coalescence thickness. The graph shows dislocation densities extracted from these TEM images as a function of the grain diameter [12].

If the ratio of lateral to vertical growth rate is approximately constant for the set of growth parameters chosen, the coalescence thickness can be taken as a direct measure of the average grain diameter in the fully coalesced films [12].

The GaN layers were grown by T. Boettcher on c-plane sapphire by metalorganic vapour phase epitaxy at a temperature of 1040 – 1050° C, a pressure of 700 Torr for the samples A, B and D and 150 Torr for C, ammonia and trimethylgallium are used as precursors.
and hydrogen as the carrier gas. The coalescence process was varied by changing the total pressure and the V/III ratio during the nucleation layer growth [21]. A 25 nm thick GaN nucleation layer was deposited at 550°C for all samples [12]. The coalescence and the total thicknesses of the samples are shown in table 3.1.

![AFM images of samples with different coalescence thickness.](image1.png)

**Figure 3.3:** AFM images of samples with different coalescence thickness. The graph shows the subsequently extracted dislocation densities as a function of the grain diameter [12].

The average grain diameter was varied between 250 and 4200 nm choosing appropriate growth parameters [66]. This variation in grain diameter resulted in a drastic change of the edge and mixed type TD density as illustrated in Fig. 3.2, which shows plan-view TEM images of samples with average grain diameter of 250 nm, 1000 nm and 4200 nm, respectively. Instead, the screw type TD remain quite constant (Fig. 3.3), showing no
dependence on the grain diameter. This suggests that the formation of screw type TD is not related to the coalescence process, i.e. these dislocations are randomly distributed.

3.2 Mosaic structure

As mentioned in section 2.5, the characteristic parameters of mosaic layers can be determined utilizing their influence on the RLPs. Fig. 3.4 shows schematically a typical mosaic structure and its parameters. The evaluation of these parameters has been done using different approaches and different x-ray diffraction geometries. An extended review of these approaches has been given in the previous chapter. Here, the results will be discussed, and a model of the structure proposed. The vertical coherence length has often been treated as being equivalent to the layer thickness as will be discussed just briefly [48].

![Diagram of a mosaic layer structure](image)

**Figure 3.4:** Illustration of a mosaic layer structure with the four characteristic parameters: lateral and vertical coherence length, tilt and twist.

3.2.1 Tilt and coherence lengths

The influence of **tilt** and **coherence lengths** on the RLPs has been treated in section 2.5. For **symmetric reflections**, the broadening perpendicular to the q_z axis in reciprocal space due to tilted crystallites is proportional to the scattering order, while the broadening perpendicular to the q_z axis in reciprocal space due to a limited lateral coherence length is independent of the scattering order (see Fig 2.16 and 2.17).

<table>
<thead>
<tr>
<th>Sample</th>
<th>Coalescence thickness (nm)</th>
<th>Total thickness (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>4200</td>
<td>5700</td>
</tr>
<tr>
<td>B</td>
<td>1000</td>
<td>2200</td>
</tr>
<tr>
<td>C</td>
<td>250</td>
<td>1800</td>
</tr>
<tr>
<td>D</td>
<td>350</td>
<td>2000</td>
</tr>
</tbody>
</table>

Table 3.1: Coalescence and total thicknesses of the samples.
A separation of these two effects is possible by recording rocking curves of the (002), (004) and (006) symmetric reflections and utilizing a Williamson-Hall plot, in which the FWHM is plotted in reciprocal space units \( (FWHM \cdot \frac{\sin \theta}{\lambda}) \) versus the reflection order in reciprocal space units (see Fig. 3.5).

**Figure 3.5:** Schematic Williamson-Hall plot for the determination of tilt and lateral coherence length of a mosaic structure.

The data are fitted by a linear regression:

\[
y = y_0 + \alpha \cdot x
\]  

(3.1)

**Figure 3.6:** Williamson-Hall plot for samples with different grain diameter. Triple-axis rocking curves were measured for \((00l)\) reflections as indicated in the figure. The lines result from a linear fit of the data.
The intersection with the y-axis \((y_0)\) gives the lateral coherence length defined as [67]:

\[
d_{lat} = \frac{0.9}{2 \cdot y_0}.
\]  

The slope \(\alpha\) is a direct measure of the tilt as shown also in Fig. 3.5. Triple-axis rocking curves of the (002), (004), and (006) symmetric reflections were measured for all samples and their broadening analyzed in a Williamson-Hall plot. Fig. 3.6 shows data for selected samples with different grain diameter and the subsequent linear fit. From the linear fit the tilt and lateral coherence lengths have been calculated for the different samples and then plotted in Fig. 3.7 as a function of the average grain diameter. The values for the lateral coherence lengths show a maximum for a grain diameter of about 2\(\mu\)m, the values are in the range 500 to 1800 nm. Also, the tilt values have a maximum at the same value of grain diameter and are in the range 170 and 290 arcsec. The evaluation of the tilt and of the lateral coherence length of the mosaic blocks from asymmetric reflections is slightly more difficult. They broaden the RLPs along different directions in reciprocal space (see section 2.5, Figs. 2.19). The superposition of the two effects causes a rotation of the RLP ellipses in the \((q_x, q_z)\) plane.

![Graph showing tilt and lateral coherence lengths as a function of the grain diameter.](image)

**Figure 3.7:** Tilt and lateral coherence lengths as obtained from Williamson-Hall plots as a function of the grain diameter.

Therefore, RSMs of the RLPs rather than single scans are necessary to get a full picture of the mosaicity. Particularly the rotation of the RLP is measured which can be quantified by the angle \(\alpha\) between the main axis of the RLP ellipses and the \(q_x\)-axis. Two extreme cases are possible: a) dominance of the lateral coherence length effect resulting in \(\alpha = 0\), and b) dominance of the tilt resulting in \(\alpha = \phi\), where \(\phi\) is the inclination angle of the
diffracting lattice planes with respect to the sample surface. A graphical illustration of the trend of the $\alpha$ angle with $\phi$ is given in Fig. 3.8. In the graph are depicted the two extreme cases of dominant tilt and dominant lateral coherence length.

**Figure 3.8:** Schematic for the orientation of RLPs as a function of the lattice plane inclination angle. The two extreme cases of dominant tilt ($\alpha = \phi$) and of dominant lateral coherence length ($\alpha = 0$) are shown as dashed lines.

**Figure 3.9:** Reciprocal space maps of the asymmetric reflections (105) and (114), corresponding to $\phi = 20.5^\circ$ and $\phi = 39.1^\circ$ respectively, for a sample with a grain diameter of $d_0 = 350$ nm.

RSMs of the (105), with $\phi = 20.5^\circ$, and (114) with $\phi = 39.1^\circ$ asymmetric reflections, are shown in Fig. 3.9 for a sample with a small average grain diameter of 350 nm.
CHAPTER 3. GROWTH INDUCED STRAIN AND DEFECTS

Figure 3.10: Reciprocal space maps of the asymmetric reflections (105) and (114), corresponding to $\phi = 20.5^\circ$ and $\phi = 39.1^\circ$ respectively, for a sample with a grain diameter of $d_0 = 4200$ nm.

Figure 3.11: Simulation of the distribution of RLPs in a mosaic structure in the case of dominant lateral coherence length.

Figure 3.12: Simulation of the distribution of RLPs in a mosaic structure in the case of dominant tilt.

The RLPs have a nearly elliptical shape, which is most obvious for the high intensity contour lines. As discussed before, the inclination $\alpha$ of the main axis of these ellipses with respect to the $q_x$ axis, is taken as a measure for the mosaicity of the layer. As can be seen in Fig. 3.9 and 3.10, the angle $\alpha$ is larger for an asymmetric reflection with a larger lattice plane inclination $\phi$. Furthermore, the inclination angle $\alpha$ of the RLP main axis depends strongly on the grain diameter as can be seen in Fig. 3.10 and 3.9 showing RSMs of the same asymmetric reflections for a sample with a larger grain diameter. The RLP of a mosaic structure can be simulated using a model published by Holy et al. [68]. The model is based on the kinematical theory of x-ray diffraction and requires the assumption of a mean block size (lateral coherence length) and an average tilt. The RLPs obtained in this way are shown in Fig. 3.11 and Fig. 3.12 for the two extreme cases of dominant lateral coherence length and dominant tilt, respectively, for the (213) asymmetrical reflection. Unfortunately,
3.2. MOSAIC STRUCTURE

the model yields identical results for a constant product of lateral coherence length and tilt as shown in Fig. 3.13. Obviously, the effect of tilt and lateral coherence length can not be separated by only measuring the angle $\alpha$. Therefore, it was assumed that the tilt is identical to the values extracted from the Williamson-Hall plots shown in Fig. 3.6 and the lateral coherence length, only, was determined comparing the orientation of experimental and simulated RLPs.

Figure 3.13: Inclination of RLP obtained from the simulation of distributions of RLPs in a mosaic structure for a constant product of tilt and lateral coherence length utilizing the model of Holy et al.

The inclination angle $\alpha$ obtained from the experimental data is shown in Fig. 3.14 as a function of the inclination angle $\phi$ of the reflecting lattice planes for GaN layers with a grain diameter of 350, 1000 and 4200 nm, respectively. For every sample the $\alpha$ angle increases with the angle $\phi$ and also with increasing grain diameter. The sample with an estimated grain diameter of 4200 nm, has a RLP inclination almost equal to $\phi$ independent of the chosen reflection. In contrast to this, the RLP inclination approaches $\phi$ only for large values of $\phi$ for the sample with 350 nm. Thus, the layers approach the limit of dominant tilt broadening with increasing grain diameter. The values obtained from the simulation are added in Fig. 3.14 to the experimental data. The values obtained from the simulations confirm the general trend of the experimental data in the case of small lattice plane inclination angles and large grain diameters. The experimental data deviates from the simulated ones only for small grain diameter at large angles $\phi$. However, as can be seen in Fig. 3.15, the high intensity contour line of the asymmetric reflection (213), for a sample with small grain diameter ($d_0 = 350nm$), has a not well defined elliptical shape, causing an indetermination in the evaluation of the inclination of the RLP of $\pm 3^\circ$, instead
the high intensity contour line of the asymmetric reflection (213), for a sample with large grain diameter ($d_0 = 4200\text{nm}$), is better defined. Now that the symmetric and asymmetric reflections have both been used to evaluate the lateral coherence lengths, it is necessary to compare their results. This is done in Fig. 3.17.

**Figure 3.14:** Inclination of RLPs ((105), (114), and (213) reflections) relative to the $q_x$-axis as a function of the lattice plane inclination angle for samples with different grain diameter. The two extreme cases of dominant tilt ($\alpha = \phi$) and of dominant finite size broadening ($\alpha = 0$) are shown as dashed lines. The open symbols are experimental data, and the filled ones represent simulated values assuming the tilt extracted from Fig. 3.6 and using the lateral size of the mosaic blocks as the lateral coherence length.

It shows a clear trend of increasing lateral coherence lengths increasing grain diameter for the results obtained from asymmetric reflections. Contrarily, the lateral coherence lengths obtained from the symmetric reflections show a maximum and are much larger compared to the values obtained from asymmetric reflections. The different lateral coherent lengths derived from symmetric and asymmetric reflections can be explained by the different sensitivity of these reflections to the various types of threading dislocations (TD). Screw type TDs with a Burgers vector $\vec{b}_s = \langle 0001 \rangle$ distort all (hkl) planes with $l$ not equal to zero. Edge type TDs with the dislocation line along $[0001]$ and a Burgers vector $\vec{b}_e = \frac{1}{3} \langle 1120 \rangle$ distort only those (hkl) planes with $h$ or $k$ being non-zero. This means, that rocking curves of symmetric reflections are not broadened by pure edge type TDs [52]. Since the edge type TDs are distributed at the grain boundaries the inverse of the lateral coherence length is a measure for the edge type TD density, it can be concluded from Fig. 3.17 that
Figure 3.15: Reciprocal space map of the asymmetric reflection (213), corresponding to $\phi = 58.9^\circ$, for a sample with small grain diameter ($d_0 = 350\,nm$).

Figure 3.16: Reciprocal space map of the asymmetric reflection (213), corresponding to $\phi = 58.9^\circ$, for a sample with large grain diameter ($d_0 = 4200\,nm$).

The increase of the lateral coherence length with increasing grain diameter derived from asymmetric reflections confirms the changes in the dislocation structure found in the TEM images shown in Fig. 3.2.

Figure 3.17: Comparison of the lateral coherence lengths as a function of the grain diameter obtained from symmetric and asymmetric reflections.

The broadening of RLPs of symmetric reflections parallel to the $q_z$ direction in reciprocal space is due to both a limited vertical coherence length and to a heterogeneous strain along the c-axis of the crystal. This heterogeneous strain is present if there is a local variation of the strain along the c-axis which is normally called microstrain and the
coalescence process produces a strain gradient at the coalescence boundaries as explained in section 2.6. Again these two effects can be separated utilizing a Williamson-Hall plot as the broadening due to a limited vertical coherence length is independent of the scattering order, while the broadening due to heterogeneous strain is proportional to the scattering order.

\[ \text{FWHM} \times \left( \frac{\sin(\theta)}{\lambda} \right) [\text{nm}^{-1}] \]

\[ \frac{1}{\text{interception}} \text{ proportional to vertical coherence length} \]

\[ \text{slope of regression} \text{ describes heterogeneous strain} \]

**Figure 3.18:** Williamson-Hall plot for samples with layer thicknesses of 1.0, 2.0 and 5.5 \( \mu \)m, but equal average grain diameters of 0.5 \( \mu \)m. Triple-axis \( \omega - 2\theta \) scans were measured for the (00\( l \)) reflections indicated in the figure. The lines result from a linear regression of the data.

Fig. 3.18 shows a Williamson-Hall plot for three GaN layers with different thicknesses, varying from 1.0 \( \mu \)m to 5.5 \( \mu \)m. By choosing identical growth parameters, the average grain diameter of (500 \( \pm \) 200) nm was constant for these layers. In the figure the \( q_z \) broadening of RLPs is plotted as a function of the reflection order as extracted from triple-axis \( \omega - 2\theta \) scans together with corresponding linear fits. The inverse of the point of interception is proportional to the vertical coherence length, and the slope of the regression describes the heterogeneous strain. As can be expected from the dislocation structure, the vertical coherence length increases with the layer thickness, varying between 370 nm, for the thinnest layer, and 6200 nm for the thickest one. The heterogeneous strain decreases by a factor of 4 with increasing layer thickness. Indeed layers with a thickness much larger than the coalescence thickness are expected to release a greater amount of the strain variation produced at the coalescence boundaries.

### 3.2.2 Twist

Until now only standard x-ray geometries have been used as only the impact of the tilt and the lateral coherence length on the RLPs in the \( (q_x, q_z) \) plane has been considered.
However in the case of in-plane rotation of the mosaic block (twist), the RLP is broadened in the \((q_x, q_y)\) plane. Its evaluation requires either a so-called in-plane measurements ((hk0) reflection), or an extrapolation of the broadening along \(q_y\) to a lattice plane inclination angle of 90°. In the previous chapter a review of non-standard diffraction geometries has been given, which are: transmission, grazing incidence or edge geometry. Examples of these measurements made by other groups on GaN can be found in the literature [69, 70, 71, 48]. In this work the twist of the mosaic blocks was determined by measuring rocking curves of the (110) reflection in edge diffraction geometry. Here, the twist is directly given by the broadening of this reflection along \(q_y\), but the strain relaxation of the sample at the sample edge or crystal damages limit the measurement accuracy.

\[ FWHM = (((f_{\text{twist}}(\phi))^n + (f_{\text{tilt}}(\phi))^n)^{1/n} \]

\( (3.3) \)
with
\[ f_{\text{twist}}(\phi) = \text{FWHM}_{\text{twist}} \cdot \sin(\phi) \exp(-m \cdot \cos(\phi)) \] (3.4)
and
\[ f_{\text{tilt}}(\phi) = \text{FWHM}_{\text{tilt}} \cdot \cos(\phi) \exp(-m \cdot \sin(\phi)) \] (3.5)
where \( m \) is a parameter characterizing the interdependence between the two distribution (tilt, twist), \( \text{FWHM}_{\text{tilt}} \) and \( \text{FWHM}_{\text{twist}} \) are the broadenings due to tilt and twist, respectively.

The RLPs are fitted by Pseudo-Voigt functions, which are a combination of gaussian and lorentzian distribution functions; \( n \) is a parameter for the convolution of Pseudo-Voigt functions and varies between 1 and 2, depending on the weight of the gaussian and the lorentzian function, respectively, in the Pseudo-Voigt function. The broadening of various \((h0l)\) reflections has to be measured in skew symmetry\[73\] to minimize the impact of the apparatus function. In order to access the twist of the layers one has to measure reflections with different \( \phi \)-values followed by an extrapolation to \( \phi = 90^\circ \). The described method has been applied to the GaN layers under investigation. The result is shown in Fig. 3.20, where the FWHM of triple axis rocking curves of RLPs measured in skew symmetry is plotted as a function of the lattice plane inclination angle. The experimental data are strongly dependent on the average grain diameter. While the FWHM increases with lattice plane inclination for layers with small grain diameter, the FWHM is quite constant for films.
3.2. MOSAIC STRUCTURE

with large grain diameters, suggesting a much lower twist of the mosaic blocks in the latter case. The dashed lines are simulation curves obtained utilizing the algorithm of Srikant et al.\cite{72}.

The extrapolation of the fitted curves to $\phi = 90^\circ$ provides the average twists of the layers which are shown in Fig. 3.19 as a function of the grain diameter. It should be noted that the twist is overestimated by this extrapolation procedure, since the lateral coherence length also contributes to the measured FWHM. The twist decreases with increasing grain diameter and approaches a value for large grain diameters which is comparable to the tilt value at large grain diameters (see Fig. 3.7). As can be seen in Fig. 3.19, the twist obtained in edge geometry is larger than the one obtained by extrapolation, but it fully reproduces the trend.

3.2.3 Defect determination

In a mosaic structure the influence of the dislocations on the broadening of the RLPs can be described by the Darwin theory, which describes an ensemble of ideal crystallites. The dislocations are randomly distributed or are localized at the boundaries of the crystallites. The latter are called low angle grain boundaries if the crystallites are only slightly rotated with respect to each other. Under the hypothesis that the mismatch angle between adjacent grains meets a Gauss distribution and that the dislocations are stochastically distributed the dislocation density $N$ is related to the broadening $\beta$ by:

$$N = \frac{\beta^2}{4.36b^2}$$

(3.6)

where $b$ is the length of the Burgers-vector of the dislocation \cite{74}.

In case that the dislocations are not randomly distributed but localized at the grain boundaries, their individual strain fields superimpose and the grain diameter $d_0$ has to be taken into account\cite{75}:

$$N = \frac{\beta}{2.1 \cdot b \cdot d_0},$$

(3.7)

where $N$ is the dislocation density and $b$ is the length of the Burgers vector of the dislocations. If one assumes that screw form to adapt the out of plane tilt of the layer and that edge type TDs accomodate the in-plane twist in the layer, then the broadening $\beta$ of the RLPs can be approximated by the FWHM of the RLPs affected from these dislocations. The FWHM of (002) reflection was found to be a good approximation of the tilt, whereas the $1.14 \cdot$ FWHM of the (302) reflection is a good approximation of the twist \cite{76, 73}.

If the FWHM of the rocking curves $\Delta \omega$ is not only due to dislocations but also due to an intrinsic broadening of the reflection or apparatus effects, these contributions have to be eliminated. In general, the rocking curves can be approximated by a gaussian distribution, and $\Delta \omega$ can be written as:

$$\Delta \omega^2 = \beta^2 + \Delta \epsilon^2 + \Delta \theta^2 + \Delta \xi^2$$

(3.8)

where $\Delta \epsilon$ is the broadening due to the apparatus effects, $\Delta \theta$ is the intrinsic broadening of the reflection, and $\Delta \xi$ are other contributions like curvature of the sample, or inhomogeneous strain.
In general the broadening of a RLP, FWHM, is also affected by finite size effects due to limited spacial coherence of the crystal lattice. This additional broadening can be estimated using the Scherrer equation[62]:

\[ d = \frac{0.9 \cdot \lambda}{\text{FWHM} \cdot \sin \theta} \]  

(3.9)

where \( d \) is the coherence length, \( \theta \) is the scattering angle, and \( \lambda \) is the wavelength of the x-rays. If the finite size effect (Scherrer equation) is taken in account, then:

\[ N_e = \frac{1}{2.1 \cdot b \cdot d} \sqrt{\Delta \omega^2 - \left(\frac{0.9 \cdot \lambda}{d \cdot \sin \theta}\right)^2} \]  

(3.10)

### 3.2.4 Dislocation densities

The edge type TD density obtained from the Eq. 3.6 and 3.7 is plotted in Fig. 3.21 and compared to the data obtained from the plan-view TEM images shown in Fig. 3.2. The model assuming a random distribution of the edge type TDs (Eq. 3.6) significantly overestimates the dislocation density determined by TEM. The discrepancy becomes larger with increasing grain diameter. In contrast, the model of correlated edge type TDs provides a reasonable agreement with the TEM data.

![Figure 3.21: Edge type TD densities as a function of the grain diameter. The dashed line is a eye guide [12].](image-url)
3.2. MOSAIC STRUCTURE

Only for lower grain diameters the dislocation density extracted from the XRD data deviates to slightly higher values. The deviations between XRD and TEM data for small grain diameter are presumably caused by finite size broadening. If the finite size effect (Scherrer equation) is taken into account in Eq.3.7, then:

\[
N_e = \frac{1}{2.1 \cdot b \cdot d} \sqrt{ \left( \text{FWHM}_{302} \right)^2 - \left( 0.9 \cdot \lambda \cdot \sin \theta \right)^2 }
\]  

(3.11)

where \( \lambda \) is the wavelength of the x-rays, FWHM\(_{302} \) is the rocking curve FWHM of the (302) reflection and \( \theta \) is the Bragg angle of the (302) reflection [76, 73]. Densities of edge type TDs evaluated from XRD data according to Eq.3.6 are shown in Fig. 3.22 together with the plane-view TEM results for selected samples. In addition to the edge type TD densities, densities of screw type TD are plotted in Fig. 3.22. They are calculated from Eq.3.6 using the Burgers vector length \( b_s \) of the screw type TD on the one hand, and measured by AFM for two samples on the other hand. An excellent agreement between XRD, TEM and AFM data is found. The edge type TD density dominates for almost all samples, but drops for larger grain diameters. In contrast, the screw type TD density is roughly constant for all samples under investigation.

The linear reduction of the edge type threading dislocations with increasing grain diameter suggests that a perfect layer, i.e. almost free of dislocations, can be obtained at very large grain diameter. Wu et al. have given experimental evidence [65, 77] of a mosaic structure in GaN MOVPE layers by using in-plane TEM micrograph. They have revealed a grain structure in layer with high dislocation density, whereas layers with low dislocation density have too large spacing between dislocations to reveal a grain structure.

\[ 0,25 \quad 0,50 \quad 1,00 \quad 2,00 \quad 4,00 \]

\[ \text{grain diameter [\( \mu \text{m} \)]} \]

\[ 10^7 \quad 10^8 \quad 10^9 \quad 10^{10} \]

\[ \text{threading dislocation density [cm}^{-2} \text{]} \]

\[ \text{screw/mixed (XRD)} \quad \text{edge/mixed (TEM)} \quad \text{screw/mixed (AFM)} \quad \text{edge/mixed (XRD)} \]

Figure 3.22: Edge and screw type TD dislocation densities as determined by XRD, AFM and plan-view TEM as a function of the grain diameter.
3.3 Strain

This part of the work will deal with the strain present in MOVPE GaN layers having different coalescence thicknesses. As already discussed in section 1.5, a biaxial tensile stress resulting from the coalescence process is supposed to be present in the layers. This stress can explain why the MOVPE GaN layers grown on (0001) sapphire are found to be under tensile rather than under compressive stress during growth [57]. The existence of a tensile stress has been proposed first by Hoffmann et al. [59] and mathematically formulated by Nix et al. [58] for polycrystalline films through the mechanism of crystallite coalescence. Nix et al. have also proposed that this stress has to be inversely proportional to the grain size, with the following formula:

\[ \sigma = \frac{E \Delta}{1 - \nu d_0} \]  

(3.12)

where E is Young modulus, \( \nu \) the Poisson ratio, \( d_0 \) the grain size and \( \Delta \) the gap between adjacent crystallites at the point of their coalescence.

Figure 3.23: \( a \) and \( c \) lattice constants as a function of the grain diameter[21].

In Fig. 3.23 the trend of \( a \) and \( c \) lattice constants with different grain diameter is shown, the two lattice constants show a strong dependence on the grain size. This is a first confirm of the existence of a coalescence dependent stress. An effective technique to separate the components of the strain is x-ray diffraction at variable temperature, as was already explained in section 2.7. The lattice constants \( a \) and \( c \) of GaN epilayers were measured in the temperature range between RT and 1020 K using HRXRD.
By utilizing theoretical data on lattice constants of unstrained GaN layers [60], the strain components were calculated. To determine the \( c \) lattice constant, the (002) and (004)

\[ \begin{align*}
(002) & \quad \text{lattice constant} = 5.19 \\
(004) & \quad \text{lattice constant} = 5.21
\end{align*} \]

\[ \text{Figure 3.24: } \text{c lattice constant as determined from the (002) and (004) reflection, respectively, versus the temperature.} \]

symmetrical reflections have been measured, whereas the \( a \) lattice constants were extracted from the (105) and (204) asymmetrical reflection.

\[ \begin{align*}
(105) & \quad \text{lattice constant} = 3.19 \\
(204) & \quad \text{lattice constant} = 3.21
\end{align*} \]

\[ \text{Figure 3.25: } \text{a lattice constant as determined from the (105) and (204) reflection, respectively, versus the temperature.} \]

\[ \begin{align*}
d_0 = 1000 \text{ nm} & \quad \text{lattice constant} = 5.19 \\
d_0 = 4200 \text{ nm} & \quad \text{lattice constant} = 5.21 \\
d_0 = 250 \text{ nm} & \quad \text{lattice constant} = 5.19 \\
\text{reference value} & \quad \text{lattice constant} = 5.21
\end{align*} \]

\[ \text{Figure 3.26: } \text{c lattice constant versus the temperature for samples with different grain sizes, the dashed line represents the literature data [60].} \]
The difference in the $c$ values obtained with the two symmetrical reflections is very low ($\Delta c \approx 0.0002$ Å, see Fig. 3.24), whereas the difference in the $a$ lattice constants obtained from the two asymmetrical reflections is considerably large ($\Delta a \approx 0.001$ Å, see Fig. 3.25).

**Figure 3.27:** $a$ lattice constant versus the temperature for samples with different grain sizes, the dashed line represents the literature data [60].

In Fig. 3.26 and in Fig. 3.27 the experimental $c$ and the $a$ lattice constants of samples with different grain sizes are shown as a function of the temperature and compared with theoretical values of unstrained GaN layers taken from the literature [60].

**Figure 3.28:** $c/a$ lattice constant versus the temperature for samples with different grain sizes. The crosses are the literature data [60].
From the comparison of the experimental data with expectations for purely biaxially or purely hydrostatically stressed GaN (see Fig. 2.22 of section 2.7) it is clear that the experimental data indicate a superposition of the two different stress situation. The temperature dependence of the two lattice constants for samples with different grain diameter is similar. The values of the $c$ lattice constant for the different layers are close to each other, whereas the values of the $a$ lattice constant are quite different. In particular the measured $a$ lattice constant intercept the curve of the reference values curve at different temperatures, indicating a higher strain at the growth temperature for layers with smaller grain diameter (see Fig. 2.24). Fig. 3.28 shows the ratio of the two lattice constants for samples with different grain size as a function of the temperature. The slope of the experimental data is similar for all samples, and for samples with large grain sizes the ratio is similar. The temperature at which the experimental data intercept the reference values varies with the grain size, i.e. at the same temperature the samples are differently strained. The point of interception, i.e. the temperature of zero biaxial stress, increases with increasing grain size. For a perfect layer the stress should vanish at the growth temperature. Therefore the close the point of interception gets to the growth temperature, the smaller is the tensile stress from the mosaic structure. This is another indication that the biaxial tensile strain decreases with increasing grain size as Eq.3.7 proposes. The components of the normal ($\sigma_{xx}, \sigma_{yy}$) stress have been calculated iteratively following Eqs. 2.16, 2.17, 2.18, 2.19. The components are plotted in Fig. 3.29 as a function of the grain size. As can be seen from Fig. 3.29 the parallel biaxial tensile strain decreases with the grain size nearly vanishing for large coalescence thickness, supporting the model of tension due to island coalescence, whereas the other two components remain quite constant.

![Figure 3.29: Normal stress components for layers of different grain size.](image-url)
More the total strain state is dominated at RT by the compressive biaxial thermally induced stress and at larger grain diameter partly release.

### 3.3.1 Elastic modulus

If the elastic constants of GaN were known with only little uncertainties, all strain components for biaxial and hydrostatic compression or tension could be obtained. Unfortunately this is not the case for GaN.

In table 3.1 are listed the published elastic constants and the ratios $2\frac{C_{13}}{C_{33}}$. It can be observed that the values scatter.

<table>
<thead>
<tr>
<th>$C_{11}$</th>
<th>$C_{12}$</th>
<th>$C_{13}$</th>
<th>$C_{33}$</th>
<th>$C_{44}$</th>
<th>$2\frac{C_{11}}{C_{33}}$</th>
<th>reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>373</td>
<td>141</td>
<td>81</td>
<td>387</td>
<td>94</td>
<td>0.42</td>
<td>[78]</td>
</tr>
<tr>
<td>390</td>
<td>145</td>
<td>106</td>
<td>398</td>
<td>105</td>
<td>0.53</td>
<td>[79]</td>
</tr>
<tr>
<td>350</td>
<td>140</td>
<td>104</td>
<td>376</td>
<td>101</td>
<td>0.55</td>
<td>[80]</td>
</tr>
<tr>
<td>367</td>
<td>135</td>
<td>103</td>
<td>405</td>
<td>95</td>
<td>0.51</td>
<td>[56, 55]</td>
</tr>
</tbody>
</table>

**Table 3.2:** Elastic stiffness constants of GaN reported in the literature. The values $C_{11}$ through $C_{44}$ are in GPa.

In Fig. 3.30 are plotted the a lattice constants of samples with different grain sizes as a function of their c lattice constants.

**Figure 3.30:** a lattice constants of samples with different grain sizes vs the respective c lattice constants for the evaluation of the elastic stiffness constants.
From these data it is possible to extract the constant $-2\frac{C_{13}}{C_{33}}$ applying a linear fit according to the equation:

$$
\frac{c - \Delta x_c - c_0}{c_0} = -2\frac{C_{13}}{C_{33}} \cdot \frac{a - \Delta x_a - a_0}{a_0}
$$

(3.13)

where $\Delta x_{c,a}$ are the hydrostatic contributions to $c$ and $a$, respectively, as the Eq.1.8 is valid only for biaxial strain. The fit yields $2\frac{C_{13}}{C_{33}} \approx 0.483 \pm 0.064$ and $\Delta x_{c,a} \approx 1.7 \cdot 10^{-4} \text{Å}$. The value of $2\frac{C_{13}}{C_{33}}$ is in good agreement with the theoretical calculation made by Wright [56]. However, considering the scatter of the data the fit can give only a rough estimation of the constant $-2\frac{C_{13}}{C_{33}}$.

### 3.4 Conclusion

The mosaicity shows a clear dependence on the grain diameter when measured in asymmetric diffraction geometry. As the edge type TDs are visible in asymmetric diffraction geometry and the screw type TDs only in symmetric diffraction geometry, the correlation between mosaicity parameters and the type of dislocations has been discussed and used to calculate the dislocation densities of edge and screw type TD present in the material. Different models of defect structure were analyzed. In particular, the edge type TD densities calculated under the assumption that the dislocations are not randomly distributed but localized at the grain boundaries agree with the TEM data. The comparison of the XRD data with dislocation densities obtained from plan-view TEM and AFM demonstrates, that the model of a mosaic crystal is well suited to utilize XRD as a tool to quantify the film perfection. On the other hand, the evaluation of strain components by temperature dependent measurements have shown that the tensile in-plane strain component is dependent on the coalescence process, as already postulated by Nix et al. [58]. The in-plane tensile strain decreases with increasing grain size as suggested by Eq. 3.7.
Chapter 4

Strain and defects in GaN layers grown by pendeoepitaxy

The fact that GaN-based devices work also in the presence of a large density of defects in the material had lead to the wrong conclusion that the defects in GaN are electrically and optically inactive. At present, a large number of studies has proved that this is not the case. Indeed dislocations act as non-radiative recombination centers[81], they create current leakage pathways, deep levels in the bandgap and act as scattering centers[82]. Therefore, there is likely room for improvements of these devices by simply reducing the dislocation density.

Although sapphire is the most common substrate for the growth of GaN an alternative substrate has been searched for a long time. As already mentioned in Chapter 1, the best alternative is SiC. However, the lattice mismatch and the difference in thermal expansion coefficients between GaN and SiC is still too large to obtain a low defect density. Considerable interest has been raised in lateral epitaxy (LE) growth techniques due to a four-to-five orders of reduction of the dislocation density in the region of lateral epitaxial overgrowth compared to the regions of conventional vertical growth.

In this Chapter the development of GaN growth on SiC will be studied, from the growth of single layers of GaN on SiC to the optimization of a particular LE technique namely pendeoepitaxy. The strain status and the dislocation density will be studied and discussed in detail. The samples were grown from the research group of Pr. R. F. Davis at the North Carolina State University, Department of Material Science and Engineering, Raleigh, North Carolina, USA, during a postdoctoral leave of Dr. S. Einfeldt.

4.1 Dislocation density reduction in GaN

As already pointed out the defects present in GaN epitaxial layers are mostly threading dislocations with a density of \(10^8\) to \(10^{16} cm^{-2}\). Also point defects are present in large number \(\approx 10^{16} cm^{-3}\). Both types of defects influence the strain state of the layers. Whereas the former reduces the strain due to the lattice mismatch, the latter is supposed to be the origin of a hydrostatic strain. A first successful step in the reduction of the dislocation density in GaN was the introduction of an AlN buffer layer as already discussed in Chapter 2. Interlayers of AlN or SiN have been also used, with some success, to reduce
both the strain and the dislocation density in GaN. Thick HVPE GaN layers provide good crystalline quality as the strain decreases with increasing thickness. Thus the GaN subsequently grown by MOVPE presents a reduced dislocation density. Lateral epitaxial overgrowth (LEO, section 1.7.1) has been shown to significantly reduce extended defects in GaN grown by MOCVD and HVPE on sapphire [83], SiC [84], and Si(111) [85]. LEO is based on selective growth through a SiO$_2$ mask/window stripe pattern formed on a pregrown GaN layer. The reduction in TD density led to an improvement in the device performances, like longer lifetime cw blue lasers [42], low reverse-bias leakage current in LEDs [36] and $p$-$n$ junctions [43] and low gate leakage current $Al_xGa_{1-x}N$/GaN field-effect transistors [86].

### 4.1.1 Pendeoepitaxy (PE)

PE is an approach to the selective epitaxy of GaN and AlGaN layers that incorporates mechanisms of growth exploited by the conventional LEO process with the substrate itself used as a pseudomask.

![Cross-sectional SEM of a GaN PE structure](image)

**Figure 4.1:** Cross-sectional SEM of a GaN PE structure: the wing and stripe regions are marked in the picture. The overgrowth thickness ($h$), the wing width ($w$) and the stripe lateral length ($s$) are indicated.

The growth does not initiate through open windows but on sidewalls of GaN stripes. GaN stripes along $[1\bar{1}00]$ with a rectangular cross section were etched from a 1 $\mu$m thick GaN layer grown by MOVPE on 0.1 $\mu$m AlN buffer layer previously deposited on 6H-SiC (0001) substrates. A cross-sectional SEM picture parallel to the (11-20) plane of an uncoalesced GaN PE layer is shown in Fig. 4.1, the stripe and the wing regions being easy to recognize. In lateral overgrowth techniques it is very important to have a high lateral growth rate to achieve rapid coalescence. The growth temperature as much as the V/III molar flow ratio were reported to significantly impact the lateral growth. It will be studied in the next sections how the growth temperature influence the formation of in-plane stress in PE structures. An increase in V/III ratio can, instead, give rise to hydrostatic stress.
4.1.2 Wing tilt

Although LEO or PE techniques are widely used to improve the performance of devices, some problems still remain in controlling the structural quality of the overgrown material. In particular the crystal planes in the wings are typically tilted with respect to those in the window (seed) regions. For the case of LEO, this has been attributed to threading dislocations which form a grain boundary along the edge of the mask [87, 88]. New dislocations can form at the coalescence front of adjacent wings if they are crystallographically tilted against each other. The goal is to minimize or avoid wing tilt such that the coalescence front has a low residual extended defect density. Initial studies have shown that the tilt boundary may be suppressed with increasing film thickness [87, 89]. GaN-based lasers fabricated on the coalescence fronts did not show enhanced degradation of the performance with this approach [90]. Fini et al. [91] demonstrated high quality coalesced LEO stripes by first growing wings with low crystallographic tilt relative to the seed regions, and then rapidly coalescing these wings using different growth condition.

Wing tilt determination

A typical high resolution x-ray diffraction RSM of the (0002) reflection of an uncoalesced GaN PE layer, with the diffraction plane perpendicular to the stripes, is shown in Fig. 4.2.

Figure 4.2: High resolution x-ray diffraction RSM of the GaN (0002) reflection showing the peaks for stripe and wing regions in an uncoalesced GaN PE layer.
The figure shows a center peak and two side peaks. The peak separation along \( q_x \) represents the wing tilt, whereas the peak separation along \( q_z \) is due to strain along the c-axis (\( \epsilon_{zz} \)). A RSM of the (0002) reflection with the sample rotated by \( \Delta \phi = 90^\circ \) (i.e. the diffraction plane along the stripes) shows only a single peak.

**Figure 4.3:** Schematization of the tilt of the wings of an uncoalesced GaN PE layer.

The XRD data of Fig.4.2 lead to the schematization of an uncoalesced GaN PE layer as shown in Fig.4.3. Here it was assumed, that the wings tilt away from the SiC substrate. A slight change of both \( a \) and \( c \) lattice constants was observed in the wing region with respect to the stripe region.

**Figure 4.4:** High resolution x-ray diffraction RSM of the (204) asymmetrical reflection of an uncoalesced GaN PE structure, showing peaks from the stripe and the wing regions.
4.1. DISLOCATION DENSITY REDUCTION IN GAN

RSMs of asymmetrical reflections can provide information on the strain along the a-axis ($\epsilon_{xx}$), but, as shown in Fig. 4.4, the intensity is not high enough to extract exact peak positions.

![Figure 4.5: Rocking curve of the (0002) GaN reflection recorded at different temperatures.](image)

The Wing tilt can be readily measured with the x-ray diffraction by recording $\omega$ rocking curves of the GaN (0002) peak (see Fig. 4.5) with the scattering plane perpendicular to the stripe direction. A schematic of this geometry is shown in Fig. 4.6. The temperature effect of Fig. 4.5 will be discussed in section 4.3.3.

![Figure 4.6: Schematization of the diffraction geometry employed to measure the crystallographic tilt of the wings relative to the stripes.](image)
Similar to the RSM’s discussed before, wing tilt has been found only along the direction perpendicular to the stripe direction ($\phi = 0^\circ$), but not along the stripe direction ($\phi = 90^\circ$). A decrease of the tilt is observed when the $\phi$-angle is varied from 0 to 90°.

A detailed study of the strain in GaN PE layers has been performed to understand the origin of the tilt of the wings and to clarify in which way it is connected with the strain and the defect structure of the layers. It has been assumed that the tensile stress due to the thermal mismatch present in the stripes is releaved in the wings, causing the wing tilt with respect to the seed. For this scope the strain present in plane GaN layers grown on AlN/SiC and stripes of GaN grown on AlN/SiC has been analyzed first and will be discussed in the following section 4.2. This data is used to analize the data on PE layers in section 4.3.

4.2 GaN on SiC

4.2.1 GaN layers

The optimization of the growth process of GaN single layers on SiC substrates is estabilished as the growth of GaN on sapphire.

![Photoluminescence spectra and HRXRD scans](image)

**Figure 4.7:** Photoluminescence spectra taken at 4 K (a) and HRXRD $\omega - 2\theta$ scans of the GaN (0002) reflection (b) of GaN layers of different thicknesses grown on SiC. [92]
GaN is generally grown on a AlN nucleation layer, due to the low lattice mismatch along the a-axis of $\sim 1\%$ between SiC and AlN. GaN layers grown directly on SiC are found to be under tensile strain at RT [93]. This tensile strain is due to the difference in thermal expansion coefficients between the GaN and the SiC substrate. On the other hand GaN layers are expected to be also under compressive strain due to the lattice mismatch with the AlN nucleation layer. This strain releases only partially with increasing thickness of the GaN layer. The compressive strain and the tensile strain superimpose such that a thickness-dependent strain in GaN results. A variation of the strain of the GaN layers grown on AlN/SiC with increasing thickness has been observed utilizing photoluminescence measurements and high resolution x-ray diffraction (see Fig.4.7 a) and b), respectively).

![Figure 4.8](image.png)

**Figure 4.8:** The strain extracted from the pl and x-ray measurements as well as wafer bending experiment is shown[94].

The thickness of the layers was varied between 0.02 and 4 $\mu$m. The fringes in Fig.4.7 b) are due to the interference of the x-rays in the GaN layer. An increase of the Bragg angle of the (002) reflection with increasing thickness of the layers is clearly observed in Fig.4.7 b). That means that the c lattice constant increases with increasing thickness (Eqs. 2.7-2.8 ) and therefore (Eq. 1.3) the strain as well. Also, PL measurements of the GaN layers show a clear redshift of the excitonic peak (FA) with increasing layer thickness as can be seen in Fig. 4.7 a) which corresponds to an increasing tensile stress (Eqs. 1.17-1.18). The strain of the layers calculated using the HRXRD and PL data is compared in Fig. 4.8. The difference in the strain values of the two techniques is mostly due to the different penetration depths of the X-rays and the laser beam used for PL, respectively. The latter penetrates only
some tenth nanometers in the layer, whereas the HRXRD technique integrates over the total volume of the layer. The data obtained in these two ways are compared with wafer curvature data obtained by optic interferometry (see Fig. 4.8). The last agree with PL measurements, but this is a volume sensitive measurement, the discrepancy can be attributed to a strain variation along the c-axis in the samples.

The small angle x-ray diffraction (SAXD) technique has been used to investigate the strain variation along the c-axis in the layers under investigation. In conventional HRXRD the depth resolution is fixed.

**Figure 4.9:** Schematic of Small Angle X-ray Diffraction (a), depth selectivity (b).

**Figure 4.10:** SAXD results (circles) and theoretical variation of the Bragg angle due to refraction (dashed line) as a function of the incident angle $\omega$. (Theoretical curve by Thomas Schmidt.)
In SAXD there is depth selectivity through the variation of the incident angle, by rotating the sample around the normal of an asymmetric lattice plane (see Fig. 4.9). The results of this measurement are shown in Fig. 4.10.

The scattering angle decreases with decreasing incident angle: In the figure is also shown the theoretical change of the Bragg angle in a layer of homogeneous strain due to the refraction correction (dashed line), the calculations were made by geometrical evaluation of the angle $\Theta$ between the incident vector in the air and the refracted vector in the sample (see Fig. 4.11).

![Figure 4.11: Schematization of the change of the Bragg angle with the refraction at the interface air/sample.](image)

Obviously this correction becomes very large when the measurement geometry is very grazing. As the measured shift of the Bragg angle is similar to the shift expected by refraction, these measurements are not suitable to extract reliable data for the strain variation in the layer.

### 4.2.2 GaN stripes on SiC

To understand the evolution of the strain during PE growth of GaN at elevated temperature it is necessary to clarify first the strain state in GaN stripes which are the starting point for PE growth. The in-plane lattice constants of the GaN stripes along the x- and y-axis ($a_x$ and $a_y$, respectively) have been measured at RT and after annealing at different temperatures, as shown in Fig. 4.12. For this purpose the (105) and (114) reflections were measured and the $a_x$ and $a_y$, respectively, lattice constants were extracted. At RT the lattice constant $a_x$ is larger than $a_y$. The expected cross section shape of the stripe at RT is represented in Fig. 4.13 a). As the unit cell is enlarged along the x-axis with respect to the y-axis an elastic relief of the compressive strain is supposed to take place. At higher temperature the x-component decreases, while the y-component increases. The values of the two components becomes equal at $\sim 900^\circ$ C, and at higher temperatures the x-component is slightly larger than the y-component. The expected cross section shape of the stripes after annealing at elevated temperatures is represented in Fig. 4.13 b). The
unit cell is shrunk along the x-axis with respect to the y-axis, i.e. an elastic relief of a tensile strain has taken place.

In conclusion the compressive strain observed both in GaN layers (compare section 4.2.1) and in unannealed GaN stripes relaxed plastically during annealing such that at the starting point of PE growth only the remaining tensile strain has to be considered in the stripes.

**Figure 4.12:** Behaviour of lattice constant along ($a_y$) and perpendicular ($a_x$) to the stripe direction at different temperatures[94].

**Figure 4.13:** Schematic of the evolution of the stress in the stripe with annealing of the stripes.
The relief of the compressive stress in the GaN stripes is related to the formation of dislocations in the c-plane as can be seen in the TEM images of Fig. 4.14.

\[ \text{Figure 4.14: Cross-sectional TEM images of GaN stripes on a AlN/SiC substrate (a) before and (b) after annealing. The formation of new defects in the c-plane is observed (which are indicated with arrows in b)[95].} \]

It is assumed that these dislocations are misfit segments formed by TDs which have been bent over into the c-plane (Fig. 4.14).

4.3 Pendeoepitaxy

\[ \text{Figure 4.15: Lateral and vertical growth rates of PE growth of GaN as a function of the growth temperature [44].} \]
GaN PE layers grown at different temperatures on AlN/SiC substrates by MOVPE have been studied by A. M. Roskowski et al. [44] In Fig. 4.15 the vertical and lateral growth rates of a pendeo structure are shown as a function of the growth temperature. Utilizing elevated temperatures the growth is forced to occur on the (11\bar{2}0) plane rather than on the (0001) plane, and the formation of hillocks on the latter plane is promoted. An optimal temperature for the growth of the layers has been found to be $\sim 1020^\circ$ C. Beyond this temperature the growth of hillocks within the stepped microstructure can hardly be suppressed.

The process of lateral epitaxial overgrowth (LEO) has been briefly described in the first Chapter. The lateral overgrowth takes place at the (11\bar{2}0) facets. The side facet growth as a function of the growth temperature has suggested that lateral growth should occur even without a SiO$_2$ mask. This maskless approach is called maskless pendeo epitaxy. In this case the GaN is etched in stripes, with an orientation similar to the stripes in the SiO$_2$ mask. The sidewalls of the GaN stripes provide the starting surface for the lateral growth. The region corresponding to the stripes is called seed and the lateral overgrowth zone is called wing as it hangs at the side of the GaN/AlN stripe. [74]

4.3.1 Lateral overgrowth

The major factor for the defect reduction in the laterally overgrown regions is the change of the predominant growth direction from vertical to lateral. Also a reduction of the stress due to the thermal mismatch between the GaN and the SiC is achieved as the lateral overgrown area is quasi free-standing. Dislocation densities are reduced in the wing to $\sim 10^5 cm^{-2}$ as evidenced by TEM. A typical TEM image of a pendeo structure is shown in Fig. 4.16. The bending of dislocations from the stripe into the wings and the formation of dislocations at the coalescence front can be observed. During the lateral overgrowth dislocations close to the edge of the seed areas tend to bend to follow the faster growth direction. As dislocation lines can not finish inside bulk material some segments extending in the c direction will inevitably be formed, particularly at the meeting front of overgrowth material.

![Figure 4.16: Cross sectional TEM image of a coalesced GaN pendeo structure](image)
Ziliental et al. proposed that threading dislocations are bent to form c-plane segments, as a result of shear stresses acting on the basal plane [96].

### 4.3.2 Local strain in wing and stripe

Low temperature micro-PL spectra taken in the wing and the seed region of a pendeo structure are shown in Fig. 4.17. The strong donor bound exciton ($D^0X$) PL peak emitted from the wing material had a FWHM smaller than 300μeV (below the resolution of the equipment), a hallmark of the markedly lower strain variation in the wing material. This FWHM value is comparable to that of completely relaxed homoepitaxial GaN films grown on bulk GaN crystals [97]. The $D^0X$ peak from the stripe material has a FWHM of 12 meV. A redshift of the $D^0X$ peak of 5 meV in the stripes with respect to the wings indicates the larger tensile strain in the stripes. The broadening of the $D^0X$ line in the stripe material and its increased intensity relative to that of the peak from the wing material can be attributed to the inhomogeneous strain and the higher dislocation density in the stripe region. A reduction of the strain in the uncoalesced wings is also observed by micro-Raman measurements as shown in Fig. 4.18. An upward shift of the $E_2$ Raman line by about 0.7 cm$^{-1}$ in the wings with respect to the stripe is observed. This shift indicates a relaxation of the tensile strain along x in the wings.

![Figure 4.17: Micro-PL spectra of an uncoalesced PE GaN layer taken at 4K from the two wing regions (a and b) and the stripe (c) region [98].](image-url)
4.4 Uncoalesced structures: temperature dependent measurements

In fig. 4.19 the \(c\) lattice parameters measured in the stripe and in the wing regions are plotted as a function of the wing tilt and of the wing width. From this figure it can be deduced that wing tilt is induced by strain, as the \(c\)-axis lattice parameter decreases with increasing wing tilt. As at the starting point of PE growth (see section 4.2.2) only the remaining strain between GaN and SiC has to be considered in the stripes, the tilt in PE is induced by the mismatch in the coefficients of thermal expansion between GaN and SiC. The \(c\)-axis lattice parameter of the wing in Fig. 4.19 is always larger than that of the stripes, indicative of a relaxed material with respect to the stripe. The \(a\) lattice parameter show no correlation with the wing tilt [99]. The wing tilt of the wings is caused by the relaxation of the compressive strain along \(z\)-axis in the stripes, and is not affected by the strain along the \(x\)-axis.

The \(c\) and \(a\) lattice constants corresponding to the stripes of PE GaN layers were measured...
4.4. UNCOALESCED STRUCTURES: TEMPERATURE DEPENDENT MEASUREMENTS

In the temperature range 300-1020 K and are shown in Fig. 4.20 and Fig. 4.21, respectively, the figures show a tensile strain along the x-axis and a biaxial compressive strain along the z-axis.

The growth parameters of the two studied samples are listed in table 4.1.

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<td>A</td>
<td>4.1</td>
<td>3.5</td>
<td>2.72</td>
<td>1100</td>
<td>3073</td>
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<tr>
<td>B</td>
<td>0.72</td>
<td>4.73</td>
<td>1.13</td>
<td>1100</td>
<td>6160</td>
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The two PE structures are uncoalesced, and they differ in the ratio $s/h$ and V/III ratio. The lattice constants are quite similar for the two samples. The small differences in the $a$ lattice constants in Fig. 4.21 are mostly due to the error for the determination of the $a$ lattice constant since the temperature dependent measurements have some limits in the $\phi$ angle adjustment, as discussed in section 2.8. The ratio $c/a$ of the PE GaN layers is shown in Fig. 4.22. The values for the PE samples are compared with the values of a MOVPE GaN layer grown on (0001) sapphire. The high $c/a$ ratio indicates compressive stress, as already mentioned in Chapter 3. As can be seen the PE GaN layers are under tensile stress as the ratio $c/a$ is below the theoretical values for the nominally stress-free layer. The high $c/a$ ratio for the layer on $\text{Al}_2\text{O}_3$ indicates compressive stress. The values of the PE GaN layers seem to be quite constant but scatter.

![Figure 4.19: Lattice parameters c for the stripes (filled circles) and wings (open circles) of different samples vs the wing tilt and wing width, respectively. The dotted lines are guides to the eye [99].](image)
The values of the ratio \( \frac{c}{a} \) of the PE GaN layers obtained experimentally at different temperatures are shown in Fig. 4.23 in comparison with the theoretical \( \frac{c}{a} \) values [60] of nominally stress-free GaN.

**Figure 4.20:** \( c \) lattice constant as a function of the temperature for two PE GaN layers.

**Figure 4.21:** \( a \) lattice constant as a function of the temperature for the two PE GaN layers.

Furthermore, the values of the ratio \( \frac{c}{a} \) for a biaxially stressed GaN layer at different temperatures, was calculated by Eq. 4.1, derived from Eq. 1.2 and 1.4:

\[
\frac{c}{a} = \frac{c_0 + \varepsilon_a (\frac{-2C_{13}}{C_{33}})c_0}{a_0 + a_0 \varepsilon_a}
\]  
(4.1)
4.4. UNCOALESCED STRUCTURES: TEMPERATURE DEPENDENT MEASUREMENTS

and for an uniaxially stressed was calculated by Eq. 4.2, derived from Eq. 1.15 and 1.16 and is shown as well:

\[
\frac{c}{a} = \frac{c_0}{a_0} \frac{1 + \epsilon_a (C_{13}C_{33} - C_{12}C_{13})}{1 + \epsilon_a (C_{12}C_{33} - C_{23}C_{13})}
\]

(4.2)

where \( \epsilon_a \) is the the biaxial strain on SiC.

![Figure 4.22](image)

Figure 4.22: c/a ratio of the two PE GaN layers as a function of the temperature. For comparison data for a MOCVD GaN layer on Al\(_2\)O\(_3\) and reference values of a nominally stress-free layer taken from literature [60] are shown as well.

The PE samples could be expected to be under uniaxial stress as parallel to the stripes, i.e. along the y-direction, the GaN layer is expanded infinitely. Therefore in this direction the stress is not reduced. Perpendicularly to the stripes, i.e. in x-direction, stress can be reduced, because the GaN stripes in this direction have a finite expansion. The layers would, then, be under uniaxial stress with the only no-zero stress component along the x-direction.

However one can not say that the stress is zero in y-direction. The strain reduction strongly depends on the geometry of the stripe. However the wings are less stressed in y-direction than the stripes. Since the stress is only partly diminished the ratio c/a of PE GaN layers should take an intermediate position between purely unaxial and purely biaxial stressed material.

The experimental values seem to be closer to the theoretical values of the uniaxially stressed or unstressed layer than to those of the biaxially stressed GaN. The PE GaN layers could be under uniaxial stress due to the stripe geometry.
CHAPTER 4. STRAIN AND DEFECTS IN GAN LAYERS GROWN BY PENDEOEPIXTA

Figure 4.23: Ratio c/a for the two PE GaN layers on SiC as a function of the temperature, compared with the theoretical values [60] for a relaxed layer, a layer under biaxial and uniaxial stress, respectively.

This supposition is not confirmed by Fig. 4.24, where the values of c lattice constant are plotted as a function of the a lattice constant of various samples. In the picture GaN layers of different thickness grown on AlN/SiC and PE GaN layers grown under different conditions are compared. The first can be fitted by Eq. 1.3, assuming a biaxial stress in the GaN layers, the value for the ratio of the elastic stiffness constants obtained by this fit are in good agreement with values reported in literature [56]. Also for uniaxial stress a linear trend should be observed as well (see Eq. 1.16), but the trend of c lattice constant versus a lattice constant for PE GaN layers is constant.

4.4.1 Wing tilt: thermal strain

Temperature-dependent high resolution x-ray diffraction measurements have been recorded to evaluate the variation of the wing tilt with the temperature. In Fig. 4.25 and Fig. 4.26 are plotted the RSMs of the sample A (see Table I) recorded at 126 °C and 726 °C, respectively. As can be seen the wing tilt decreases slightly with increasing temperature. In Fig. 4.27 are plotted the RSMs of the (002) reflection of the sample B recorded at 326 and 726 °C. In this case the tilt is reduced drastically with increasing temperature. The tilt even almost disappeared at 726 °C.

The wing tilt of the two PE GaN layers as a function of the temperature is shown in Fig. 4.28. The values of the wing tilt at RT of the two layers differ slightly. The wing tilt for both layers decreases linearly with the temperature, but the slope is larger for the sample B such that at growth temperature the wing tilt of this layer is expected close to zero, i.e. the stress is completed releaved. In contrast the wing tilt of the sample A is only
4.4. UNCOALESCED STRUCTURES: TEMPERATURE DEPENDENT MEASUREMENTS

3.188 3.190 3.192 3.194
Lattice parameter $a$ [Å]

5.188 5.190 5.192 5.194
Lattice parameter $c$ [Å]

Figure 4.24: $c$ lattice constants as a function of $a$ lattice constants for plain GaN layers of different thicknesses and for the stripes of pendeo structures [44].

partly reduced. In this case only part of the stress is released. Temperature-dependent high resolution x-ray diffraction measurements have shown that the wing tilt in maskless pendeoepitaxy samples is primarily thermally induced, which is opposite to the findings for LEO [100].

Figure 4.25: RSM of the (002) reflection of a PE GaN layer (sample A) recorded at 126 °C.

A rest tilt remains at the growth temperature whose value varies from sample to sample. Stress is also induced in the GaN epilayer from the mismatch between the AlN buffer layer
and the GaN, this stress contributes to the remaining part of the wing tilt not relieved thermally.

A comparison of finite element (FE) simulations, assuming a fully thermally induced wing tilt, with experimental results reveals marked inconsistencies [99]. FE simulations results shown in Fig. 4.29 reveal that pendeo structure with the largest wing tilt should have the highest strains both along z-axis and x-axis. This agrees only partly with the experimental results, as it was found a correlation of the wing tilt with the strain along the z-axis, but not with the strain along the x-axis [99].

Figure 4.26: RSM of the (002) reflection of a PE GaN layer (sample A) recorded at 726 °C.

Figure 4.27: RSMs of a PE GaN layer (sample B) measured at two different temperatures, 326 °C a) and at 726 °C b).
FE simulations predict a correlation between the wing tilt and the aspect ratio [99] particularly the ratio of the overgrowth thickness \( h \) to the stripe width \( s \) (see Fig. 4.29).

![Figure 4.28: Wing tilt of two PE GaN layer measured at different temperatures.](image)

It was found that as \( s/h \) decreases, the wing tilt decreases as schematized in Fig. 4.30. This ratio is directly dependent on the growth conditions like the V/III ratio or the substrate temperature [99]. The experimental tilt values plotted versus the stripe aspect ratio show no clear correlation [99].

![Figure 4.29: Wing tilt and averaged strain obtained from Finite Element simulations as function of \( s/h \) ratio [99].](image)
Figure 4.30: Schematic for the expected wing tilt from FE simulation for different ratios of stripe width $s$ to overgrowth thickness $h$. The tilt decreases with increasing of this ratio $s/h$.

The different behaviours of sample A and B with the temperature could relate to the different growth conditions. Some of the data indicate that the wing tilt decreases with increasing V/III ratio as shown in Fig. 4.31.

Figure 4.31: Wing tilt as a function of the V/III ratio[94]

A significant fraction of the wing tilt is not a consequence of an elastic stress but is of inelastic nature as it is related to dislocations. Most probably the bending of dislocations and their final arrangement in the PE structure is heavily influenced by the V/III ratio. It
is well-known that the surface morphology, i.e. the formed facets, of uncoalesced LEO or PE structures is determined by the V/III ratio and the growth temperature, and the surface morphology determines the bending of the dislocations. Thus it is obvious to assume that also in our samples the defect structure and consequently the wing tilt changes with the V/III ratio [101].

4.4.2 Wing tilt: dislocation effect

As the temperature dependent XRD data shows a remaining wing tilt at the growth temperature, which even varies from sample to sample the exact origins of the wing tilt are unknown. This remaining wing tilt could be attributed to threading dislocations. The TDs have been found to induce the wing tilt in LEO samples. Wing tilt in LEO samples increases only slightly during the cooldown to RT as observed by Fini et al. [100]. They have done in-situ measurements of the wing tilt during the growth of LEO GaN layers utilizing x-ray diffraction rocking curves and observed the formation and the increase of the wing tilt during growth at high temperature. Since the wing tilt is developed in LEO GaN layers before cooldown, it must be concluded that it forms during growth. The dislocations producing the wing tilt in LEO samples can be divided in two groups named $D_1$ and $D_2$ after Sakai et al. [87] (see Fig. 4.32). Both types of dislocations are aligned along the [0001] direction. The $D_1$ dislocations are at the center of the SiO$_2$ mask, and the $D_2$ dislocations are at both edges of the mask. These two kinds of defects were found to originate from edge type TDs in the stripe propagating laterally into the wings. These dislocations are sufficiently dense to form the tilt boundary.

![Figure 4.32: Schematic diagram showing two types of dislocations ($D_1$ and $D_2$) in the overgrown region after Sakai et al. [87].](image-url)

A complete study of the dislocations formed in LEO GaN samples has been done also by Liliental-Weber et al. [96] utilizing plan-view and cross-section TEM. They have observed two types of dislocations with segments in the basal plane (see Fig. 4.33 b)). They propose that the orientation of one sort of dislocations are generated by shear stress operating parallel to the stripe direction. The bowing of these dislocations is due to glide under the action of the Peach-Kohler force which acts perpendicular to the dislocation line. The mechanism is illustrated in Fig. 4.33a). The second type of dislocations observed by
Liliental-Weber et al. can be considered as grain boundary dislocations. These dislocations are similar to the dislocations observed by Sakai et al. [87].

**Figure 4.33:** (a) Schematization of the dislocations half loops forming at the stripe/wing interface. (b) Plan-view TEM image showing the dislocation arrangement at the seed/wing interface along the stripe direction in an LEO GaN sample. The threading parts are marked with a T [96].

Fig. 4.34 is a cross-sectional TEM image of a PE sample [40] showing the overgrowth region near the edge of the GaN stripe along the [11-20] direction. As can be seen there are many bending TDs in the GaN wing.

### 4.5 Conclusions

In this Chapter the possible origins of the wing tilt of PE GaN layers grown on a SiC substrate were discussed. For this purpose the strain state of single layers and stripes of GaN grown on SiC was studied. It was found that an elastic relief of the biaxial tensile stress, due to the thermal mismatch between GaN and SiC, takes place in the stripes, before the overgrowth of the PE GaN layer. The biaxial compressive stress, due to the lattice mismatch between the GaN layer and the AlN buffer layer is plastically relieved before overgrowth. It has been found that, different from LEO findings, the wing tilt in
4.5. CONCLUSIONS

PE GaN layers is partly strain induced due to the difference in the thermal coefficient expansion of the GaN with the SiC. The different temperature dependent change of wing tilt indicates that the growth conditions of the measured samples impact the wing tilt too. As the growth conditions determine the density and distribution of the defects, the wing tilt in PE GaN layers can be related to its dislocations structure. The presence of bent dislocations in PE GaN layers have been revealed by TEM pictures. As the wing tilt, in LEO samples, has been demonstrated to be produced by the bending of TDs, also the remaining part of the wing tilt could be induced by dislocations also in PE GaN layers.

Figure 4.34: TEM cross section image of an uncoalesced maskless pendeoepitaxy structure showing dislocations with segments in the basal planes marked by arrows [40].
Chapter 5

Strain and defects in layers of inhomogeneous composition

AlGaN layers have a wide range of applications in optoelectronic devices [102, 103]. The process control in the fabrication of the corresponding heterostructures requires the determination of the chemical composition, the thicknesses and the strain of the epitaxial layers. The strain state and the chemical composition of a ternary structure can be determined using x-ray diffraction. However, the quantification of the chemical composition is more difficult in case the layer is partially or totally strained. In fact there is not a direct method for determining the Al content in a AlGaN layer using x-ray diffraction because it depends on the lattice distortion due to the strain induced by the substrate or underlying buffer layers.

To characterize an unstrained ternary layer the variation of the lattice parameters with the composition has to be known. This variation is usually assumed linear which is known as Vegard’s law such that it is sufficient to know the lattice parameters of the two binary constituents [104]. If the layer is coherent in the (001) growth plane, the in-plane lattice parameters of the layer and the substrate will be matched. In this case the amount of strain can be determined most directly by measuring a RSM for an asymmetrical reflection [62] and the chemical composition by scans on both a symmetrical and an asymmetrical reflection.

Low angle x-ray reflectivity is an alternative way to study thin layers. In case of superlattices, it derives the period from peak positions and individual layer thicknesses and chemical compositions from peak intensities independently from the strain state. Unfortunately, the chemical composition can be determined for flat layers only. The difference between the two methods, i.e. x-ray diffraction and x-ray reflectivity, is in the sampling area and sampling depth.

In this Chapter, both high resolution x-ray diffraction and x-ray reflectivity, are used to study the composition, the strain and the crystalline defects in layers based on Al$_{1-x}$Ga$_x$N. First the nucleation mechanism of AlGaN on SiC substrates is investigated using HRXRD and compared with data from TEM and energy dispersive x-ray analysis (EDS). In the second part Al$_{1-x}$Ga$_x$N/GaN superlattices will be characterized by using low angle x-ray reflectivity.
5.1 AlGaN nucleation layers on SiC

The n-type conductivity of SiC wafers allows one to fabricate vertical GaN-based devices utilizing backside contacts on the substrate. The realization of such a device has long been hampered by the commonly used AlN nucleation layer, as the AlN is an isolator. Later Al$_{1-x}$Ga$_x$N with low Al content was found to be a good alternative to AlN as nucleation layer [105]. Furthermore, the lattice mismatch between GaN and AlGaN is lower than between GaN and AlN. Similar structural and optical properties are found for GaN films grown on AlN or Al$_{1-x}$Ga$_x$N nucleation layer [92].

Reflectivity measurements during the growth of Al$_{1-x}$Ga$_x$N layers, with different Al content, directly on SiC show that the higher the Al content the faster the flattening of the surface [106]. At maximum of roughness, i.e. minimum of reflectivity, the Al$_{1-x}$Ga$_x$N nucleation layer consists of isolated islands on a thin continuous film that completely covers the substrate. The thin film was found to be almost pure AlN.

The strain of GaN grown on Al$_{1-x}$Ga$_x$N/SiC as a function of the GaN thickness is shown in Fig. 5.1.

![Figure 5.1: Strain of GaN layers of different thickness grown on 6H-SiC (0001) using an AlGaN nucleation layer [92].](image)

Obviously, the thickness of the GaN layer influences its average biaxial strain. GaN layers were determined to be under compression in the growth plane due to incomplete relaxation of the coherent stress with respect to the AlGaN nucleation layer. From a comparison of Fig. 5.1 with Fig. 4.8 it is clear that the strain is larger for a GaN layer grown on AlN nucleation layer than on a AlGaN nucleation layer as the lattice mismatch between AlN and GaN is larger than the lattice mismatch between AlGaN and GaN. With increasing thickness, this stress is progressively relieved.
To study the growth of AlGaN layers directly on a (0001) 6H-SiC substrate two $\text{Al}_{1-x}\text{Ga}_x\text{N}$ layers of different thicknesses have been investigated with HRXRD: sample A (100 nm) and sample B (1000 nm), both of a nominal Al mole fraction of $x = 0.15$. The samples were grown from the research group of Pr. R. F. Davis at the North Carolina State University, Department of Material Science and Engineering, Raleigh, North Carolina, USA, during a postdoctoral leave of Dr. S. Einfeldt. The $\text{Al}_{1-x}\text{Ga}_x\text{N}$ films were grown via MOVPE at 20 Torr and 1010° C, trimethylallumium, triethylgallium and ammonia were used as precursors with flow rates ranging from 2.3 $\mu\text{mol/min}$ to 26.9 $\mu\text{mol/min}$ and 3 slm, hydrogen was the carrier gas with 3.0 slm flow rate [107].

A RSM of the (105) reflection of the 100 nm $\text{Al}_{1-x}\text{Ga}_x\text{N}$ layer and of the (1015) reflection of the SiC substrate is shown in Fig. 5.2. The model of the relaxation line can not be used in this case as formulated in chapter 2 [63] as the $c/a$ ratios of AlGaN and SiC are different.

The difference with respect to former measurements is that not the GaN (i.e. one of the binary constituents of the ternary alloy AlGaN) has been used as a reference point in reciprocal space but the SiC. Therefore the relaxation line can still be drawn through the AlGaN reflection, but it does not longer pass through the reference point.

![Figure 5.2: RSM of the (105) reflection of a 100 nm AlGaN nucleation layer and (1015) reflection of the SiC substrate. The blue line indicates the theoretical position of the strain-free AlGaN, the magenta lines are relaxation lines, the filled circles indicate the position of the maxima of the RSMs.](image_url)

The theoretical position of the (105) reflection of strain-free AlGaN shown by the blue line in Fig. 5.2, was derived using the lattice parameters of nominally strain-free GaN,
and AlN, and correcting the scaling of the RSM regarding the measured position from the SiC(1 0 15) reflection. The magenta lines are relaxation lines. They correspond to biaxially strained AlGaN with two distinct compositions. The figure shows that at least two phases of Al$_{1-x}$Ga$_x$N are present simultaneously. Filled circles indicate their maxima. In average the two phases of Al$_x$Ga$_{1-x}$N layer are fully relaxed with respect to the substrate, but completely strained with respect to each other. The Al mole fraction of the two phases calculated from the positions of the peaks are x = 0.1 and 0.18, respectively.

**Figure 5.3:** (a) High resolution cross section TEM micrographs of a 20 nm AlGaN layer on SiC substrate. (b) GaKα EDS map of this film [107].

Fig. 5.3 a) shows a HRTEM cross-sectional image of the nominally 20-nm-thick AlGaN film. The image was taken along the [0110] zone axis and shows the 0002 lattice fringes. Distinct islands were found showing a height of about 50 nm with flat surface and diameters of about 100 nm. In addition, islands with diameter of several hundred nanometers and a thickness of only 10 nm were observed between the tall islands.

**Figure 5.4:** (a) and (b) High resolution cross section TEM micrographs of a 100 nm AlGaN layer on SiC substrate. (c) AlKα EDS map of this film [107].

EDS mappings of the nominally 20-nm thick layer were taken in cross section using the intensity of the GaKα and AlKα signals from an area covering the edge of a thick island and a part of a thin island. The results are shown in Fig. 5.3 b). The GaKα signal is significantly stronger in the thick island. A quantitative EDS point analyses reveals an Al mole fraction of 0.15 to 0.18 ±0.01, compared to a value of about 0.035±0.01 in the large islands. These results also suggest the formation of at least two AlGaN phases upon
nucleation and confirm the results obtained by XRD. The EDS measurements may not be representative of the entire film, thus the value of $x = 0.1$ determined by XRD could be the average Al mole fraction of the Al-deficient phase.

![Figure 5.5: RSM of the (105) reflection of a 1000 nm AlGaN nucleation layer and of the (1015) reflection of SiC. The lines correspond to biaxially strained AlGaN ($x = 0.204$) and fully relaxed AlGaN of varying composition.](image)

High resolution cross sectional TEM images of a 100 nm thick AlGaN film are shown in Fig. 5.4 (a) and (b). Fig. 5.4 (c) shows a color coded EDS maps of the AlKα signals of the same area with red and blue indicating areas of high and low intensities, respectively. Clearly visible is a fluctuating Al mole fraction at the SiC interface and at the top of the layer. The Al content extracted from the EDS map varies between 0.05 and $>0.15$. Fig. 5.5 is a RSM of a 1 $\mu$m AlGaN layer. In this case only one AlGaN phase is present. The broadening of the (105) AlGaN reflection along the $q_z$ direction is due to the presence of a region with inhomogeneous Al concentration at the interface with SiC substrate [106]. The layer appears to be almost fully relaxed. The Al mole fraction extracted from the RSM is 20%. This value is higher than the nominal one. This could be due to the use of the SiC reflection as a reference point in the RSM. HRXRD data has allowed for a fast characterization of the complex growth process of AlGaN layers on SiC. The strain state of the layers has been determined, despite the presence of a layer with varying Al concentration.
5.2 X-ray reflectivity

Low angle x-ray reflectivity is an alternative technique for the evaluation of the structural parameters of thin layers. This method is capable of providing the period of a SL and the relative thicknesses of the layers forming a period [108, 109, 62]. In comparison to several other techniques it does not require a relatively thick sample, and it is non-destructive. However, a large difference in the electronic density and thus the atomic scattering factor between the layers forming the SL is necessary for the structural characterization of the sample. Since in a conventional x-ray experiment intensities rather than the electromagnetic field are measured, direct access to the structure of the superlattice through Fourier transformation is generally precluded by the lack of phase information. For this reason, the structural information is extracted by fitting the recorded reflectivity with theoretical models.

5.2.1 Theory

An example of an algorithm for the calculation of the reflection of x-rays at small angles was given by L.G. Parratt [110]. His recursive formula gives the total reflected intensity of any multilayer. The contribution of the reflection and transmission of the x-ray beam at the interfaces of the thin layers have to be added. As the refractive index for x-rays is less than unity, total reflection is typically observed at an incident angle of about 0.3°.

A sample of n layers of different materials is sketched in Fig. 5.6. The layers are stacked along the z-axis. The x-ray beam with wavelength $\lambda$ hits the layer surface under an angle $\phi$. The x-ray beam is partly reflected and partly transmitted at the interfaces. The electrical field $E_m \{\vec{r}, t\}$ in the m-th layer is the sum of the transmitted $E_t^m \{\vec{r}, t\}$ x-ray beam at the (m, m-1)interface and the reflected $E_r^m \{\vec{r}, t\}$ x-ray beam at the (m, m+1) interface.

\begin{align*}
E_r^m \{\vec{r}, t\} &= E_r^m \exp \left\{ i \left[ \omega t + Q_{m,x}^r x - Q_{m,z}^r z \right] \right\} \\
E_t^m \{\vec{r}, t\} &= E_t^m \exp \left\{ i \left[ \omega t + Q_{m,x}^t x + Q_{m,z}^t z \right] \right\}
\end{align*}  

where $E_r^m$ and $E_t^m$ are the amplitudes of the reflected and transmitted x-ray wave, respectively. $Q_{m,x}^r$ and $Q_{m,z}^r$ are the parallel and perpendicular components of the wavevector $Q_m^r$. The $Q_{x}^r$-component is the same in all layers. The $Q_{z}^r$-components have opposite signs for both x-ray waves, and the value of this component is dependent on the material of the layer. The value of the $Q_{m,z}$-component of the wavevector in the m-th layer is given by:

\begin{align*}
Q_{m,z}^r &= Q_0 \sqrt{\sin^2 \phi - 2\delta_m - 2i\beta_m} \\
\delta_m &= \frac{2\pi r_0}{Q_0^2} \sum_{j=1}^{N} (\rho_{m,j} f_{1,j}) \\
\beta_m &= \frac{2\pi r_0}{Q_0^2} \sum_{j=1}^{N} (\rho_{m,j} f_{2,j})
\end{align*}
5.2. X-RAY REFLECTIVITY

Figure 5.6: Representation of reflection and transmission at the layer interface. The contribution of the electrical field and wavevector are explained in the text.

with \( f_1 \) and \( f_2 \) are the atomic scattering factors, \( \rho_{m,j} \) is the density of the j-th atom and \( r_0 \) is the classic radius of the electron. The sum is over all the different atoms in the material \((j=1...N)\). The parallel components of the electric field for all layers are equal, while the perpendicular components of the electric field are related in the following:

\[
\epsilon_{m-1} E_{m-1,x} = \epsilon_m E_{m,x} \tag{5.6}
\]

with \( \epsilon \) the dielectric constants of the material of the layer. The reflectivity at the interface \((m-1,m)\) is given by the recursive formula:

\[
R_{m-1,m} = a_m^4 \frac{R_{m,m+1} + F_{m-1,m}}{R_{m,m+1}F_{m-1,m} + 1} \tag{5.7}
\]

with \( a_m \) the phase factor \( e^{iQ_{m,z}h_m/2} \) and the so-called Fresnel reflectivity at the interface \((m-1,m)\):

\[
F_{m-1,m} = \frac{Q_{m-1,z} - Q_{m,z}}{Q_{m-1,z} + Q_{m,z}}. \tag{5.8}
\]

The total reflectivity of the sample \( R = I_R/I_0 \), i.e. the ratio of the reflected to the incident intensity of the beam, can be expressed as:

\[
R = I_R/I_0 = |R_{0,1}|^2 \tag{5.9}
\]

with:

\[
R_{0,1} = \frac{R_{1,2} + F_{0,1}}{R_{1,2}F_{0,1} + 1}. \tag{5.10}
\]
Assuming the substrate to be infinitely thick there is no reflection at its backside. The equations given above are valid in the case that the interfaces do not show any roughness. This is not the case for real multilayer structures. Therefore, a roughness parameter $\sigma$ is usually introduced. This parameter is given by the standard deviation of the roughness function $h(x, y)$ from the average value $\langle h(x, y) \rangle$. If the distribution of the roughness is assumed to be gaussian then the roughness at the interface $\sigma_{m-1,m}$ is considered in the Parrat formula by multiplying the reflectivity $R_{m,m+1}(\sigma = 0)$ with a factor similar to the Debye-Waller factor:

$$R_{m,m+1}(\sigma) = R_{m,m+1}(\sigma = 0) e^{-Q_{m-1}Q_{m}\sigma_{m-1,m}^2/2}.$$  \hfill (5.11)

Analysis of interface roughness solely through the specular reflectivity is limited in that it can not differentiate surface roughness from interdiffusion.

### 5.2.2 Experiment: Analysis of AlGaN/GaN superlattices

The thickness of a total period in a superlattice is easily determined by high-resolution x-ray diffraction from the spacing between the satellite peaks in an 2$\theta$/\omega scan of the (002) reflection [108]. Superlattice periods are typically less than 10 nm in case of AlGaN/GaN superlattices used in laser-diodes.

![Small angle x-ray reflectivity of two AlGaN/GaN superlattice grown on a GaN/sapphire substrate. The two curves have been shifted with respect to each other.](image)

**Figure 5.7:** Small angle x-ray reflectivity of two AlGaN/GaN superlattice grown on a GaN/sapphire substrate. The two curves have been shifted with respect to each other.

The determination of the thicknesses of the individual AlGaN and GaN layers is less straightforward, since for multilayer structures the peak positions are determined by both
the Al content and the thickness ratio of the GaN to the AlGaN layer [108, 109]. Usually the 
Al content in AlGaN/GaN superlattices is determined from high resolution x-ray curves.

Figure 5.8: Small angle x-ray reflectivity of two AlGaN/GaN superlattice grown on a 
GaN/sapphire substrate.

However, high resolution x-ray curves alone do not give information on the Al content, 
unless the strain state and the thickness ratio is known. The strain state is extracted from 
RSMs of asymmetrical reflections as was already explained in section 2.9.1 and shown in 
the first part of this chapter.

In x-ray small angle measurements the chemical composition has a significant influence not 
only on the positions but also on the contrast of the peaks. However, the measurements 
might not been capable of distinguishing between different thickness ratios. Moreover, the 
experimental data might not be collectable to a high enough angle. In order to compre-
hensively extract the structural composition of a sample, ideally high-resolution diffraction 
and reflectivity measurement should be combined. MOVPE AlGaN/GaN superlattices 
have been studied utilizing x-ray reflectivity and compared with HRXD results. All the 
samples were grown by M. Diesselberg at 1030°C, 75 Torr, and 0.6 sccm of SiH₄, the V/III 
ratio is varied from sample to sample, the amounts of V/III ratio are listed in table 5.3 
and 5.2. The layers have the following structure:

$$100 \times (5 \text{ nm GaN}/5 \text{ nm AlGaN})/1 \mu\text{m GaN:Si}/Al_2O_3$$

The Al content and the strain state of the ternary alloys in the heterostructures were 
determined by M. Diesselberg using high resolution x-ray diffraction. The results are 
presented in Table 5.1. It is interesting to notice that for Al mole fractions larger than 
20% the superlattices partially relax [111].
Table 5.1: Strain state, averaged Al mole fraction (±5%) and period of the superlattice as determined by HRXRD, more the V/III ratio, growth parameter. (by M. Diesselberg)

<table>
<thead>
<tr>
<th>Sample</th>
<th>γ (%)</th>
<th>( x_{Al} ) %</th>
<th>period [nm]</th>
<th>V/III</th>
</tr>
</thead>
<tbody>
<tr>
<td>A 180</td>
<td>100</td>
<td>14.4</td>
<td>9.3</td>
<td>2441/2184</td>
</tr>
<tr>
<td>B 183</td>
<td>100</td>
<td>18.4</td>
<td>9.6</td>
<td>2533/2184</td>
</tr>
<tr>
<td>C 182</td>
<td>57-100</td>
<td>20.5</td>
<td>9.6</td>
<td>2623/2184</td>
</tr>
<tr>
<td>D 181</td>
<td>55</td>
<td>23.6</td>
<td>9.5</td>
<td>2720/2184</td>
</tr>
</tbody>
</table>

Figure 5.9: Small angle x-ray reflectivity of the AlGaN/GaN superlattice A and corresponding simulations assuming different Al content.

Another set of MOVPE AlGaN/GaN superlattices with a smaller superlattice period have been also studied. Their structure is:

\[
100 \times (2.5 \text{ nm GaN}/2.5 \text{ nm AlGaN})/2 \mu\text{m GaN}/\text{Al}_2\text{O}_3
\]

The Al mole fraction and thicknesses were obtained from x-ray diffraction measurements and are presented in Table 5.2:

Small angle x-ray reflection curves measured on these samples are shown in Fig. 5.7 and Fig. 5.8, respectively. The reflectivity data have been analyzed using the software of the center for X-ray Optics (CXRO) at Lawrence Berkeley National Laboratory (LBNL) which applies an algorithm based on Parrat’s recursive application of the Fresnel equations using the Nevot-Croce factor for the roughness [112, 113]: http://www-cxro.lbl.gov/.

Simulations of the superlattice A assuming a period of 10 nm repeated 100 times and a ratio \( s = t_{AlGaN}/t_{AlGaN+GaN} = 0.5 \) at three different Al content are shown in Fig. 5.9.
5.2. X-RAY REFLECTIVITY

Table 5.2: Strain state (± 5%), averaged Al content (± 5%) and period of the superlattice as determined by HRXRD, more the V/III ratio, growth parameter. (by M. Diesselberg).

<table>
<thead>
<tr>
<th>Sample</th>
<th>γ %</th>
<th>x_{Al} %</th>
<th>period [nm]</th>
<th>V/III</th>
</tr>
</thead>
<tbody>
<tr>
<td>E 201</td>
<td>89</td>
<td>14.8</td>
<td>4.5</td>
<td>4400/3900</td>
</tr>
<tr>
<td>F 202</td>
<td>89</td>
<td>15.0</td>
<td>4.6</td>
<td>2940/2600</td>
</tr>
<tr>
<td>G 203</td>
<td>89</td>
<td>14.0</td>
<td>4.7</td>
<td>2200/1950</td>
</tr>
</tbody>
</table>

The chemical composition x is considered by the AlGaN mass density $\rho_{\text{AlGaN}}$ which is a linear superposition of the AlN and GaN mass densities ($\rho_{\text{AlN}}$ and $\rho_{\text{GaN}}$):

$$\rho_{\text{AlGaN}} = \rho_{\text{GaN}} \cdot (1 - x) + \rho_{\text{AlN}} \cdot x$$  \hspace{1cm} (5.12)

with: $\rho_{\text{GaN}} = 6.1 \text{ g/cm}^3$, and $\rho_{\text{AlN}} = 3.25 \text{ g/cm}^3$.

The experimental data are in good agreement with an Al content of 15%.

Figure 5.10: Small angle x-ray reflectivity of the AlGaN/GaN superlattices B and C, and a corresponding simulation assuming an Al mole fraction of x = 20%.

Additional information on the superlattices is provided by x-ray reflectivity measurements. There is a further reflectivity peak in Fig. 5.10 as indicated by the box. This reflectivity maximum is much less in intensity than others. This is caused by an intensity envelope function whose minima are most sensitively determined by the ratio s of the individual thickness $d_{\text{AlGaN}}$ of the superlattice and the superlattice period [109, 114]. From the angular spacing between the diffraction peaks in the reflectivity curves, which is correlated...
to the periodicity of the structure, the superlattice period is derived. From a fit to the experimental peak positions and intensities not only a superlattice period of 9.3-9.5 nm for the first series of superlattices (samples A, B, C, D) is derived in good agreement with results from the (002) diffraction experiment, but also the individual thicknesses of the AlGaN layer [(4.7±0.2) nm] and GaN layer [(4.6±0.2) nm] is obtained. For the second series of superlattices (samples E, F, G) the fit results in a period of 4.7 nm. The layer thicknesses should be exactly half of the period, since no further peak is present in the reflectivity curves of these samples (see Fig. 5.8).

As can be seen in Fig. 5.9 the Al content influences only the intensity of the reflectivity peak. Broadening of the reflectivity peaks is due to structural inhomogeneity as variation in thickness or in Al content. The Al mole fraction calculated for the first series of superlattices is in the range 15-23% in good agreement with the results of x-ray diffraction. The parameters of the first series of samples obtained from x-ray reflection are summarized in table 5.3.

In the case of the second series of samples the value of the Al content extrapolated from x-ray reflectivity measurement is lower than the value obtained from x-ray diffraction, as shown in Fig. 5.11. This can be attributed to the interface roughness of the samples. A strong reduction of the reflectivity immediately beyond the critical angle θc indicates a considerable roughness of the top surface and the upper interfaces of the sample [115]. This is because the x-ray penetration depth close to the critical angle is very small (1-4 nm) such that the reflected intensity is determined by the top surface layers. For incident angles θ ≫ θc the penetration depth is larger, and scattering from areas far below the surface is revealed. The reflectivity curves shown in Fig. 5.7 of the first series of samples have well pronounced higher order peaks and, therefore, the interfaces have to be reasonably smooth. In contrast the reflectivity curves of the second series of samples show much weaker and
5.2. X-RAY REFLECTIVITY

Table 5.3: Al content and period of the superlattice as determined by x-ray reflection.

<table>
<thead>
<tr>
<th>Sample</th>
<th>x_{Al} %</th>
<th>period [\text{nm}]</th>
<th>SL [\text{nm}]</th>
</tr>
</thead>
<tbody>
<tr>
<td>A 180</td>
<td>15</td>
<td>9.3</td>
<td>4.4</td>
</tr>
<tr>
<td>B 183</td>
<td>20</td>
<td>9.6</td>
<td>4.5</td>
</tr>
<tr>
<td>C 182</td>
<td>20</td>
<td>9.6</td>
<td>4.5</td>
</tr>
<tr>
<td>D 181</td>
<td>23</td>
<td>9.6</td>
<td>4.5</td>
</tr>
</tbody>
</table>

higher order peaks. In this case the surface and interfaces should be rougher. In Fig. 5.12 simulations of the influence of the roughness on x-ray reflectivity data are shown for a sample of the first series.

![Reflectivity Graph](image)

Figure 5.12: Small angle x-ray reflectivity of the AlGaN/GaN superlattices D and corresponding simulations made with different roughnesses and a constant Al mole fraction of x = 15%.

As can be seen it produces a decrease of the intensity after the highest maxima not observable in the experimental data, in the simulation of the x-ray reflectivity data only the Gaussian-distributed microroughness is considered. The experimental data have to be simulated using a more complex model for the evaluation of the surface or interfaces roughnesses. The calculations can be made with the assumptions of the presence of a roughness distribution which varies linearly from the substrate to the superlattices [114] and roughness correlation [116].
Chapter 6

Summary

The stress present in GaN epitaxial layers and its heterostructure is mainly due to the lattice mismatches as well as to the difference in thermal expansion coefficients with its substrates. The stress is partly relieved by the formation of dislocations, that hampers the device performances. Considerable work has been done in the last years to reduce stress in GaN epitaxial layers in order to improve the performance of GaN-based devices. Nucleation layers grown on sapphire substrates are usually utilized to decrease the nucleation density as the subsequent GaN growth is island-like with nearly defect-free lateral growth. The island coalescence process determines the edge type TDs as well as the strain in the epilayers. The layers with larger grain diameters have lowest edge type TDs and highest compressive stress.

The third chapter of this thesis treats of strain and dislocations in MOVPE GaN layers. The MOVPE GaN epilayers on GaN nucleation layer exhibit a typical columnar growth. This can be generally described with a mosaic structure. The mosaic structure of metalorganic vapour phase epitaxy (MOVPE)-grown GaN layers was studied in dependence on the grain diameter utilizing high-resolution XRD. Different geometries and models have been utilized and discussed. In asymmetric diffraction geometry the derived parameters of the mosaic structure vary with the grain diameter, in this geometry only edge type TDs are visible. Therefore, a correlation between edge type TDs and the coalescence process must exist. Different models for the defect structure were analyzed, the edge type TD densities were calculated under the assumption that the dislocations are not randomly distributed but localized at the grain boundaries. The edge type TD densities assuming localization of TD at grain boundaries agree with the TEM data. Therefore, the grain diameters determine the edge type TDs.

The comparison of the XRD data with dislocation densities obtained from plan-view TEM and AFM demonstrates, that the model of a mosaic crystal is well suited to utilize XRD as a tool to quantify film perfection.

Moreover, in situ measurements have shown that the layers are under tension in the c-plane when a nucleation layer is used [57], in spite of the compressive lattice mismatch between GaN layers and sapphire. It has been supposed that the stress in the layers is due to the superposition of an intrinsic tensile stress associated with the coalescence process and the extrinsic compressive stress due to the cooling of the layers to RT. The evaluation of stress components by temperature dependent measurements have shown that the tensile in-plane stress component is dependent on the coalescence process, indicating the formation of the
The second part of this thesis treats a particular approach to reduce dislocations in MOVPE GaN layers, i.e. maskless pendeo epitaxial growth of MOVPE GaN layers. In general a reduction of the TDs of some orders is observed in laterally overgrown layers, due to the decoupling from the substrate. Though the lateral regions are crystallographically tilted respect to the seed, the exact origin of this tilt is still unknown. In LEO samples this is associated with grain boundary TDs, as well as with changes in the mask density, composition and stress state during the early stages of lateral overgrowth [100]. In maskless PE epilayers the results are contradictory. FE simulations assuming the strain to be completely induced during cooling of the structures after growth agree only partly with experimental data. The possible origins of the wing tilt of PE GaN layers grown on a SiC substrate were discussed. The strain state of single layers and stripes of GaN grown on SiC was studied to exploit the evolution of the strain in the different phases of the PE growth. It was found that an elastic relief of the biaxial tensile stress, due to the thermal mismatch between GaN and SiC, takes place in the stripes, before the overgrowth of the PE GaN layer. The biaxial compressive stress, due to the lattice mismatch between the GaN layer and the AlN nucleation layer is plastically relieved before overgrowth. Temperature dependent measurements show a linear reduction of the wing tilt with increasing temperature varying from sample to sample, indicating that it partly results from the mismatch in the coefficient of thermal expansion between the GaN layer and the substrate. The remaining wing tilt could be due to grain boundary TDs as in LEO samples. Bent TDs have been observed in TEM images of maskless PE samples, a shear stress has been associated with these dislocations by Lilienthal-Weber et al. [96]. Stress induced from the mismatch between the AlN buffer layer and the GaN also contributes to the remaining part of the wing tilt not relieved thermally.

It has to be noted that the rest tilt value varies from sample to sample at the growth temperature, indicating that it relates to the different growth conditions. In fact some of the data indicate that the wing tilt decreases with increasing V/III ratio. A significant fraction of the wing tilt is not a consequence of an elastic stress but is of inelastic nature as it is related to dislocations. Most probably the bending of dislocations and their final arrangement in the PE structure is heavily influenced by the V/III ratio. As the surface morphology, i.e. the formed facets, of uncoalesced LEO or PE structures is determined by the V/III ratio and the growth temperature and the surface morphology determines the bending of the dislocations. Thus it is obvious to assume that also in samples the defect structure and consequently the wing tilt changes with the V/III ratio [101].

In the last Chapter the application of x-ray techniques for the analysis of strain and composition in layers of inhomogeneous composition is explored. In the first part of the Chapter the strain state and the Al content of AlGaN buffer layers grown directly on (0001) 6H-SiC substrates have been studied by high resolution x-ray diffraction at both symmetrical and asymmetrical reflections. An inhomogeneous Al distribution was found in the film at the substrate interface. This is attributed to the strain present during the initial stage of growth at which Al rich and Al-deficient islands of different morphology are formed. The Al fluctuations disappear at a film thickness of 100 nm. The results have been compared with TEM and EDS data, and a reasonably good agreement was found.

In the second part of the Chapter the x-ray reflectivity technique has been utilized for the characterization of AlGaN/GaN superlattices. The fundamental parameters of the superlattices, i.e. period and individual layer thicknesses could be determined for ideally
flat surface. Roughness at the surface or the interfaces of the superlattices were found to render the determination of Al content more difficult. In contrast partially or totally strained layers hamper a direct determination of the composition by x-ray diffraction. The combination of both methods is recommended for the analysis of complex structures.
Bibliography

[38] D. Hull, D. J. Bacon, D. J. Bacon, Introduction to dislocations, BH.
[76] H. Heinke, L. Haase, V. Kirchner, and D. Hommel, phys. stat. sol. (a) 180, 189 (2000).


Publications

Papers:

- "A critical assessment of different models of the metastability in a-Si:HF"
  R. Chierchia, S. Loreti, V. Loreto, L. Mariucci, C. Minarini, A. Mittiga

- "Light emitting porous silicon diode based on a silicon/porous silicon hetero-junction"
  M. Allegrini, S. Trusso, C. Vasi, P. J. Ventura, L. C. Costa, M. C. Carmo and O. Bisi

- "All Porous silicon optical devices and Si/SiO2 multilayers: recent results"
  V. Mulloni, R. Chierchia, C. Mazzoleni, G. Pucker, L. Pavesi and P. Bellutti

- "Light emitting diodes based on anodically oxidized silicon/porous silicon heterojunction"
  Z. Gaburro, R. Chierchia, V. Mulloni, L. Pavesi, P. Bellutti

- "Near-Field Optical Investigation of Porous Silicon Samples"
  M. Allegrini, F. Fusco, M. Labardi, L. Pardi, and F. Sbrana, V. Mulloni, C. Mazzoleni,
  R. Chierchia, and L. Pavesi

- "X-ray scattering from Gan epitaxial layer - an example of highly anisotropic coherence"
  H. Heinke, V. Kirchner, H. Selke, R. Chierchia, R. Ebel, S. Einfeldt and D. Hommel

- "The role of high temperature island coalescence in the development of stresses in GaN films"
  T. Böttcher, S. Einfeldt, S. Figge, R. Chierchia, H. Heinke and D. Hommel

- "Mosaicity of GaN epitaxial layers: Simulation and experiment"
  R. Chierchia, T. Böttcher, S. Figge, M. Dieselberg, H. Heinke, D. Hommel
"Microstructure of heteroepitaxial GaN revealed by x-ray diffraction"
R. Chierchia, T. Böttcher, H. Heinke, S. Einfeldt, S. Figge, D. Hommel
J. Appl. Phys. 93, p. 8918

"On the microstructure of AlxGa1-xN layers grown on 6H-SiC (0001)

"Influence of electrical, chemical and morphological properties of inorganic/organic interface on light emitting device performances"
P. Vacca, M. Petrosino, R. Chierchia, A. Guerra, C. Minarini, A. Rubino

Conference Proceedings:

"Compositional Fluctuations in AlxGa1-xN Layers grown on 6H-SiC (0001) by Metal Organic Vapor Phase Epitaxy"
R. Kröger, S. Einfeldt, Z. J. Reitmeier, R. Chierchia, P. Ryder, D. Hommel and R. F. Davis

"Towards an Understanding of Strain Phenomena in GaN Layers by High-temperature X-ray Diffraction"
R. Chierchia, L. Kahrs, H. Heinke, T. Bottcher, D. Hommel, S. Einfeldt, A. Roskowski and R. Davis
Proceedings of the Nitride Workshop held in Denver, CO, 7/01

Oral contributions:


"Toward an understandig of mosaicity and strain in GaN epitaxial layers" R. Chierchia, T. Boettcher, L. Kahrs, H. Heinke, D. Hommel, E-MRS Strasbourg 2001


Posters:

"International Conference on Organic Electronics (ICOE) : Application of new functionalized poly(fluorene)s (PFs) in polymer light-emitting diodes (PLEDs)"
P. Vacca, R. Chierchia, C. Minarini, D. della Sala, C.F. Nobile, Mastrorilli, G.P.Suranna, A. Rubino

- "AIM 2005 Napoli: Application of new functionalized poly(fluorene)s (PFs) in polymer light-emitting diodes (PLEDs)"
  R. Chierchia, P. Vacca, A. Guerra, T. Fasolino, C. Minarini, D. della Sala, C.F. Nobile, Mastrorilli, G.P.Suranna, A. Rubino

- "AIM 2005 Napoli: Blue electroluminescence from films of poly(N-vinylcarbazole) and new segmented polyethers containing the oxadiazole unit"
  P. Vacca, R. Chierchia, T. Polichetti, L. Ferrara, D. della Sala, M.G. Maglione, A. Rubino, S. Bellone, S. Concilio, P. Iannelli

- "TOP 2006 Ischia: Influence of electrical, chemical and morphological properties of inorganic/organic interface on light emitting device performances"
  P. Vacca, M. Petrosino, R. Chierchia, A. Guerra, C. Minarini, A. Rubino

- "TOP 2006 Ischia: Influence of hole transporting layer on the improved performances of OLEDs by the surface treatments of ITO layer"
  R. Chierchia, A. Guerra, C. Minarini, P. Vacca, M. Petrosino, A. Rubino, M. G. Maglione

Enea technical notes:

- "Application of new functionalized Poly(fluorene)s (PFs) in Blue Polymer Light Emitting Diodes (PLEDs): Devices Preparation and Characterization"
  R. Chierchia, P. Vacca Sigla di identificazione: 2P99J

- "Thin film transistor"

- "OLED Prototypes"

- "Organic Light Emitting Diode: OLED"

- "PLED Fabrication"
• "Laser Crystallization on polymeric substrates"
  E. Calo’, R. Chierchia, D. Della Sala, P. Di Lorenzo, T. Fasolino, L. Ferrara, A.
  Guerra, A. Imparato, C. Minarini, D. Palumbo, T. Polichetti, A. Rubino, P. Tassini,

• "Active Matrix Organic Light Emitting Diode: AMOLED"
  E. Calo’, R. Chierchia, D. Della Sala, P. Di Lorenzo, T. Fasolino, L. Ferrara, A.
  Guerra, A. Imparato, C. Minarini, D. Palumbo, T. Polichetti, A. Rubino, P. Tassini,
  P. Vacca, F. Villani. Sigla di identificazione: RT/2006/30/MAT
Acknowledgment

First I would like to thank Pr. Hommel who has given me the chance to develop an interesting research theme and for his support during my PhD.

Naturally I want to thank all the Hommel group who has supported me from the beginning and making me feel at home, also helping me in all the bureaucracy like Verena Kirchner and Michael Fehrer my first officemates and Gisela Schuettrup.

In particular I want to thanks Heidrun Heinke for introducing me in the x-ray diffraction. She was the chef of the x-ray diffraction team: Gabriela Alexe, Claudia Roeder and I. We could always count on her. Gabriela, Claudia and I have supported each other in the difficulties and fought to share the use of the diffractometers.

And then the grower team: Sven Einfeldt, Tim Boettcher and Stephan Figge who have provided me the samples to characterize, without them I could not finish this work. Thanks for making me understood of the growth processes giving me always attention.

Thank to Matthias Klude for helping me with the computer stuff, he had a lot of patience, Sonia Hesselmann and Kalle Vennen-Damm for helping me with equipment running, Roland Kroeger, Angelica Venneman, Jens Dennemark and Lueder Kahrs for samples characterizations.

I wouldn´t have managed to bring my work at the end if I wouldn´t have found friendship in this group. I still remember the evenings spent with my friends Gabriela, Matthias, Stephan, Sven, Tim, Lueder and Akio drinking beer, sharing opinions and kino evenings.

I want also to remember also other component of the II-VI team: Carsten Kruse, Thorsten Passow, Elena Rowenta.

I want to thanks my friends Tiziana, Sabina and Claudio who have encouraged me along this years.

And at last my family who have supported me and my decisions, in particular my sister Patrizia and finally my niece and my nephew who love me so much that they couldn´t leave me alone writing this work.
Curriculum Vitae

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I was born in Naples on 9th January 1969.

In 1989 I’ve got a scientific degree at High-School.

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I have done an experimental thesis at the ENEA research center at Portici (Naples, Italy) under the supervision of Prof. Giuseppe Iadonisi.
After the thesis I have won a research stage under a grant of the “Istituto Nazionale per la Fisica della Materia (INFM)” at the University of Trento, Italy.
From the 01/05/99 to the 31/08/03: I was phd student at the University of Bremen, Germany at the solid state physic institute.
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