Magnetron Sputter Epitaxy of GaN

Muhammad Junaid
In the name of God, most gracious, most merciful.
Abstract

Electronic-grade GaN (0001) epilayers have been grown directly on Al₂O₃ (0001) substrates by reactive DC-magnetron sputter epitaxy (MSE) from a liquid Ga sputtering target in an Ar/N₂ atmosphere. The as-grown GaN epitaxial film exhibit low threading dislocation density on the order of $\leq 10^{10}$ cm$^{-2}$ obtained by transmission electron microscopy and modified Williamson-Hall plot. X-ray rocking curve shows narrow full-width at half maximum (FWHM) of 1054 arcsec of the 0002 reflection. A sharp 4 K photoluminescence peak at 3.474 eV with a FWHM of 6.3 meV is attributed to intrinsic GaN band edge emission. The high structural and optical qualities indicate that MSE-grown GaN epilayers can be used for fabricating high-performance devices without the need of any buffer layer. GaN (0001) thin films were grown on Al₂O₃ substrates by reactive high power impulse magnetron sputtering of liquid Ga targets in a mixed N₂/Ar discharge. A combination of x-ray diffraction, electron microscopy, atomic force microscopy, μ-Raman microscopy, photoluminescence, time of flight elastic recoil detection, and cathodoluminescence showed the formation of both relaxed and strained domains in the same films. While the strained domains form due to ion bombardment during growth. The relaxed domains exhibit superior structural and optical properties comparative to the strained domains, including room temperature luminescence.
Preface

The work presented in this Licentiate thesis is part of my PhD studies from June 2007-February 2011 in the Thin Film Physics Division at Linköping University. In the first two and half years I spent my time in developing a sputtering system where liquid Ga target can be sputtered. After mastering the technique and having a good control on the growth process, I also demonstrated the possibility to grow high quality GaN epitaxial layers directly onto sapphire without using a buffer layer. My project is funded by the Swedish Foundation for Strategic Research via the MS²E and Nano-N programs.
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Included Papers

Paper 1
Electronic-grade GaN(0001)/Al₂O₃(0001) grown by reactive DC-magnetron sputter epitaxy using a liquid Ga target

M. Junaid, C.-L. Hsiao, J. Palisaitis, J. Jensen, P. O. Å. Persson, L. Hultman and J. Birch
Submitted to Applied Physics Letters, 2010

Paper 2
Epitaxial Growth of GaN (0001)/Al₂O₃(0001) by Reactive High Power Impulse Magnetron Sputter Deposition

Manuscript in final preparations
Related Papers (not included)

Paper 3
Growth and characterization of thick GaN layers grown by halide vapour phase epitaxy on lattice-matched AlInN templates

C. Hemmingsson, M.Boota, R.O.Rahmatalla, M. Junaid, G. Pozina, J. Birch, and B. Monemar


Paper 4
Standard-free composition measurements of Al\textsubscript{1-x}In\textsubscript{x}N by low-loss electron energy loss spectroscopy

Justinas Palisaitis, Ching-Lien Hsiao, M. Junaid, Mengyao Xie, Vanya Darakchieva, Jean-Francois Carlin, Nicolas Grandjean, Jens Birch, Lars Hultman, and Per O. Å. Persson


Paper 5
Synthesis and characterization of textured single phase (Al,B)N thin films

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Submitted to Thin Solid Films (2010)
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Chapter 1

Introduction

The group III-Nitrides (III-N) InN, GaN and AlN have very good optical and electrical properties. By using ternary alloys of these materials, we can tailor the band gap as well as the electrical and optical properties which can make world faster and brighter. III-N based devices have applications from LED TVs to 4th generation wireless communication enabling us to use high speed data trafficking while on the move. Almost all the devices made of III-N contain GaN. Huge research efforts are being made on these materials and their ternary alloys to improve their structural and optical properties.

The main epitaxial growth techniques to grow the GaN epitaxial layers are chemical vapor deposition (CVD) and molecular beam epitaxy (MBE). In case of CVD growth temperatures are very high > ~1000 °C and temperature sensitive substrates cannot be used. Scalability is not a big issue in case of CVD. For MBE growth, it is possible to grow at lower temperatures, around 700 °C but the running costs are high and it is difficult to scale up for industrial epi-layer production on large areas of substrate material. Magnetron sputter epitaxy (MSE) has the potential of epi-layer synthesis of high quality GaN at low temperatures thanks to the inherent possibility to exploit a concurrent flux of low energy process gas ions to promote adatom mobility during growth. MSE can also easily be scaled up for deposition over large areas while maintaining excellent control over impurity incorporation. However, for reactive sputter deposition of electronic quality GaN there are difficulties in obtaining stable growth conditions, mainly caused by nitridation of the target surface and the low melting point (29 °C) of metallic Ga. For example, the Ga source material needs to be kept in a horizontal trough and sputtering gas can be trapped in liquid gallium with bubble bursts in the source as a consequence, etc. On the other hand, from a technological point of view, mastering reactive sputtering from a liquid target will give clear process advantages
such as high deposition rate, elimination of target erosion track effects, and a continuous supply of source material.

Since the early 80s till to date there exists less than 50 reports about the growth of GaN by magnetron sputtering but only two groups have shown evidence of semiconductor quality GaN and these are made by RF and DC magnetron sputtering.[1,2]

Thin Film Physics Division at Linköping University has a history of exploring new materials and developing sputtering process for their synthesis. There is also a strong tradition of working with wurtzite structures nitrides, especially with AlN, AlInN, and ScAlN. This knowledge and experience of sputtered growth of nitrides in a UHV system encouraged us to try the growth of GaN and try to achieve the high quality GaN epitaxial layers by sputtering, which has not been reported since the early 80’s.

In my ongoing research I have shown that it is possible to grow GaN film with good structural and optical properties. Two techniques were employed to grow these films by DC magnetron sputtering and high power impulse magnetron sputtering (HiPIMS). We have optimized the growth conditions and shown the possibility to grow GaN. There is, however, a lot of room to play with the process and to improve the quality of the material.

In Chapter 2, we will learn briefly about the application, properties and epitaxial growth techniques of GaN. In Chapter 3, the construction of the growth chamber for the MSE of GaN will be described. The characterization techniques used to analyze the films will be described briefly in Chapter 4. Chapter 5 summarizes experimental results and Chapter 6 is about ongoing and future research.
Chapter 2

Applications, Properties and Growth Techniques for GaN

In this chapter applications and properties of GaN and also epitaxial growth methods commonly used to grow epitaxial GaN, will be described.

2.1 Applications

Group III-N such as GaN, AlN and InN are highly interesting material systems, since they combine desired properties like direct band gaps ranging from 0.8 to 6.1 eV (see fig 2.1) with a high breakdown voltage and high electron mobility. [3,4,5] Due to such opto-electronic properties group III nitrides have attracted much attention in the last two decades. Ternary alloys based on Group III-N allow for the tuning of the band gap, ranging from near IR to deep UV regions (see fig. 2.1).

Figure 2.1: Lattice parameters of III-Ns and their corresponding bandgap energies
The band gap engineering offers a lot of applications as light emitting diodes (LED)s and laser diodes (LD)s covering the spectral wavelength from infrared to ultraviolet. [6,7,8] In a few years time solid-state lightening devices based on Group III nitride materials such as LEDs are believed to replace incandescent light bulbs and florescent lamps with a substantial impact on the energy saving and environmental conservation. [9] In this work we have focused on the GaN, which is an important material that is used in a majority of the electro-optical devices based on the III-Ns.

2.2 Properties

Structural Properties

GaN has two crystal structures, wurtzite and zincblende. During this work only wurtzite GaN is being studied, so we will only consider the properties of the wurtzite structure. Fig. 2.2 below shows the unit cell of wurtzite GaN. It will have two lattice parameters $c$ and $a$ and their values are $5.185 \ \text{Å}$ and $3.189 \ \text{Å}$, respectively.[4]. The space grouping for the wurtzite structure is P63mC6v4. [10]
Depending on the growth conditions and type of growth technique GaN wurtzite crystal can be grown with two faces, Ga-face and N-face (see fig. 2.3).[11] Usually, GaN grown directly on the sapphire has an N-face. During this work GaN was grown directly on sapphire and we confirmed the N-face by KOH etching. After the KOH etching, the nitrogen face forms a pyramidal shape features on the surface, but in case of the Ga-face, it remains undetached. Details of the KOH etching recipe can be found in the reference11.

![Figure 2.3](image)

**Figure 2.3**: Different polarities of wurtzite GaN crystal, left hand side figure shows the Ga-face and the right hand side figure shows the N-face.

**Summary of Properties of GaN**

Table 2.1: Important properties of GaN [5,10]

<table>
<thead>
<tr>
<th>Material</th>
<th>GaN</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lattice Parameters [Å]</td>
<td>( a = 3.189, \ c = 5.185 )</td>
</tr>
<tr>
<td>Band gap [eV]</td>
<td>3.42 at 300 K</td>
</tr>
<tr>
<td>Density [g/cm(^3)]</td>
<td>6.15</td>
</tr>
<tr>
<td>Melting point [°C]</td>
<td>29</td>
</tr>
<tr>
<td>Boiling Point [°C]</td>
<td>~2400</td>
</tr>
<tr>
<td>Electron Mobility [cm(^2)/Vs]</td>
<td>1400 at 300 K</td>
</tr>
<tr>
<td>Breakdown Voltage [V/cm]</td>
<td>5 x 106</td>
</tr>
</tbody>
</table>
2.3 Epitaxial Growth Techniques

2.3.1 Chemical Vapor Deposition (CVD) of GaN

In CVD GaN is grown on the substrate by the chemical reactions close to the equilibrium conditions. This method is used for both bulk and epitaxial growth. A general sketch of a CVD reactor is shown in the fig 2.4. Different so called precursors are allowed to flow through tube and they react with each other to form GaN on the heated surface of the substrate. The substrates typically have temperatures of more than 1000 °C, heated by using RF coils around the quartz tube. On the basis of different type of precursors, CVD can be classified in two types mainly used for GaN growth:

1: Metal Organic Vapor Phase Epitaxy (MOVPE)
2: Hydride Vapor Phase Epitaxy (HVPE)

![Figure 2.4: Schematic diagram of a CVD reactor](image)

High growth rates can be achieved by CVD methods and large area depositions are possible. However, In CVD growth, substrates sensitive to high temperatures and harsh chemical environments cannot be used. Harmful residual gases may also be produced which are not good for human health and environment.

2.3.2 Molecular Beam Epitaxy (MBE) of GaN

MBE is a physical vapor deposition (PVD) technique where growth occurs in non-equilibrium conditions. MBE growth is done in ultra high vacuum at lower temperatures than of nearly 700 °C. As a Ga source effusion cells are used where Ga is evaporated by
heating a crucible. The source of atomic N is more complicated due to the high binding energy of the N$_2$ molecules. So for producing N atoms source either an RF-plasma is used or NH$_3$ is cracked in an effusion cell at very high temperatures. Fig. 2.5 shows a rough sketch of an MBE chamber. Growth rates are much lower than the MOVPE or HVPE. Typical growth rates are 0.5-1µm/h [5] which are suitable for epitaxial growth thanks to the UHV conditions assuring a very high purity level of grown films. High running costs and scalability make it a less favorable method for industrial use.

![Figure 2.5: Schematic diagram of an MBE chamber](image)

### 2.3.3 Magnetron Sputter Epitaxy (MSE) of GaN

“*Magnetron Sputter Epitaxy is defined as epitaxial growth by magnetron sputter deposition of GaN under the same stringent vacuum and sample handling conditions as in practice in MBE*” [12]

In the present work, GaN was grown by MSE on (0001) oriented c-plane Al$_2$O$_3$ substrates. Growth was performed in a UHV chamber having a base pressure of 1.0E-8 Torr. Liquid Ga (99.99999% pure), contained in a horizontal water cooled stainless steel trough of 50 mm diameter, was used as the magnetron sputtering target. To form GaN, a mixture of Ar (99.999999% pure) and N$_2$ (99.999999% pure) was used. To achieve such a high purity of gases special gas purifiers are used.
Sputtering

In the sputtering process the target material is bombarded by ions having high kinetic energy and as a result of this bombardment atoms are ejected from the target material. These ejected atoms are then transported in a gas phase to the substrate and where they condense on the surface to form a film as shown in the figure 2.6. To produce the ions for the sputtering process, sputter gases are introduced into the vacuum chamber and a negative potential is applied to the target. Plasma is generated and glow discharge process is maintained in the deposition chamber. Interactions of the ions with the target surface not only sputter the atoms but also cause the generation of secondary electrons. These secondary electrons are accelerated away from the target due to the presence of the negative potential on the target. The secondary electron emission is needed to sustain the discharge since these electrons help the gas ionization process. [13]
**Magnetron Sputtering**

To enhance the ionization process by using magnetic field is called magnetron sputtering. In the presence of magnetic and electrical fields the ejected secondary electrons follow a cycloid path close to the target surface due to the Lorentz force experienced by these electrons. The electrons that are trapped in this region further ionize the gas atoms. Magnetrons can be classified into three types according to their magnetic field configuration [14]

- Balanced magnetron (center and outer poles have equal strength)
- Unbalanced magnetron type I (center pole is stronger than the outer pole)
- Unbalanced magnetron type II (outer pole is stronger than the inner pole)

In this work, unbalanced magnetron of type II was used during the MSE of GaN, because the magnetic field of this type of magnetron not only traps electrons and enhance the ionization at the target surface, but also extend the plasma to the substrate and the chamber space (see fig. 2.6). This will increase the ion density in the vicinity of the substrate which can be used to influence the film growth process [14,15].

**Reactive Sputtering**

Usually a metal film is deposited in the presence of an inert gas e.g. Ar. In such a case the gas is only used to sputter the atoms from the target. In some cases a sputtering gas is chosen which chemically reacts with the target atoms and forms a new compound and this new compound is deposited on the substrate surface. This type of sputtering is called reactive sputtering. [15] These reactive gases can be used separately or as a mixture with Ar. In my experiments, for the deposition of GaN, a mixture of Ar and N2 was used, where N2 reacts with the sputtered atoms of sputtered Ga.
Direct Current and High Power Impulse Magnetron Sputter Deposition

In the present work two techniques were used for the magnetron sputter epitaxy of GaN.

1. Direct Current Magnetron Sputter Epitaxy (DC-MSE)
2. High Power Impulse Magnetron Sputter (HiPIMS) Deposition

The main difference between these two techniques is the type of potential applied to the sputtering target. To switch between these two types of sputtering method we just need to switch the power supplies. DC-MSE is a simple process and easy to handle. In my growth experiments for DC-MSE, a stable process is achieved for lower pressures (~5 mTorr total pressure) and at lower powers (~10 W) compared to HiPIMS. In DC-MSE, also nearly 2 times higher growth rates can be achieved as compared to the HiPIMS.

In the case of HiPIMS, during my experiments, in order to achieve a stable growth process a minimum of 16 mTorr total pressure was required at an average power of 14W. HiPIMS is a promising technique for improving common magnetron sputtering for thin film deposition [16], since the HiPIMS process generates a highly ionized plasma with large quantities of energetic target material ions [17]. These beneficial modifications of the discharge process are due to the increased plasma density, which is 2-3 orders of magnitude higher than for example, standard direct current magnetron sputtering plasmas. It results in a decrease of the ionization mean free path from ~50 cm for DCMS to ~1 cm in the case of HiPIMS [18,19].
Chapter 3

Construction of a UHV-system for Reactive Magnetron Sputter Epitaxy of GaN

To grow the GaN by MSE, a major challenge was to develop a sputtering system in which we could sputter from a liquid Ga target. The melting point of Ga is 29 °C [20] but during sputtering, the temperature of the target surface may reach a few hundred degrees Celsius, which can cause melting of the Ga. Therefore special measures must be taken to use it as a sputtering target. A few reports can be found in the literature regarding the sputtering of liquid Ga but no one has explained the challenges involved in this development. In this chapter I will explain the challenges and obstacles I faced in construction of the system. I hope this will help many others who are still trying or will try to sputter from a liquid Ga target. In addition to the synthesis of the III-N materials, it will make synthesis of Ga containing alloys. This will also open new fields of research like ion-liquid interactions and new theoretically predicted phases can be grown, e.g. TiGaN and others.

3.1 Growth Chamber

A UHV growth chamber was used for MSE of GaN. The growth chamber is connected to a common load lock and transfer tube system which also connects it to another UHV chamber used for the MSE of AlN and AlInN. The vacuum system of the growth chamber is shown in the figure 3.1. Thanks to the load lock system, we do not need to vent the chamber every time during loading and unloading of the sample. The base pressure inside the growth chamber is $1 \times 10^{-8}$ Torr. To control the pumping speed a butterfly throttle valve was designed and installed. The flow of gases is controlled by electronic mass flow controllers (see fig. 3.2). For precise measurement of the pressure during growth, a capacitance manometer is used. Very high purity Ga (99.99999% pure) is used as the sputtering target. Due to the low melting point of Ga, it will be in liquid
phase during sputtering and there is a need to do keep the liquid Ga target in a trough in a horizontal position to avoid the spilling of liquid Ga inside the chamber. In the present system I used a water cooled 2 inch magnetron. In its original design, the magnetron was designed to be mounted at a flange size of CF60 but the only available horizontal port has the flange size of CF40 (see fig 3.2-top), therefore I modified the existing magnetron to fit into that flange.

The magnets in the magnetron were chosen to give a type II configuration (see fig. 3.2-bottom), because the magnetic field of this magnetron not only traps electrons and enhance the ionization close to the target surface but also the plasma can be extended to the substrate and the chamber space. Figure 3.2-bottom shows a schematic sketch of the magnetron. The gallium is placed in a stainless steel (SS) trough which is clamped tightly to the magnetron. This gave a good surface contact between the bottom surface of the SS trough and the water cooled magnetron surface.

Figure 3.1: Vacuum system for the growth chamber
3.2 Construction of the Sputtering Target

Ga has a very high surface tension $735E-5$ N/cm [21] and pure Ga does not wet any surface [22,23]. Due to this property Ga spreads like beads on a surface just like mercury. The Ga surface reacts with oxygen and forms an oxide layer [24] which changes wetting capabilities of Ga. Thus the selection of the material to make the trough was another challenge. In the literature there is no such data available showing which material Ga wets more and these materials should be UHV compatible. Three materials, molybdenum, graphite and stainless steel (SS) were tested. Molybdenum and carbon
were selected based on their high surface energies which would facilitate wetting. SS is quite commonly used and it was reported in literature [1,2,25] to be used as a trough to contain liquid Ga. Ga has a very corrosive effect for Al, which therefore cannot be used. Graphite and stainless steel (316-British = 2343-Swedish standard) are quite resistant [26,27,28]. For molybdenum corrosive data could not be found.

Figure 3.3: (a) Liquid Ga droplet on a flat SS surface. (b) & (c) liquid Ga in cylindrical-shape SS crucible. (d) Liquid Ga in concave shape SS crucible.

According to my observation, I found that

1: Ga wets stainless steel more than any of the other two materials. But it still forms a large droplet and does not spread on the surface as water does (see fig. 3.3a).
2: For both cylindrical-shape and concave-shaped trough made of molybdenum and graphite, during the sputtering, the Ga shrinks and forms into beads. So there is no continuous film or layer of Ga covering the entire trough.
3: During sputtering, in the case of a SS cylindrical-shaped trough the Ga layer also shrinks in diameter after a short time of sputtering. In this case Ga remains in a big droplet shape and does not form beads. Due to shrinkage of the Ga layer some part of the SS crucible is exposed to the plasma. This is not usable since SS then also could be sputtered (see fig. 3.3c).
Another disadvantage of using a cylindrical shape container is that if the gallium does not wet the corners, there will be some empty space left in the corner as can be seen in the fig. 3.1b, which may cause a virtual leak in the vacuum chamber.

The concave shaped SS-crucible shown in the fig. 3.3d is the most optimized shape in order to keep the Ga target in contact with the SS, creating as large flat target area as possible without formation of any droplets or voids during sputtering.

### 3.3 Temperature Calibration

To grow the semiconductor materials precise temperature control is required. In our growth chamber the substrate is heated by radiative heating and the distance between the substrate and the heater is ~2 cm. For this purpose a careful calibration was performed. In the present scenario all the technologically interesting substrates to grow GaN on them are transparent and are also transparent for infrared radiation. So the temperature on the surface of the substrate can be very low as compared to the heater temperature. A thermocouple use to control the heater is placed in between the heater and the back side of the substrate (see fig. 3.4).

![Experimental setup for the temperature measurement at the substrate surface.](image)

The thermocouple is hanging in vacuum and it is not touching any surface. To calibrate the thermocouple, three temperatures were recorded verses the current which was passing through the graphite heater. The first one was the control thermocouple (Thermocouple 1), second one was the substrate temperature measured by IR-pyrometer through a view point and the third one was from a thermocouple attached to the surface...
of substrate (Thermocouple 2) facing the sputtering target. A detailed sketch of the experimental set up is shown in fig 3.4. From the results (see fig. 3.5) it is clearly seen that there is a difference of 100 to 150 °C in the readings of the back controlling thermocouple and the front substrate thermocouple at high temperatures ~ above 500 °C.

Figure 3.5: Calibration graph showing three temperatures, one from the thermocouple 1, thermocouple 2 (sample surface) and pyrometer measurements on sample surface.

3.4 Formation of Bubbles and Nitride layer on The Target Surface

In the fig. 3.6 an event is recorded demonstrating the formation of bubbles, bursting of these bubbles, and Ga wetting of the SS. Fig. 3.6a shows the start of the sputtering process in the mixture of Ar and N₂ and the plasma is confined to a limited region and a nice plume of plasma can be observed emerging from the target. In fig. 3.6b, an arrow is indicating a bubble formed just under the surface of the liquid Gallium target. A possible reason of the formation of these bubbles can be the trapping of the sputter gas into the liquid.
Figure 3.6: Bubble formation and bursting, also the increased wetting of the Ga is shown in this set of pictures.
Figure 3.7: This set of pictures shows the formation of nitride layer on the target surface. Two types of motions were observed, 1: Clock wise rotation (follow the arrow position, where arrow is indicating a crack in the film) and 2: contraction and expansion of the layer that causes the variation in the target voltage.
As we learnt early in this chapter that the magnetron is water cooled and also the temperature of the target surface can rise up to a few hundred degrees Celsius due to the radiative heat from the heater and also due to the energy transferred by the bombardment of the sputtering ions.

Due to the local differences in the temperature of the melt there can also be convection in the liquid and that can cause the movement of the bubbles in the liquid which was observed during this event and it is also reported [29]. N\textsubscript{2} is used as a reactive gas therefore a thin nitrided layer will form on the top of liquid Ga target which may hinder the escape of trapped gas from the liquid, promoting coalescence of smaller bubbles, thus causing the formation of large bubbles. These bubbles can burst after reaching some critical size, overcoming the surface tension of the liquid Ga. In fig. 3.6c arrow 1 shows the start of the Ga wetting of the SS after a bubble burst and the arrow 2 indicates a crack formation in solid the nitrided layer. In fig. 3.6e the arrow 1 shows the burst of the bubble and arrow 2 indicates the development of an extra crack in the nitrided layer. The burst of the bubbles cause a lot of splashing of Ga droplets in all directions, some of those Ga droplets can be seen on the ground shield (see fig. 3.6f indicated by arrow 2). Another possible reason for the formation of the bubbles could be the boiling of the liquid Ga. However, the boiling temperature of Ga at nearly 5 mTorr pressure is nearly 1100 °C, which is not possible. To know the exact temperature of the melted target during sputtering an experiment is described in the section 3.5.

To avoid the formation of a nitrided target and to reduce the formation and bursting of bubbles an experiment was designed. In this experiment the Ar partial pressure was set at a certain level and then the N\textsubscript{2} partial pressure was increased. Due to the increase in the partial pressure the plasma color was changed from purple to more pink (see fig. 3.7a-c). With the initial increase of N\textsubscript{2} partial pressure the nitrided layer coverage increased (see fig. 3.7a & b), but at a certain N\textsubscript{2} pressure the layer started to shrink again to a certain size (see fig. 3.7c). At this stage the increase in N\textsubscript{2} was stopped and an interesting phenomenon was observed. The layer coverage is not static and it is demonstrating two types of motions.
Figure 3.8: Top image shows a cross-sectional TEM view graph of GaN film grown before improving the base pressure and without proper clamping the sputtering target. Bottom image shows cross-sectional TEM view graph after applying the changes.

The whole layer is rotating in a clockwise direction as indicated by the arrow (pointing at a certain feature at the layer) in fig. 3.7c-h and secondly it is periodically shrinking and expanding, evident by comparing fig. 3.7c & e and also fig 3.7i & j.

The observed bubble formation and the formation of the nitrided layer on the surface of the liquid target were problems occurring early in the experiments and we identified two reasons for these problems. The first one was too high base pressure and the second one was inadequate cooling of the target.

A stable process was achieved after working on the vacuum system and reducing the base pressure to \(~1 \times 10^{-8}\) Torr and after better clamping the SS trough to the magnetron backing plate to get a better thermal contact to improve the cooling of the target. These actions also led to drastically improved film quality as can be seen in fig. 3.8. As the film
quality improved, it was also possible to grow thicker films under stable conditions. Although the dynamics of the liquid target, i.e., bubble formation, periodic coverage and rotation of the nitride layer are extremely interesting features of this process, it is beyond the scope of this work to investigate them in detail. The observations are presented here since they may be useful for others who will work with high base pressures, in an oxygen containing environment, or in the field of liquid ion interactions.

3.5 Temperature on the Target surface

To confirm that the liquid Ga target was far from the boiling temperature of Ga, an experiment was designed to see how much temperature can rise on the surface of the liquid Ga target during heating the substrate. The distance between the target and the substrate heater is ~ 11 cm. The experimental setup is shown in the figure 3.9. During heating the substrate to 840°C the temperature rose from room temperature to 105°C.

![Figure 3.9: Experimental Setup to measure the temperature of the surface of the liquid target. Ceramic tubes are used to avoid contact with the ground shield and chamber walls.]

After cooling down the target to the room temperature the target was sputtered in mixture of Ar and N$_2$ atmosphere at total pressure of 10 mTorr for 10 minutes using a magnetron power of 25W. The temperature was measured on the surface right after the stopping the sputtering and the measured temperature was ~330°C. During the real sputtering experiments the total gas pressure was 5 mTorr. Vapor pressure curves for Ga indicate that it should boil at 1100 °C at 5mTorr pressure. Measured temperature is much lower than 1100 °C, so there is no chance of boiling of the Ga in our setup.
Chapter 4

Characterization Techniques

Several characterization techniques were used to analyze the as-grown GaN films. This chapter introduces each technique used and the information which it can give about the samples.

4.1 Transmission Electron Microscopy

Transmission electron microscopy (TEM) is an important tool for material science and also for life science studies. Using TEM a magnification allowing imaging with resolution on the atomic scale is achievable. We can obtain information about the microstructure and crystal structure i.e. how the atoms are arranged in a sample. Using the diffraction pattern it is easy to figure out the structure and orientation of the crystal and we can find the epitaxial relationship between the substrate and film. Using analytical TEM elemental composition and spatial distribution of elements in the material can also be identified. The working principle of the TEM can be found in the Ref. 30. Contrast is a variation in intensities in adjacent areas. Two basic ways to form contrast are bright field (BF) imaging and dark field (DF) imaging. In BF contrast regions that scatter the electrons most will appear dark, this means that, e.g. thicker regions or regions with high atomic number, or the parts of the samples that diffract the electron will appear darker and thin areas with small atomic number without diffracting the beam will appear brighter. In DF, a selected part of the scattered or diffracted electrons are used in the imaging, making it possible to highlight certain structures in the sample. In the present work for imaging, BF contrast is used in TEM mode. In scanning transmission electron microscopy (STEM), we used DF contrast by using high angle annular dark field (HAADF) detector. This also gives a bright contrast to thick areas or areas with high atomic numbers.
Special sample preparation is required to make a thin sample which is transparent for electron beam. Cross-sectional specimens for TEM were prepared by mechanical polishing followed by Ar ion milling at 5 keV. Final polishing was done using low energy ions at 2 keV for removing damage on the sample surface in the previous step. Structural characterization was performed using an FEI Tecnai G2 TF 20 UT field-emission TEM operated at 200 kV in high-angle annular dark field imaging (HAADF-STEM) mode. In order to selectively make cross-sectional samples of individual features in the epilayers, cross sectional samples were prepared by ion etching method using Carl Zeiss Crossbeam 1540 EsB focused ion beam milling instrument.

### 4.2 X-ray Diffraction

X-ray diffraction (XRD) is a powerful tool for investigating the crystalline structure of materials. For semiconductor epilayers, XRD is mainly used to evaluate the quality of the film, determine the composition of alloys, and investigate the thickness and strain condition of the epilayers.[31,32]

X-rays are electromagnetic radiation of the same nature as light, but with much shorter wavelength (usually of the order of Å), X-rays used in XRD typically have wavelengths of 0.5~2.5 Å, which is close to the spacing of atoms in crystals. Since atoms are arranged periodically in a lattice, constructive interference of the scattered X-ray from the lattice occurs when the Bragg’s law is fulfilled: \( n\lambda = 2d\sin\theta \), where \( n \) is an integer representing the order of diffraction, \( \lambda \) is the X-ray wavelength, \( d \) is the inter planar spacing of the diffracting planes, and \( \theta \) is the incidence angle of the X-ray beam. Details about the crystal structure can be obtained from the maxima in an XRD pattern using Bragg’s law. The Ewald’s Sphere construction provides a relation between Bragg’s law and reciprocal space representation of the crystal which is used to interpret the reciprocal space maps (RSM). [32]
Overview 0-20 x-ray diffraction scans were performed with a Philips 1820 Bragg-Brentano diffractometer. For high resolution X-ray diffraction (HRXRD) measurements, a Philips X’Pert MRD diffractometer ($\lambda = 0.15406$ nm) was used, equipped with a graded parabolic X-ray mirror and a channel cut Ge(220) single crystal monochromator. The diffracted beam was analyzed using an asymmetric double-bounce Ge(220) crystal collimator. High resolution reciprocal space mapping (RSM) measurements were carried out in symmetric and asymmetric scattering geometries using the GaN 0002 and 1010 reflections, respectively. Information about the $a$ and $c$ lattice parameters is obtained from the peak position in these RSMs. The shape and orientation of the RSM contains the information about the orientation of the grains, strain levels, mosaicity, lateral coherence length, etc. Examples of XRD, HRXRD scans, and RSMs can be found in Paper 1 and 2.

4.3 Scanning Electron Microscopy / Cathodoluminescence.

When an electron beam interacts with a material different radiations come out of it, e.g., X-rays, Auger electrons, secondary electrons, and cathodoluminescence. By detecting these radiations a lot of information about the irradiated sample can be obtained, including microstructure, surface morphology, composition, and optical properties. [33] In SEM, the primary electron beam is steered to raster the area to imaged and secondary electrons are used. In this work SEM was used to study the surface morphology and to look at sample cross sections to measure the thickness.

Cathodoluminescence (CL) can be added to an SEM platform. For that mode of operation, energetic electrons come into interaction with the material and light radiation is emitted. One example is the cathode-ray tube. Using CL, information about bandgap of the semiconductor materials is obtained. It also helps in identifying different areas in the samples with different optical properties, by CL imaging.[34] I used a Zeiss-LEO field emission scanning electron microscope (FEG-SEM) equipped with an Oxford Research Instrument cathodoluminescence spectrometer. The experimental details can be found in Ref. 35.
4.4 Atomic force microscopy

In atomic force microscopy (AFM) a very small tip moves toward a sample, it may interact with the sample surface when they are sufficiently close. The tip-surface interactions depend on the distance between the tip and sample. AFM measures changes in the tip-sample forces to obtain surface characteristics of the sample. In different measurement modes, these forces may vary due to physical features on the sample, or arise from magnetic or electric forces between the tip and the sample. AFM primarily measures surface topography, but has other variants that measure electrical and magnetic properties [36]. In the present work AFM operated under tapping mode was used to investigate the surface morphology of GaN grown under different conditions.

4.5 Elastic Recoil Detection Analysis

When highly energetic ions hit the sample, recoiled ions are emitted and their mass and energy are detected. It is very useful in order to determine the light elements e.g. hydrogen, in the film. Using 40 MeV iodine ions a depth of ~1 µm of the film can be probed by this technique. ERDA was used to determine the stoichiometry of the GaN films and the amount of impurities like oxygen, carbon and hydrogen.[37] During the experiments the elemental composition of the deposited films was obtained by time-of-flight elastic recoil detection analysis (ToF ERDA). 40 MeV $^{127}$I$^{9+}$ ions were used as projectiles and a recoil angle of 45° with the incident angle set to 22.5° relative to the surface. The measured recoil ToF ERDA spectra were converted into relative atomic concentration profiles using the CONTES code.[38,39]
4.6 Photoluminescence

Photo luminescence (PL) is an important tool to measure the optical properties of semiconductor materials. It is a non-destructive method and it also does not require any sample preparation. Information about band gap, excitonic states, involved impurities, effects of externally applied electric or magnetic fields can be obtained from PL.[37] In the present work low temperature (at 4K) and room temperature PL were used to measure the band gap related luminescence and the yellow luminescence related to impurities in the sample. PL was performed in a backscattering geometry. A continuous-wave (CW) excitation from a Coherent Verdi/MBD-266 laser system ($\lambda_{\text{exc}} = 266$ nm) was used as the excitation source with the laser beam focused down to $\sim 2$ $\mu$m diameter by a 50X refractive objective. The collected PL light was dispersed by a single-grating monochromator with a spectral resolution better than 0.2 nm in the 300–600 nm range and detected by a liquid-nitrogen-cooled charge coupled device (CCD).

4.7 Raman Spectroscopy

Raman spectroscopy lies in the category of the vibration analysis of the materials at atomic scale. Each free standing perfect crystal has its natural vibration frequency depending on the lattice and basis of the material. This technique uses a monochromatic light source, usually lasers, and when this radiation interacts with a material it scatters inelastically. The frequency of the scattered radiation shifts up or down compared to the original radiation frequency. This shift given in wave number units (cm$^{-1}$) provides information about the material’s properties, e.g., composition, stress/strain, crystal symmetry and orientation, quality of the crystal, and the sample thickness.[34,37] To characterize the spatial distribution of strained material, Micro-Raman mapping and spectroscopy (Jobin-Yvon T64000, 0.35 cm$^{-1}$ resolution) was performed on the GaN samples via backscattering geometry at room temperature. The experimental details can be found in Refs. 40 and 41.
Chapter 5

Summary of the results

Paper 1

The epitaxial growth of electronic-grade GaN(0001) directly onto c-plane Al₂O₃ by reactive DC-MSE from a liquid Ga target is demonstrated at a moderate temperature of 700 °C. The film material has excellent structural and optical properties. This method enables large-scale production of GaN epilayers onto very large substrates at growth conditions as pure as MBE. The as-grown GaN epitaxial film exhibits a low threading dislocation density of $\leq 10^{10}$ cm$^{-2}$, as obtained by TEM and modified Williamson-Hall plot. X-ray rocking curves show narrow full-width at half maximum (FWHM) of 1054 arcsec of the 0002 reflection. A sharp 4 K PL peak at 3.474 eV with a FWHM of 6.3 meV is attributed to intrinsic GaN band edge emission. In addition, our material reveals strong room-temperature $\mu$-PL band edge (BE) luminescence at 3.4 eV with a FWHM of 73.3 meV. The high structural and optical qualities indicate that MSE-grown GaN epilayers can be used for fabricating high-performance devices without the need of any buffer layer of AlN or low-temperature GaN nucleation layer.

Paper 2

GaN(0001) was grown on Al₂O₃ substrates using high power impulse magnetron sputter epitaxy. A series of films with thickness less than 1 µm were grown to optimize growth conditions in terms of N₂ partial pressures. The growth of high-quality single-crystal and stoichiometric GaN films was thus demonstrated. Under these conditions samples of thickness ~1100 nm were grown. These thicker samples demonstrated the formation of two types of domains in terms of strain level within the epitaxial film. High resolution X-ray diffraction (HRXRD) technique and $\mu$-Raman microscopy was used to identify these
domains and the amount and type of strains. These domains were also identified by morphological studies in an atomic force microscope (AFM). AFM and cross-sectional transmission electron microscopy (XTEM) results of the morphology and microstructure of thick and thin samples reveal that the relaxed domains are disc-to-cone-like and embedded in the strained film. Relaxed and strained domains both demonstrated good structural and optical properties. Strained domains have an XRD $\omega$ FWHM value of 1024 arcsec and the relaxed domains have corresponding FWHM 825 arcsec as well as the expected Raman peak shift at 569 cm$^{-1}$. A low-temperature photoluminescence (PL) and a low-temperature BE luminescence peak at 3.48 eV with FWHM of 14 meV, was observed for strained domain and for relaxed domain BE luminescence is at 3.47 eV with FWHM of 10 meV. Relaxed domains demonstrated room-temperature luminescence in by cathodoluminescence (CL).
Chapter 6

Future Work

For the remainder of my PhD research, I plan to further address some items concerning the growth of GaN (0001) films by UHV reactive DC magnetron sputter epitaxy. Growing GaN directly on c-plane sapphire can cause extensive biaxial stress generation due to 16% lattice mismatch and also due to the difference in the coefficients of thermal expansion in GaN epilayer and substrate. This stress in the film can cause generation of defects in the crystal structure and it also will affect the optical and electronic properties of the GaN.

The next step will be to study how to reduce the stresses and improve crystal quality. This will first be done by studying the growth of GaN on all technologically important substrates e.g. Si (111), 4H and 6H SiC, and ZnO by MSE. I will study the in-situ stress evolution during the growth on these substrates. It will also be interesting to learn about the polarity of GaN and which face of GaN will appear after the growth on these substrates by MSE. Use of buffer layers, such as AlN, low temperature GaN or AlInN will also affect the structural properties and also the polarity of the GaN. Therefore I plan also the growth on different buffer layers.

AlInN ternary alloy with the 18% In content has a lattice match to GaN. GaN/AlInN quantum well emission can cover the whole UV spectrum and even the blue domain with improved internal quantum efficiency. One of my originally defined goals for the PhD thesis is to grow GaN/AlInN (In-18%) hetero-structures and study the structural and opto-electronic properties of these structures.
References

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