Magnetron Sputter Epitaxy of GaN
Epilayers and Nanorods

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The Cover Image

The cover image shows, cross-sectional scanning electron microscopy image of GaN Nanorods grown on Si(111) substrate by reactive DC Magnetron Sputter Epitaxy.

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

In this research, electronic-grade GaN(0001) epilayers and nanorods have been grown onto Al$_2$O$_3$(0001) and Si(111) substrates, respectively, by reactive magnetron sputter epitaxy (MSE) using liquid Ga as a sputtering target. MSE, employing ultra high vacuum conditions, high-purity source materials, and low-energy ion assisted deposition from substrate biasing, is a scalable method, lending itself to large area GaN synthesis.

For the growth of epitaxial GaN films two types of sputtering techniques, direct current (DC) magnetron sputtering and high power impulse magnetron sputtering (HiPIMS) were studied. The GaN epitaxial films grown by DC-MSE directly on to Al$_2$O$_3$(0001) in a mixture of Ar and N$_2$, feature low threading dislocation densities on the order of ≤ 10$^{10}$ cm$^{-2}$, as determined by transmission electron microscopy (TEM) and modified Williamson-Hall plots. X-ray rocking curves reveal a narrow full-width at half maximum (FWHM) of 1054 arcsec of the 0002 reflection. A sharp 4 K photoluminescence (PL) peak at 3.474 eV with a FWHM of 6.3 meV is attributed to intrinsic GaN band edge emission. GaN(0001) epitaxial films grown on Al$_2$O$_3$ substrates by HiPIMS deposition in a mixed N$_2$/Ar discharge contain both strained domains and almost relaxed domains in the same epilayers, which was determined by a combination of x-ray diffraction (XRD), TEM, atomic force microscopy (AFM), µ-Raman microscopy, µ-PL, and Cathodoluminescence (CL). The almost fully relaxed domains show superior structural and optical properties evidenced by a rocking curves with full width at half maximum of 885 arc sec and a low temperature band edge luminescence at 3.47 eV with the FWHM of 10 meV. The other domain exhibits a 14 times higher isotropic strain component, which is due to higher densities of point and extended defects, resulting from bombardment of energetic species during growth.

Single-crystal GaN(0001) nanorods have been grown directly on Si(111) substrates by DC-MSE in a pure N$_2$ environment. The as-grown GaN nanorods
exhibit very high crystal quality from bottom to the top without any stacking faults, as determined by TEM. The crystal quality is found to increase with increasing working pressure. XRD results show that all the rods are highly 0001 oriented. All nanorods exhibit an N-polarity, as determined by convergent beam electron diffraction methods. Sharp and well-resolved 4 K µ-PL peaks at ~3.474 eV with a FWHM ranging from 1.7 meV to 22 meV are attributed to the intrinsic GaN band edge emission and corroborate the exceptional crystal quality of the material. Texture measurements reveal that the rods have random in-plane orientation when grown on Si(111) with its native oxide while they have an in-plane epitaxial relationship of GaN[11\bar{2}0] // Si[\bar{1}10] when grown on Si(111) without the surface oxide. The best structural and optical properties of the rods were achieved at N\textsubscript{2} partial pressures of 15 to 20 mTorr. By diluting the reactive N\textsubscript{2} working gas in DC-MSE with Ar, it is possible to achieve favorable growth conditions for high quality GaN nanorods onto Si(111) at a low total pressure of 5 mTorr. With an addition of small amount of Ar (0.5 mTorr), we observe an increase in nanorod aspect ratio from 8 to ~35, a decrease in average diameter from 74 nm to 35 nm, and a 2-fold increase in nanorod density compared to pure N\textsubscript{2} conditions. By further dilution, the aspect ratio continuously decreases to 14 while the diameter increases to 60 nm and the nanorod density increases to a maximum of 2.4×10\textsuperscript{9} cm\textsuperscript{-1}. The changes in nanorod morphology upon Ar-dilution of the N\textsubscript{2} working gas are explained by a transition from N-rich growth conditions, promoting the diffusion induced nanorods growth mode, to Ga-rich growth conditions, in qualitative agreement with GaN nanorods growth by MBE. At N\textsubscript{2} partial pressure of 2.5 mTorr, the Ga-target is close to a non-poisoned state which gives the most perfect crystal quality which is reflected in an exceptionally narrow band edge emission at 3.479 eV with a FWHM of only 1.7 meV. Such structural and optical properties are comparable to rods previously grown at 3 to 4 time higher total working pressures of pure N\textsubscript{2}. 
Populärvetenskaplig Sammanfattning

Denna avhandling behandlar magnetronsputterepitaxi, eller MSE (förkortning av engelskans "Magnetron Sputter Epitaxy"), som en ny metod för att framställa halvledermaterialet galliumnitrid (GaN). Galliumnitrid är ett viktigt material inom modern elektronik där det t.ex. ingår som en grundkomponent i energibesparande vita lysdioder. Ett annat exempel där GaN utnyttjas är för nya typer av transistorer som klarar högre strömmar och spänningar med mindre effektförluster än vad dagens konventionella elektronik klarar.

GaN tillhör en klass av material som heter "grupp III-nitrider" där även materialen aluminiumnitrid och indiumnitrid ingår. För att kunna framställa fungerande elektronikkomponenter måste GaN kombineras med de andra grupp III-nitriderna, oftast som en lagrad struktur där de olika lagren i sin tur består av specifika legeringar mellan de olika grupp III-nitriderna. Varje lager fyller sin speciella funktion i komponenten och kan ofta vara mycket tunna, från några få atomlagers tjocklek och uppåt. GaN är oftast ett av de aktiva lagren där elektroner rör sig med hög hastighet eller där elektrisk energi omvandlas till ljus. För att det ska kunna ske krävs det att GaN-lagret är så perfekt som möjligt, både vad det gäller hur atomerna sitter ordnade i sin kristallstruktur och hur rent från föroreningar det är. Sådana tunna lager benämns ofta episkikt. En annan typ av GaN strukturer som spås ha viktiga tillämpningar i framtids elektronik är så kallade nano-stavar (nanorods) som består av stav-formade kristaller, upp till några µm långa men endas några tiotal nm i diameter. Tack vare sina små dimensioner kan sådana nano-stavar bildas till synes helt utan kristalldefekter och de får även nya fysikaliska egenskaper, dikterade av kvantmekanikens lagar.

De metoder som idag används för att framställa GaN-komponenter bygger på att man låter episkikten bildas på ytan av ett substrat. Metoderna är dock förknippade med vissa svårigheter eller nackdelar. Det renaste och mest perfekta materialet framställs genom en metod som kallas MBE (Molecular Beam Epitaxy) där ångor av rent gallium och atomärt kväve fås att reagera på substratytan för


Efter att de tekniska problemen med att kontrollera plasmat och den flytande Ga-källan lösats har vi lyckats att tillverka GaN-episkikt med MSE, direkt på substrat av safirkristall (Al₂O₃) vid en temperatur av drygt 700 °C. Dessa episkikt skapades genom användandet av ett likströmsplasma. Kvaliteten på episkiten analyserades med hjälp av ett stort antal avancerade materialtekniska analysmetoder, såsom t.ex. högupplöst transmissionselektronmikroskopi (HRTEM), röntgenspridning (XRD), etc., och vi kunde visa att kristallkvaliteten är lika hög som motsvarande episkikt tillverkade med andra metoder. Syntestemperaturen är upp till 300 grader lägre för MSE vilket kan vara en fördel om man vill använda ett känsligt substrat. Experiment med en pulsad MSE-
teknik, så kallad HIPIMS, som ofta är till fördel vid syntes av tunna skikt, visade sig dock generera episkikt innehållande olika områden där GaN-kristallen var olika mycket töjd. Orsaken till detta förklarades av växelverkan mellan det energirika pulsade plasmat som används i HIPIMS och atomerna på ytan av det växande episkiktet. I en speciell studie visade vi att spänningarna i GaN-skikten är kompressiva om temperaturen är över 600 °C samt att spänningen ökar och blir än mer kompressiv med ökande skikttjocklek. Förklaringen tros vara att ytatomerna har hög rörlighet på ytan under tiden skikten växer vilket gör att skikten bildas som 2-dimensionella lager redan från tillväxtens början.


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Preface

The work presented in this doctorate thesis is a result of my PhD studies from 2007 to 2012 in the Thin Film Physics Division at Linköping University. First two and half years were fully dedicated to develop a new sputtering system where liquid Ga target can be sputtered and to achieve a good control on the growth process, I also demonstrated the successful growth of high quality GaN epitaxial layers and nanorods. This project is funded by the Swedish Foundation for Strategic Research via the MS²E and Nano-N programs. The results are presented in five appended papers. The introductory chapters in this thesis are to a large extent based and expanded on my previous published licentiate thesis \(^1\).

Muhammad Junaid
2012-10-03
Linköping

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Signed

Muhammad Junaid
Linköping, 2012-10-04
Included Papers

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

**Paper II**
Two-domain formation during the epitaxial growth of GaN (0001) on c-plane Al₂O₃ (0001) by high power impulse magnetron sputtering

**Paper III**
Stress Evolution during Growth of GaN (0001)/Al₂O₃ (0001) by Reactive DC Magnetron Sputter Epitaxy
M. Junaid, P. Sandström, J. Palisaitis, V. Darakchieva, C.-L. Hsiao, P.O.Å. Persson, L. Hultman and J. Birch, (Submitted), August 2012

**Paper IV**
Liquid-target Reactive Magnetron Sputter Epitaxy of High Quality GaN(0001̅) Nanorods on Si(111)
Paper V
Effects of N$_2$ partial pressure on Growth, Structure, and Optical Properties of GaN Nanorods Grown by Liquid-target Reactive Magnetron Sputter Epitaxy
M. Junaid, Y.-T. Chen, J. Lu, J. Palisaitis, C.-L. Hsiao, P. O. Å. Persson, L. Hultman, and J. Birch (in Manuscript)

My Contributions to the Papers
In all the papers included in this thesis, I planned and performed the growth experiments. I myself used XRD, SEM, and AFM as characterization tools. I analyzed the results and wrote the all the papers.
Related Papers, not Included in the Thesis

Paper VI
Composition tunable Al$_{1-x}$In$_x$N nanorod arrays grown by ultra-high-vacuum magnetron sputter epitaxy
C.-L. Hsiao, J. Palisaitis, M. Junaid, P. O. Å. Persson, J. Jensen, and J. Birch,
Thin Solid Films (Accepted), 2012

Paper VII
Synthesis and characterization of (0001)-textured wurtzite Al(1-x)B(x)N thin films

Paper VIII
Effect of strain on low-loss electron energy loss spectra of group III-nitrides
J. Palisaitis, C.-L. Hsiao, M. Junaid, J. Birch, L. Hultman, and P. O. Å. Persson,

Paper IX
Standard-free composition measurements of Al$_x$ In$_{1-x}$N by low-loss electron energy loss spectroscopy
Paper X
Spontaneous Formation of AlInN Core–Shell Nanorod Arrays by Ultrahigh-Vacuum Magnetron Sputter Epitaxy
Ching-Lien Hsiao, Justinas Palisaitis, Muhammad Junaid, Ruei-San Chen, Per O. Å. Persson, Per Sandström, Per-Olof Holtz, Lars Hultman, and Jens Birch, Appl. Phys. Express, 4, 115002 (2011)

Paper XI
Growth and characterization of thick GaN layers grown by halide vapor phase epitaxy on lattice-matched AlInN templates
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Papers
Introduction

1.1 Background

GaN belongs to the family of semiconductors known as Group III-Nitrides (III-N). Other important semiconductor materials in the same family are InN and AlN. GaN is a direct wide band gap semiconductor material with excellent properties, which makes it suitable for optical [1,2,3], high power [4,5,6], and high frequency devices [7]. By using ternary alloys of group III-N materials, we can tailor the band gap as well as the electrical and optical properties, which can make our world faster and brighter. III-N based devices have applications from solid-state lighting sources to 4th generation wireless communication enabling us to use high speed data trafficking while on the move. Huge research efforts are being made on these materials and their ternary alloys to improve their structural and optical properties. GaN nanostructures, such as nanorods/nanowires [8,9], nanobelts [10], and nanowalls [11] have drawn an interest due to their great prospects in novel nanotechnology applications as well as in fundamental physics during the last decade. A few GaN nanorods based nanoelectronic and optoelectronic devices have been reported [12,13].

The main growth techniques for GaN epitaxial layers and nanorods are chemical vapor deposition (CVD) and molecular beam epitaxy (MBE). Growth of
semiconductor quality, (i.e. with high crystal quality and good optical properties) GaN epilayers and nanorods by the sputter deposition method is yet to be explored. Since the early 80s to date there exists close to 50 reports about the growth of GaN epilayers by magnetron sputtering (except from the presented report), but only two groups have shown evidence of semiconductor quality GaN epilayers and these were made by RF and DC magnetron sputtering in 1991 and 1998, respectively [14,15]. Afterwards, no further exploitation of the sputter deposition technique has been pursued to refine GaN for electronic applications.

The Thin Film Physics Division at Linköping University has a history of exploring new materials and developing sputtering processes for their synthesis. There is also a strong tradition of working with wurtzite structures nitrides, especially with AlN [16], AlInN [17,18], and ScAlN [19,20] epilayers. Recently AlInN based nanostructures like nanorods [21] and nanograss [22] have been grown by sputter deposition technique. This knowledge and experience of sputter growth of nitrides in a UHV system encouraged me to study the growth of GaN epilayers and nanorods and try to revisit and advance the sputtering techniques for semiconductor quality GaN material. The main challenges involved during the sputter growth process of GaN are presented next.

1.2 Research Objectives

For reactive sputter deposition of 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 is liquid and needs to be kept in a horizontal trough, sputtering gas can be trapped in the liquid gallium with bubble bursts in the source as a consequence. The first objective of my research was to overcome these problems and have a full control of the sputtering process. Mastering reactive sputtering from a liquid target can give clear process advantages such as high deposition rate, elimination of target erosion track effects, and a continuous supply of source material.
The second objective is to optimize the growth conditions for semiconductor quality GaN epilayers and nanorods by the sputter deposition method. I have successfully demonstrated that it is possible to grow GaN epitaxial films and nanorods with good structural and optical properties. Papers I, II, and III deal with the growth of GaN epitaxial layers directly onto Al₂O₃ substrates. Papers IV and V explain the growth of GaN nanorods on Si(111) substrates. To determine the structural, chemical, and optical properties different characterization techniques were used. Although the epilayers and nanorods have demonstrated very good properties, there is, however, a lot of room to play with the process and to improve the quality of the material.

1.3 Outline of the Thesis

This thesis is divided into two parts, the first part is the introduction part and the second half is the collection of papers, which are the basis of my research. The introductory part consists of six chapters. In Chapter 2, we will learn briefly about the material of interest in this research, i.e., GaN. Chapter 3 deals with details of magnetron sputter epitaxy and the construction of the growth system. The characterization techniques used to analyze the films are described in Chapter 4. Chapter 5 summarizes all the results, and Chapter 6 presents my contributions to the field.
GaN

2.1 Properties and Applications

GaN can be grown in two different crystal structures, wurtzite (hexagonal) and zincblende (cubic). The wurtzite phase is stable and relatively easy to grow, while zincblende is a meta-stable phase and is difficult to grow. During this work only wurtzite GaN is being studied, so we will only consider the properties of the wurtzite structure. Figure 2.1 shows the unit cell of wurtzite GaN. It has two lattice parameters \(c\) and \(a\) and their values are 5.185 Å and 3.189 Å, respectively [33,23].

![Wurtzite unit cell of GaN](image)

Figure 2.1: Wurtzite unit cell of GaN
Polarity is an inherent property of wurtzite III-Ns. Depending on the growth conditions and type of growth technique GaN wurtzite crystals grown with the c-axis in the growth direction, so called c-plane GaN, can be terminated on top with Ga-atoms or N-atoms known as Ga-face and N-face, respectively (see figure 2.2) [24]. 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 as reported in Paper 1. After the KOH etching, the nitrogen face forms pyramidal shape features on the N-face surface, but the Ga-face, is unaffected. Details of the KOH etching recipe can be found in the reference [25]. The polarity of GaN nanorods can also be determined by the convergent beam electron diffraction (CBED) method [26] which showed that the nanorods exhibit an N-polarity and it is discussed in Paper IV.

![Figure 2.2: Different polarities of c-plane wurtzite GaN crystals, left hand side shows the Ga-face and the right hand side shows the N-face.](image)

Some important properties of GaN utilized in different optical and electrical applications are listed in table 2.1. GaN has a direct wide band gap of 3.4 eV at room temperature, which makes it a suitable material for optical devices. Alloying GaN with other III-N materials AlN and InN, with band gaps of 6.1 eV to 0.7 eV, respectively, makes it possible to tune the band gap from infrared (IR) to
deep ultraviolet (UV) energies (see fig 2.3) [27,28,29]. The band gap engineering offers a lot of applications such as light emitting diodes (LEDs) and laser diodes (LDs) covering the spectral wavelength from IR to UV. In a few years time solid-state lighting devices based on III-N 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 [30].

Table 2.1: Important properties of GaN [31,23]

<table>
<thead>
<tr>
<th>Lattice Parameters [Å]</th>
<th>a = 3.189, c = 5.185</th>
</tr>
</thead>
<tbody>
<tr>
<td>Band gap [eV]</td>
<td>~ 3.4 at 300 K and ~ 3.47 at 4K</td>
</tr>
<tr>
<td>Density [g/cm³]</td>
<td>6.15</td>
</tr>
<tr>
<td>Melting Point [°C]</td>
<td>2500</td>
</tr>
<tr>
<td>Electron Mobility [Vs/cm²]</td>
<td>1400 at 300 K</td>
</tr>
<tr>
<td>Breakdown Voltage [MV/cm]</td>
<td>5 at 300 K</td>
</tr>
<tr>
<td>Thermal Conductivity (Wcm⁻¹K⁻¹)</td>
<td>2.3 at 300K</td>
</tr>
<tr>
<td>Thermal Expansion Coefficient (K⁻¹)</td>
<td>Δa/a = 5.59×10⁻⁶</td>
</tr>
</tbody>
</table>

Figure 2.3: Lattice parameters of III-Ns and their corresponding band gap energies.

GaN also has high breakdown voltage and high electron mobility [31,32,33]. Due to such properties it has attracted much attention in the last two decades. High electron mobility transistors based on GaN material are now commercially available and have applications in power amplifiers in radio frequency modules, and wireless communication applications. GaN based power semiconductor
devices used as switches or rectifiers in power electronic circuits are also available commercially. GaN has a variety of applications which makes it a material of the future.

All the commercially available devices in the market are based on GaN epitaxial layers. There are many potential devices ranging from LEDs, solar-cells, and hydrogen generation [34,35,36] based on GaN nanostructures, proposed and demonstrated at research level, but no such device is available commercially yet.

2.2 Growth Techniques

Each growth technique used for the growth of GaN epilayers and nanostructures has its pros and cons. The most common techniques to grow GaN epilayers and nanorods are chemical vapor deposition (CVD) and molecular beam epitaxy (MBE).

2.2.1 Chemical Vapor Deposition of GaN

In CVD, GaN is grown on the substrate by chemical reactions at close to equilibrium conditions. This method is used for bulk, epitaxial, and nanostructure growth of GaN. Different 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. For GaN growth on the basis of types of precursors CVD can be classified in two types, mainly:

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

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.
2.2.2 Molecular Beam Epitaxy 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 temperatures lower than or near 700 - 800 °C. Effusion cells are used as the Ga source, where Ga is evaporated by heating a crucible. The source of atomic N is more complicated due to the high binding energy of the N₂ molecules. So for producing N atoms either an RF-plasma is used or NH₃ is cracked in an effusion cell at very high temperatures. Growth rates are much lower than the MOVPE or HVPE. Typical growth rates are 0.5-1µm/h, which are suitable for epitaxial growth thanks to the UHV conditions assuring a very high purity level of grown films. High running costs and difficult scalability, however, make it a less favorable method for industrial use.

2.3.3 Magnetron Sputter Epitaxy of GaN

Sputter deposition is also a PVD method. For the growth of GaN epilayers and nanorods, it is not very well explored. Other group III-N epilayers and nanorods grown by the magnetron sputter epitaxy (MSE) method have been reported [17,37]. According to reference [16]:

"Magnetron Sputter Epitaxy is defined as epitaxial growth by magnetron sputter deposition under the same stringent vacuum and sample handling conditions as in practice in MBE”

MSE can employ low-energy (20-30 eV) ion bombardment to enhance adatom mobility allowing for low substrate temperatures. Scalability and technological maturity in industrial applications are major advantages in using sputtering. However, for reactive sputter deposition of electronic-grade GaN, there are difficulties in obtaining stable growth conditions. These are mainly caused by the low melting point (29 °C) of the metallic Ga target and formation of a non-conducting GaN layer on its surface. Liquid-target MSE can give clear process advantages over MBE and solid-target MSE such as high deposition rate, elimination of target erosion effects, and the possibility of a continuous supply of
source material. A disadvantage of using MSE is energetic sputtered species and back-scattered neutrals from the target that can create defects in the growing films.

2.3 Substrates

Bulk substrates with different orientations are now available for the homoepitaxy of GaN, but they have a rather higher cost. As a result, most of the GaN based devices today are grown on foreign substrates. The most common substrates used for heteroepitaxial growth of GaN are Al₂O₃, SiC, and Si [38,39]. Especially for the growth of GaN-based light-emitting diodes, Al₂O₃ substrates are widely employed [39]. During the presented research Al₂O₃ (0001)-oriented substrates were used for the growth of GaN epilayers and Si (111)-oriented substrates were used for the growth of nanorods. Table 2.1 shows the lattice mismatch and the dislocations densities of commercially available GaN epilayers grown on SiC, Al₂O₃, and Si substrates [40].

<table>
<thead>
<tr>
<th>Table 2.1 Bulk GaN vs Foreign Substrates</th>
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<tbody>
<tr>
<td>In-plane Lattice Constant Mismatch</td>
</tr>
<tr>
<td>--------------------------------------</td>
</tr>
<tr>
<td>Dislocation Density (cm⁻²)</td>
</tr>
<tr>
<td>10⁴ – 5 x 10⁶</td>
</tr>
</tbody>
</table>

2.4 Strain and Defects

Stress generation is a major issue in hetroepitaxially grown Group III-N materials. There is mainly biaxial stress due to the lattice mismatch and difference in the thermal expansion coefficients between the substrate and the film. This stress is released by the generation of misfit dislocation in the material. Also, strain induced by point defects, which can be either interstitials and/or vacancies in the material is called the hydrostatic strain. Total strain present in the film is a combine response of biaxial and hydrostatic stresses. In GaN epilayers grown by MSE combination of biaxial and hydrostatic strain was found
as reported in Papers I, II, and III. In sputtered MSE-grown GaN material, point defects can be generated because of the bombardment of energetic species during the growth process as discussed in section 2.4.3 and as well as in the first three papers.

Another common type of dislocations found in GaN [41,42] which we also observed in the present films grown by MSE, are threading dislocations. Threading dislocations are of different types: edge, screw, or mixed threading dislocations. The source of threading dislocation is mainly considered to be the nucleation stage, when small islands of GaN start to form and there is coalescence between the islands, threading dislocations are formed. In our work threading dislocations were not observed in GaN nanorods and the reason for that is the annihilation of the dislocations to the side wall of the nanorods because of the low dimensionality of the structure.

Wurtzite materials should grow with an ABABAB stacking sequence. However, if this sequence is disturbed during growth, stacking faults are generated. Stacking faults were observed in GaN epilayers and nanorods. The presence of strain and defects in the GaN can cause the degradation of electronic and the optical properties of the material.

2.5 GaN Nanorods

Nanorods are two dimensional nano structures and their small cross-sections can accommodate much larger lattice mismatch and thermal expansion difference compared to epilayers. Due to smaller dimensions the defects in the rods are annihilated to the sides of the nanorods [43] and this is the reason of having very high structural and optical quality. Nanorods offer a larger design freedom for the heteroepitaxy of highly lattice-mismatched materials, which is crucial for the integration of high performance III-N semiconductors with Si technology [44].
GaN nanorods are grown either by catalyst driven methods or by catalyst free methods [36]. The most common growth techniques to grow GaN nanorods are MOCVD and MBE. For the growth of catalyst free GaN nanorods mostly MBE is used. Very good structural quality and also very good optical properties, with e.g., a full width at half maximum (FWHM) of band edge (BE) luminescence of 0.3 meV have been reported [45]. In Paper IV and V we have reported the growth of GaN nanorods by DC-MSE yielding nanorods with a FWHM of BE luminescence of nearly 1.7 eV. Such a good optical response of the nanorods demonstrates the potential of DC-MSE technique as a method for the growth of semiconductor quality nanostructures. In Paper IV and V nanorods were also grown on a Si(111) substrates having a thin layer of SiO₂ on top. In Paper IV rods were also grown on a Si(111) substrate after stripping the oxide layer by dipping it in to hydro-fluoric acid (HF), which gave a different morphology. During my research I have successfully grown GaN nanorods also on other substrates e.g., SiN, Si (001), 4H-SiC(0001) and also Ti and Mo metal substrates (1×1 cm² in size) but these results are not reported in this thesis.
Magnetron Sputter Epitaxy of GaN

3.1 Thin Film Growth by Sputter Deposition

3.1.1 Basics

Sputtering is a process of removing the atoms from a material by bombarding it with ions having high kinetic energy. The material exposed to the bombardment of the energetic ions is called the target, which can be solid or liquid. In the presented research a liquid target is used and the details will be discussed later in this chapter.

Ions are used to sputter the material from the target. To produce ions a sputtering gas is introduced into a vacuum chamber, a negative potential is applied to the target and a plasma is generated in the chamber. Positive ions in the plasma are accelerated towards the target material due to the negative potential. As a result of collisions between the ions and the target material, energy is transferred to the target atom. The energy transferred to the target atom by the incident ion is given in the equation 3.1 [46],

\[ E_{\text{transfer}} = \frac{4M_i M_f}{(M_i + M_f)^2}, \quad (3.1) \]
where $M_i$ and $M_t$ represent the masses of the incident ion and the target atom, respectively. If the transferred energy to the target atoms is sufficient enough to overcome the surface binding energy, the atoms of the target may be sputtered away. The number of atoms ejected from the surface per incident particle is called sputtering yield [47]. It is an important measure of the efficiency of the sputtering process. The sputtering process is illustrated in figure 3.1. The interaction of the ions with the target surface not only sputters the atoms but also causes the generation of secondary electrons and reflected neutrals. The striking ions can also be implanted into the target material with or without the ejection of the target atoms. The secondary electrons are repelled away from the target due to the application of a negative potential on the target. These secondary electrons are needed to sustain the discharge since they help the gas ionization process. The sputtered atoms from the target material reach the substrate and form a thin film on the substrate surface.

![Figure 3.1: Illustration of the Sputtering process on the target surface.](image)

Figure 3.2 shows a schematic illustration of the chamber in which the sputtering process occurs. In the present research Ga was used as a sputter target and $N_2$ and Ar were used as the sputter gases. Ar is an inert gas and the sole purpose of using this gas is to sputter the Ga atoms from the target, where $N_2$ is used not only for sputtering the Ga atoms but also for the nitrogen source to form the GaN
on the substrate. Normally the chambers used for sputtering are evacuated and
the purpose of this vacuum is two fold: First, to reduce or remove the impurities
in the chamber, which otherwise may can be incorporated in the film synthesized
in this chamber. Secondly, to increase the mean free path of sputtered species,
this helps to increase the probability of the sputtered species to reach the
substrate.

![Figure 3.2: Illustration of a sputter deposition process in a vacuum chamber.](image)

The mean free path, $\lambda$, tells in average, how far an atom can move between two
collisions. It can be calculated by equation 3.2 [48]:

$$\lambda = \frac{RT}{N_a \pi d^2 P} \text{[m]}, \quad (3.2)$$

where $R$ is the ideal gas constant, $T$ is the temperature, $N_a$ is the Avogadro’s
number, $d$ is the molecular diameter (which is on average $3 \times 10^{-10}$ m), and $P$ is the
pressure in the chamber. For the working pressures during different conditions,
e.g., during the growth of a GaN epilayer at 700 °C and ~5 mTorr pressure, $\lambda$ will
be nearly 13 cm. This distance is larger than that between the target and the
substrate. In case of nanorods growth at 20 mTorr pressure and 1000 °C
temperature, the mean free path reduces to ~5 cm.
3.1.2 Magnetron Sputtering

The ionization process during sputtering can be enhanced by using a magnetic field and this is called magnetron sputtering. A magnetron cathode is basically a target holder inside the sputtering chamber having magnets on the backside of the target. 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.

Figure 3.3: Different types of magnetron effecting the shape of the magnetic field: (a) Unbalanced Type I magnetron with the stronger inner pole and the weaker outer poles, (b) Balanced magnetron with inner and outer poles having the same strength, (c) Unbalanced type II magnetron with stronger outer poles and weaker inner poles.

The net result is that the electrons are trapped near the target until they lose their energy. The electrons that are trapped in this region increase the ionization probability of the gas atoms. A sputtering plasma can therefore be maintained at much lower gas pressures when using a magnetron source. Magnetrons can be classified into three types according to their magnetic field configuration [49] as shown in figure 3.3.

Magnetrons can be classified as;
- Balanced magnetron
- Unbalanced magnetron type I and
- Unbalanced magnetron type II.

In case of balanced magnetron the outer and the inner magnetic poles are equally strong. In unbalanced type I configuration the center pole is stronger than the outer pole and in the type II configuration the outer pole is stronger that the center one.
A 50 mm diameter circular type II magnetron was used during the sputter deposition experiments in my research work. Using a type II magnetron, the magnetic field not only traps the electrons and enhances the ionization close to the target surface but also extends the plasma into the chamber space and towards the substrate as can be seen in figure 3.4. The center pole of the magnetron is small and cannot fully close the magnetic field of the outer ring magnet. Some of the magnetic lines then curve away toward the substrate. Since electrons in a plasma traveling in the same direction as the magnetic field experience no Lorentz force, they can escape along the magnetic field lines toward the substrate, where they can ionize the sputtering gas, and due to charge neutrality requirements they may also be pulling the positive ions along with them. This will increase the ion density in the vicinity of the substrate which can be used to influence the film growth process [49,50].
3.1.3 Reactive Sputtering

Metal films are deposited in the presence of an inert gas. For example, to deposit a thin layer of Ti on a substrate, Ti atoms are sputtered by using Ar gas. In such a case the gas is only used to sputter the atoms from the target. In some cases, a sputtering gas, which chemically reacts with the target atoms and forms a new compound on the substrate surface, is chosen. This type of sputtering is called reactive sputtering [47]. 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 N\textsubscript{2} or pure N\textsubscript{2} was used, where N\textsubscript{2} reacts with the sputtered atoms of Ga. In case of reactive sputtering, a thin compound layer can form on the surface of the target which may reduce the sputtering yield. If the sputtering yield of the compound covered target is dramatically lowered or if the compound forms an insulating layer, the sputtering becomes difficult to maintain, this phenomenon is called target poisoning.

3.1.4 Types of Sputtering

Sputtering techniques can be classified in three types depending on the type of the potential applied on the target (cathode). These types are direct current (DC) sputtering, radio frequency (RF) sputtering and DC pulsed sputtering. The RF sputtering technique is used for insulating targets or when insulating compounds are formed on the target, to avoid charge accumulation on the target. In the present work the following two techniques were used for the growth of GaN epilayers and nanorods.

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

To switch between DC-MSE and HiPIMS techniques, it is only required to change the power supplies. DC-MSE is a simple process and easy to handle. HiPIMS is a promising pulsed technique for improving common magnetron sputtering for thin film deposition [51], since the HiPIMS process generates a highly ionized
plasma with large amount of energetic sputtered material ions \[52\]. These beneficial modifications of the discharge process are due to the increased plasma density, which is 2-3 orders of magnitude higher than standard DC magnetron sputtering plasmas. It results in a decrease of the ionization mean free path from \(~50\) cm for DC magnetron sputtering to \(~1\) cm in the case of HiPIMS \[53,54\] growth. In HiPIMS, however, the growth rates are nearly 2 times lower compared to DC-MSE. Stable growth conditions for both techniques will be discussed later in this chapter.

### 3.1.5 Nucleation and Growth

In a sputtering process, the sputtered species are transported to the substrate in a vapor phase from the target to the substrate. Atoms arriving on the substrate surface are called adatoms. These adatoms diffuse around on the surface depending on their energy and interact with the surface of the substrate or with other adatoms, or they leave the surface by re-evaporation/desorption. The adatoms will eventually form small clusters. These clusters may also be mobile. Clusters are formed and disintegrated continuously, only those reaching a size larger than a critical size will become stable nuclei and continue to grow. During this nucleation stage, stable nuclei are formed until a maximum number density is reached. The density of this primary nucleation decreases with increasing growth temperatures, since the adatom mobility is increased. As the growth process continues these islands start to merge and this stage is called coalescence, and a continuous thin film is formed.

**Growth Modes**

Thin film growth can be classified into three categories \[55\] and are demonstrated in figure 3.5.

1: **Frank-van der Merwe mode:** This growth mode is known as a *layer by layer* growth mode or *2-dimensional (2D)* growth mode. In this case interaction between the adatom and the substrate is stronger than the interaction between the adatoms. Epitaxial semiconductor films are often grown in this fashion.

2: **Volmer-Webber mode:** This growth mode is also called an *Island* or *3-D* growth mode. In this case the interaction between the atoms is stronger than the
interaction with the substrate. For example, metal and semiconductors often grows on oxides in the 3-D growth mode.

**3: Stranski-Krastanov mode:** This growth mode is the combination of 2-D and 3-D growth modes. This growth mode is very common and is observed in metal-metal, and metal-semiconductors systems.

![Figure 3.5: Illustration of different growth modes. a) Represents a layer by layer growth mode, b) represents 2-D growth mode and c) represents Stranski-Krastanov growth mode.](image)

**Epitaxy**

Epitaxy is the process of growing a single crystal onto a single crystal substrate. The word epitaxy is a combination of the two Greek words; *epi* = upon or over and *taxis* = arrangement [56] indicating that the crystallographic orientation of the growing film depends on the substrate. Thus there is a certain epitaxial relationship between an epitaxial film and its substrate.

This can be classified into two categories:

**1: Homo-epitaxy:** If the film material is the same as that of the substrate, the deposition process is called homo-epitaxy, e.g., growing Si on top of a Si substrate.

**2: Hetero-epitaxy:** If the film material is different form substrate, the epitaxial growth is called hetero-epitaxy, e.g., growth of GaN on SiC substrates. In most cases of hetero-epitaxial growth there is a crystal lattice mismatch between the substrate and the film, which may cause strain in the film and may lead to the formation of dislocations in the film.
3.2 Magnetron Sputter Epitaxy of GaN Epilayers and Nanorods

3.2.1 Chamber for Magnetron Sputter Epitaxy of GaN

A UHV growth chamber was used for MSE growth of GaN epilayers and nanorods as shown in figure 3.6-top. The growth chamber is connected to a common load lock and transfer tube system which connects it to another UHV chamber used for the MSE of AlN and Al\textsubscript{1-x}In\textsubscript{x}N. The vacuum system for the growth chamber is shown in the figure 3.7. 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 in the range of $1 \times 10^{-8}$ to $4 \times 10^{-9}$ Torr. To control the pumping speed, a butterfly throttle valve was installed, which was designed and built in-house. Gas flow rates during the sputtering process are controlled by electronic mass flow controllers. For precise measurement of the pressure during the growth process, a capacitance manometer is used.

Very high purity Ga (99.99999% pure) is used as the sputtering target and very high purity process gasses (achieved by using special gas purifiers), Ar (99.999999% pure) and N\textsubscript{2} (99.999999% pure) are used. In the present system a water cooled 50 mm-diameter magnetron is installed and there is also provision of adding two more magnetrons to grow Ga based alloy materials, e.g., AlGaN and InGaN.

The magnetic field configuration of the magnetron lies in the category of type II magnetron as discussed earlier (in section 3.1.2) and this enhances the ionization close to the target surface but also extend the plasma in to the chamber space, towards the substrate. Figure 3.6-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 gives a good surface contact between the bottom surface of the SS trough and the water cooled magnetron Cu surface.
Figure 3.6: Top diagram shows the growth chamber used for MSE of GaN. Bottom diagram shows the enlarged and detailed description the target and water cooled unbalanced magnetron.

Figure 3.7: Vacuum system for the growth chamber used for MSE of Group III-N.
3.2.2 Construction of the Sputtering Target

Due to the low melting point of Ga (29 °C), it will be in liquid phase during sputtering and there is a need to keep the liquid Ga in a trough in a horizontal position to avoid the spilling of liquid Ga inside the chamber. Construction of the Ga target is shown in figure 3.8 (a) and (b). Small Ga pellets are melted to form a uniform thickness target. To solidify the target it was placed on a metallic platform dipped into liquid nitrogen.

![Figure 3.8: a) Ga Pellets inside the stainless steel trough are being heated to melt, b) uniform Ga target after cooling it by using a metallic platform dipped into liquid nitrogen.](image)

3.3 Challenges and Observations

There were many challenges involved during the development of the sputtering system and I observed many interesting things which I will discuss in this section.
Ga has a very high surface tension $735 \times 10^{-5}$ N/cm \[57\] and pure Ga does not wet any surface \[58,59\]. Due to this property the Ga spreads like beads on a surface just like mercury. The Ga surface reacts with oxygen and forms an oxide layer \[60\] which changes wetting capabilities of Ga. Thus the selection of the material to make the trough was challenging. In the literature there is no such data available showing which material Ga wets more. Moreover, the trough material must also be UHV compatible. Three materials, molybdenum, graphite, and stainless steel (SS) were tried. Molybdenum and carbon were selected based on their high surface energies which would facilitate wetting. SS is quite commonly
used in UHV systems and it was reported in the literature [14] to be used as a trough to contain liquid Ga.

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 easily (see figure 3.9a).

2: For both cylindrical-shaped and concave-shaped troughs 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 but does not form beads. Due to shrinkage the perimeters 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 figure 3.9c and 3.10).

4: 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 figure 3.9b, which may cause a virtual leak in the vacuum chamber.

5: The concave shaped SS-crucible shown in the figure 3.9d 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.

Bubble formation is also a major issue when using a Ga liquid target. In the figure 3.11 an event was recorded demonstrating the formation of bubbles, bursting of these bubbles, and Ga wetting of the SS crucible. Figure 3.11a shows the start of the sputtering process in the mixture of Ar and N<sub>2</sub> and the plasma is confined to a limited region and a nice plume of plasma can be observed emerging from the target. In figure 3.11b, an arrow is indicating a bubble, formed just under the surface of the liquid gallium target.
Figure 3.11: Bubble formation and bursting, also the increased wetting of the Ga is shown in this set of pictures.

Figure 3.12: Ga droplets on the substrate and also on the substrate holder due to the spitting of liquid Ga after the bubble burst.
A possible reason of the formation of these bubbles can be the trapping of sputter gas into the liquid. The temperature of the target surface can rise up to few hundred degrees Celsius due to the radiative heat from the substrate 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 surface of the melted target and the water cooled backside 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.

$\text{N}_2$ is used as a reactive gas so 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 figure 3.11c, arrow 1 shows after a bubble burst the Ga wetting of the SS starts to increase and the concave shaped surface of liquid Ga becomes flatter. Reason for this increased wetting is unknown. The arrow 2 indicates a crack formation in the nitrided layer. In figure 3.11e the arrow 1 shows the burst of the bubble and arrow 2 indicates the development of an additional crack in the nitrided layer. The burst of the bubbles causes a lot of splashing of Ga droplets in all directions, some of those Ga droplets can be seen on the ground shield (see fig 3.11f indicated by arrow 2). Figure 3.12 also shows droplets on the substrate and substrate holder after the bubble bursts.

Figure 3.13 shows an interesting observation that was recorded in a sequence at different timings during the growth of GaN epilayers. A floating and rotating nitrided layer on liquid surface of Ga target can be seen in the image which decreases in diameter going from left to right in the image. In the presence of nitrided layer it was difficult to run a stable growth process and the growth rates were very low.
Figure 3.13: A nitrided layer floating on the surface of the liquid target.

Figure 3.14: 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 the cross-sectional TEM view graph after applying the changes.

Figure 3.15: Condition of Ga target after sputtering in pure N$_2$ environment with total pressure varying from 5 to 20 mTorr.
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 figure 3.14. 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 nitrided 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.

For the growth of GaN nanorods, a liquid Ga target was sputtered in a pure nitrogen environment using working pressures ranging from 5 to 20 mTorr (as reported in Paper IV). When sputtering in pure N\(_2\) conditions at very high working pressures like 15 or 20 mTorr, target poisoning is a major issue. For example, it is known to strongly limit the achievable deposition rate. Also a high process pressure leads to gas scattering of the sputtered Ga which in turn, leads to a lower degree of utilization of the source material. The condition of the Ga target after sputtering in pure nitrogen environment at very high pressures can be seen in figure 3.15. After the growth of GaN epilayers the target surface is usually very flat because of the liquid Ga, but in the case of growth in pure N\(_2\) at higher pressures the target surface looks uneven and solid like. The texture of the Ga also changes and it becomes more like a paste. The reason for change in texture can be the mixture of GaN crystallites into the liquid Ga which makes it thick like paste. After sputtering in a pure nitrogen environment target poisoning effects make it impossible to grow GaN epilayers, which requires an Ar/N\(_2\)
mixture, using the same nitrided target. Sputter cleaning of the poisoned liquid Ga target in an inert gas environment is not practically possible as it leads to liquid Ga droplet contamination of the deposition chamber. The solution of this problem is presented in Paper V.
4 Characterization Techniques

4.1 X-ray Diffraction

X-ray diffraction (XRD) is a powerful tool for investigating the crystalline structure of materials. For semiconductor materials, XRD is mainly used to determine the phase, evaluate the crystal quality, determine the composition of alloys, investigate the thickness, amount of strain, and to estimate the defects. [61]

X-rays are electromagnetic radiation of the same nature as light but with much shorter wavelength (usually in 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-rays from the lattice occurs when the Bragg’s Law (equation 4.1) is fulfilled:

\[ n\lambda = 2d\sin\theta \]  \hspace{1cm} (4.1)

where \( \lambda \) is the wavelength of incident X-ray beam, \( d \) is the interplanar spacing, \( \theta \) is the angle of the incidence and \( n \) is the order of the diffraction.
The real space interpretation of the Bragg’s law is based on the concept of constructive interference between X-rays scattered from neighboring crystal planes with spacing, d (See figure 4.1). If the path difference, which is $2d \sin \theta$, equals an integer number of wavelengths, $n \lambda$, then there will be constructive interference and the diffracted intensity will be a maximum in the direction given by the $\theta$.

Lattice planes in the crystal are visualized as a stack of parallel planes, where each plane contains a sheet of lattice points (see figure 4.1). All of the planes are identical and the crystal is created by repeating the sheet of lattice points at a regular interval. The planes are described by the so called Miller indices $(h \ k \ l)$, that are related to the unit cell axes and unit cell dimensions of the crystal. Note the use of parentheses: $(h \ k \ l)$ is used to specify the single plane and; $\{h \ k \ l\}$ is used to specify the set of planes that share the same atomic arrangements and have the same the spacings, but are differently oriented with respect to the crystallographic axes. The use of the brackets; $[h \ k \ l]$ is to specify a unique direction and $<h \ k \ l>$ is used to specify the set of directions that share the same properties.

Three Miller indices, $\{h \ k \ l\}$, to describe the planes in cubic crystals and four Miller indices, $\{h \ k \ i \ l\}$, to describe planes in hexagonal crystals where $i = -(h+k)$. The four Miller indices for hexagonal system are required to conveniently...
describe the six fold symmetry. For example the planes \((1 \bar{1} 2 0)\) and \((2 1 1 0)\) belong to the same set of equivalent planes \(\{1 \bar{1} 2 0\}\), but with three Miller indices they would be written \((1 \bar{1} 0)\) and \((2 1 0)\), respectively, and could mistakenly be thought of as belonging to different sets.

For group III-Ns the interplanar distance of \(\{h k l\}\) planes is related to the lattice parameters \(a\) and \(c\) by equation 4.2

\[
d_{hkl} = \frac{1}{\sqrt{(h^2 + k^2 + l^2) \frac{4}{3a^2} + \frac{t^2}{c^2}}}
\]  

(4.2)

Diffraction experiments yield the information in the so called reciprocal space, which is a Fourier transform of the real space structure of the crystal and outcome is the reciprocal lattice points (RLP) denoted by \(h k l\) where each point represents the set of parallel crystal planes \((h k l)\). The Ewald Sphere construction provides a relation between Bragg’s law and reciprocal space representation of the crystal. [61, 62]. The radius of the Ewald sphere is equal to the wave vector of the incident X-rays, \(|\mathbf{K}| = \frac{2\pi}{\lambda}\), and diffracted beam with wave vector \(\mathbf{K}\), is determined from \(\mathbf{K} = \mathbf{K}_0 + \mathbf{Q}\), where \(\mathbf{Q}\) is the scattering vector, which is normal to the set of planes involved in the scattering event (see figure 4.5). The diffraction conditions are satisfied only if there is a reciprocal lattice point on the Ewald sphere surface at \(Q\). Each set of planes \((h k l)\) with interplanar distance \(d_{hkl}\) can be interrelated with a corresponding reciprocal lattice vector \(\mathbf{Q}\) by equation 4.3.

\[
|\mathbf{Q}| = \frac{2\pi}{d_{hkl}}
\]  

(4.3)

During my research different equipment and experimental setups have been used to determine the different structural properties of the material by using XRD in low resolution and high resolution modes.
Low Resolution Mode:
Overview θ-2θ x-ray diffraction scans were performed with a Philips 1820 Bragg-Brentano diffractometer (experimental setup is shown in the figure 4.2). The purpose of these scans is to quickly determine the crystallinity and phase of the crystal. It is a low resolution method but quick and it is easy to align the sample. An example of such a scan is shown in figure 4.3.

![Figure 4.2: Experimental setup used for θ-2θ measurements](image)

![Figure 4.3: Long range, low resolution θ-2θ scan. In the inset, a HRXRD scan is shown around the 0002 GaN peak and it is clearly seen that the 0002 GaN peak splits into two peaks (from Paper II).](image)
High Resolution Mode:
For high-resolution X-ray diffraction (HRXRD) measurements, a Philips X’Pert MRD diffractometer which is equipped with a graded parabolic X-ray mirror and a channel-cut Ge (220) single-crystal monochromator which produces a highly collimated beam of pure Cu Kα-radiations (λ = 0.15406 nm). The diffracted beam was analyzed using an asymmetric double-bounce Ge(220) crystal collimator. Experimental setup is shown in figure 4.4. Different scan modes are shown in figure 4.5.
Using HRXRD it is possible to resolve much more closely spaced peaks and also to determine the 2θ value with a high precision which can be used to accurately calculate the corresponding lattice parameters. An example of well resolved peaks is shown in the inset of figure 4.3. The FWHM of rocking curves, or ω-scans is a qualitative way to determine the crystal quality of semiconductor materials are also measured by using HRXRD. The narrower the rocking curves the better the crystal quality. The rocking curve of a 0002 peak of a GaN epilayer is shown in figure 4.6.

![Figure 4.6: ω-scan for a 0002 GaN peak](image)

**Reciprocal Space Mapping**

Two dimensional reciprocal space mapping (RSM) was realized by performing consecutive coupled 2θ-ω scans, each with a small difference in ω-value along symmetric and asymmetric directions as shown in figure 4.7. RSMs are therefore presented as diffraction intensity contours in the reciprocal space coordinate system. The shape and distribution of the reciprocal lattice point gives information about in-plane and out-of-plane lattice parameters, crystal quality, strain, relaxation, mosaicity etc. of the epilayers.
High resolution RSM was carried out in symmetric and asymmetric scattering geometries using the GaN 0002 and 1015 reflections, respectively. A typical example of symmetric and asymmetric RSMs of GaN epilayers grown on Al₂O₃ is shown in figure 4.8.
Measuring Threading Dislocation Densities in GaN epilayers

Distortion in the lattice is associated with each type of dislocation; edge dislocations accommodate a lattice twist, screw dislocations accommodate a lattice tilt and mixed dislocations both. These distortions are often approximated by a mosaic model, which assume that the film consists of perfect blocks which are tilted or twisted with respect to each other. Accurate values of lattice tilt and twist can therefore be related to dislocation densities [63].

**Tilt:**

ω-scans of 000l reflections are used to measure the lattice tilt from mixed or screw dislocations. Edge dislocations do not distort these (000l) planes as their Burgers vectors lie within the planes [63, 64].

**Twist:**

Twist is caused by the edge and mixed dislocations and is usually measured with ω-scans of off specular reflections. There are different ways to measure the twist by XRD but in the presented research we used the asymmetric ω-scan measurements [63, 65].

From Williamson Hall plot analysis using the 0002, 0004, and 0006 symmetric reflections, we have extracted the value of tilt angle and lateral coherence length and the screw threading dislocation density was calculated by using the obtained tilt angle according to the method described by Metzger et al. [64]. The density of edge threading dislocations was calculated by using the twist angle, from the method described in reference 64. The value of the twist angle was estimated by using the broadenings of the 0002, 101, 1013, 1014 and 3032 rocking curves, plotting their full width at half maxima (FWHM) vs. inclination angle ψ and fitting the data using the model proposed by Srikant et al. [65].
**Pole Figure Measurements**

Pole figure measurements were used to determine the in-plane orientation of the GaN nanorods. A PANalytical Empyrean system equipped with a 4-axis cradle, a capillary X-ray lens as the primary optics, and a parallel plate collimator as the secondary optics was used for the pole-figure measurements. For the pole-figure measurements, $2\theta$ was fixed to probe the orientations of the corresponding plane spacing $\{h k i l\}$ in the sample by rotating the sample (along $\phi$ and $\psi$) while the intensity was monitored. This gives a 3-dimensional map of the orientations of the scattered intensity, i.e., the orientation of the measured planes $\{h k i l\}$. The measurements were performed for the GaN(10$\bar{1}$5)-plane spacing with the fixed $2\theta$ angle of $\sim 105.3^\circ$, $0^\circ \leq \phi \leq 360^\circ$ and $0^\circ \leq \psi \leq 85^\circ$ with step sizes of $5^\circ$.

![Figure 4.9: 10$\bar{1}$5 Pole-figure measurements of GaN nanorods grown on Si(111) substrate (from Paper V).](image)

A representative $\{10\bar{1}5\}$ pole-figure from GaN nanorods grown on Si(111) is shown in figure 4.9 and it reveals a ring of higher intensity at $\psi \sim 20^\circ$, corresponding to an azimuthally random orientation of the $(10\bar{1}5)$ planes, i.e. the nanorods are grown with a so called (0001) fiber texture. Three reflections are
also visible at ψ ~35°, separated by ~120° in φ, which corresponds to \{440\} for Si, showing its three-fold symmetry.

### 4.2 Atomic Force Microscopy

To study the surface topography of the different materials atomic force microscope (AFM) is a very common technique. AFM has become a universal tool in material research, especially in nanotechnology [66]. Other than surface morphology, AFM can also be used to measure the electrical, magnetic, and mechanical properties [67].

A sharp tip, several microns long (~100 to 200 µm), is located at the free end of a cantilever. The inter-atomic forces between the tip and sample surface atoms cause the cantilever to deflect. The cantilever displacement is then measured by a deflection sensor. The surface topography can then be mapped while the tip is scanned over the sample. There are two primary modes of operation for AFM under ambient conditions: contact mode and tapping mode. In contact mode, the AFM tip is in physical contact with the sample all the time during the scan and is subjected to repulsive forces. The tip-sample interaction causes the cantilever to bend whenever its encounters changes in surface topography. This method is preferred for atomically flat surfaces that cannot be easily damaged. A more commonly used scan mode is tapping mode, where the tip is in intermediate contact with the surface. In this case, the cantilever is oscillated at its resonance frequency, and the tip ‘taps’ the surface during scanning, where the amplitude of tip oscillation is used as the feedback signal. The resolution of this mode may be slightly lower than for contact mode, but it significantly prevents sample damage.

During my research I operated the AFM under tapping mode to investigate the surface morphology of GaN epilayers and these results are used in **Paper II** and **Paper III**. An example of an AFM image is shown in figure 4.10, which is a 3D image of a surface of GaN epilayer grown by HiPIMS.
4.3 Photoluminescence

To measure the optical properties of semiconductor materials, photoluminescence (PL) technique is used quite often. It is a nondestructive method and it also does not require any sample preparation. Information about band gap, excitonic states, involved impurities, effect of externally applied electric or magnetic field can be obtained from PL [68]. If we want to focus on a particular area or to study the optical response from a particular region, we can use micro-PL (µ-PL) where a micrometer sized laser beam is focused on the sample. With µ-PL a spatial resolution of ~1 µm can be achieved [69]. In the present work low temperature (at 4K) and room temperature µ-PL was used to measure the optical properties of both epilayers and nanorods. The details about the experimental setup can be found in references 70 and 71. At room temperature, PL emission is thermally broadened. As the temperature is lowered, features tend to become sharper, and PL is often stronger due to fewer nonradiative centers [72].
Figure 4.11: Low temperature (4K) µ-PL spectrum from GaN pillars and film (from Paper II).

Figure 4.10 shows GaN epilayer that contains two different regions. One is like pillars and the other is the surrounding plane areas. The optical responses from these two areas were recorded by using 4K µ-PL and figure 4.11 shows the PL spectra. Sharp peaks around ~3.47 eV represents the band edge luminescence from GaN. The FWHM of the PL peaks also represents the crystal quality, qualitatively. The better the crystal quality better will be the FWHM of the luminescence.

### 4.4 In-situ Stress Measurement

In Paper-III, to measure the real time stress evolution during growth, *in-situ* curvature measurement based on the laser deflection method was used. For this purpose a multi beam optical stress measurement system was used. A schematic diagram is shown in the figure 4.12. Multiple beams of a laser are shined on the sample and the reflection is recorded by a charged coupled camera (CCD). A pattern of spots appear on the CCD. The distance between the spots changes as the curvature in the substrates changes.
Figure 4.12: Multiple laser beam setup for the in-situ stress measurement during the growth of GaN directly on sapphire.

The change in radius can be measured by using the equation 4.4 [73].

\[
\frac{1}{R} = -\frac{\Delta D}{D_o} \cos \alpha \frac{\cos \alpha}{2L},
\]  

(4.4)

where \( R \) is the radius of the curvature, \( D_o \) is the distance between the spots before growth, \( \Delta D \) is the change in the distance between the spots at any instant, \( L \) is the distance between the sample and the mirror and \( \alpha \) is the angle between the incident and reflected laser beam with the surface normal to the sample.

This system is sensitive to the small changes and it is very fast and vibration insensitive. We can measure the radius of nearly \( 6 \times 10^3 \) m. However, it requires very thin substrate to yield good data, free of noise. Usually the substrate thickness is > 300 micrometer and it is difficult to see the effect of the curvature change which gives noisy data. To see a prominent effect of the curvature changes, special ~100 micrometer thick \( \text{Al}_2\text{O}_3 \) substrates were used.

The relationship between the curvature \( R \) and the stress-thickness product of the film is given by Stoney’s equation (see equation 4.5) [74,75].
where $M_s$ is the biaxial modulus of the substrate, $t_s$ is the thickness of the substrate and $t_f$ is the thickness of the film.

### 4.5 Transmission Electron Microscopy

Transmission electron microscopy (TEM) is an important analytical and imaging tool used commonly in material science and also for life science studies. Information about crystal structure, chemical composition/elemental distribution at nanometer scale, crystal orientations, epitaxial relationships and defects in thin film can be obtained by TEM using different configuration [76].

In TEM electrons are generated and accelerated by using an electron gun. A beam of highly energetic electrons is focused on the sample by using a set of condenser lenses. The electron beam is transmitted through a thin specimen having a thickness of < 200 nm. The transmitted scattered electrons are then projected on a screen by using a combination of objective, intermediate and projection lenses. The advantage of using a beam of highly energetic electrons is to get atomic resolution. For example, using 200 kV microscope (named Galadriel) gives electrons having a wavelength of 2.5 pm. Due to lens imperfections a resolution of ~ 1.4 Å is finally achieved. Using our latest 300 kV TEM (named Arwen), the beam of electron have a wavelength of 1.97 pm and a resolution of 60 pm is achievable. In figure 4.13 low magnification cross-sectional TEM (XTEM) micrograph is shown. It shows a ~500 nm thick GaN film directly grown on Al$_2$O$_3$ substrate with threading dislocations.
Figure 4.13: XTEM micrograph and selected area electron diffraction pattern of film and substrate (from Paper I). In the SAED pattern, indices in italic font represent the film and non-italic fonts represent the substrate. The zone axis is [1120] in the GaN crystal.

From the diffraction patterns, information regarding crystallinity of the material, orientation of the crystal and epitaxial relationship between the substrate and film is obtained. In the inset of figure 4.13, the diffraction pattern from both substrate and film is shown which gives an epitaxial relationship between the film and the substrate.

Two basic ways to form contrast in an image are bright field (BF) imaging and dark field (DF) imaging. In an image, contrast is a variation in intensities in adjacent areas. Basic ray diagram is shown in figure 4.14 illustrating the formation of BF and DF image. In BF imaging the direct beam is allowed to pass through and the diffracted beam paths are blocked while in DF imaging the direct beam is blocked and diffracted beams are allowed to pass. In BF imaging thicker regions and/or regions with high atomic number will appear dark and thin areas and/or regions with small atomic number will appear bright and vice versa in case of DF imaging. In the present work both kind of imaging modes are used and examples can be found in Paper I and II.
Figure 4.14: Ray diagram to illustrate the formation of bright field and dark field images.

Figure 4.15: Cross-sectional HRTEM image showing the interface between the GaN nanorods and the Si(111) substrate with native oxide layer, grown at 5 mTorr pressure in N$_2$/Ar mix environment (image from Paper V). Arrows indicate the stacking faults in the nanorods.

In high resolution TEM (HRTEM) mode lattice resolved imaging of the material is possible. From lattice resolved images it is possible to get detailed information regarding the crystal structure, interfaces between the substrate and the film, and crystal defects such as dislocations in the crystal. Figure 4.15 shows HRTEM
image of GaN nanorods close to interface between the nanorods and the Si(111) substrate with presence of native oxide on the surface. Arrows in the figure indicate the stacking faults in nanorods.

Figure 4.16: HAADF-STEM image is shown in (a) and STEM-EDX elemental map in the box for Ga, Si and N is shown in (b)

When the electrons interact with the material, characteristic X-rays are produced which are used as fingerprints to identify the elements in the material. To detect these X-rays an energy dispersive X-ray spectrometer (EDX) is used. To get the elemental distribution at nanometer scale scanning transmission electron microscopy (STEM) is used. The difference between TEM and STEM modes is that the spot size of the electron beam ≤ 1 nm in the STEM mode and the beam is scanned over the selected area. A High-Angle Annular Dark Field (HAADF) detector is used as detector for imaging in STEM mode which gives the contrast due to atomic mass variations. Figure 4.16(a) shows the STEM-HAADF image of the GaN nanorods grown on a Si substrate without native oxide layer. Figure 4.16(b) shows the EDX map of elemental distribution of Ga, N and Si in the scanned area in STEM mode.
4.6 Elastic Recoil Detection Analysis

Elastic recoil detection analysis (ERDA) is used to determine the composition and distribution of different elements along the thickness in the thin films. Highly energetic accelerated ions hit the sample, recoiled target ions come out and their energies are detected. It is very useful to determine the amount of the light elements e.g., oxygen, hydrogen, etc., in the film. Using 40 MeV iodine ions a depth of ~1 µm of the film can be probed by this technique [77]. 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$^{+}$ 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 [78,79]. This technique was used in Paper I and Paper II to determine the stoichiometry of the GaN and presence of C and O in the films and figure 4.17 is an example of ERDA results.

Figure 4.17: Elemental depth profile of a ~200nm thick GaN film obtained by ToF-ERDA (from Paper I).
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.

Figure 4.18: (a) In the inset the optical image from the GaN film grown by HiPIMS is shown (from Paper II). Area in the square box is the area of interest showing two different domains. µ-Raman spectra from two different domains indicated by the arrows. (b) Two µ-Raman maps over the same area using the wave numbers indicated in the spectra.
This technique uses monochromatic light sources, usually lasers, and when this radiation interacts with a material, it scatters elastically. The frequency of the scattered radiation shifts up or down compared to the original radiation frequency. This shift provides information about the material properties, e.g., composition, stress/strain, crystal symmetry, and orientation, quality of the crystal, and the amount of the material (thickness) [80]. To characterize the spatial distribution of strained material, Micro-Raman (µ-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 references 81 and 82. Figure 4.18 (a) shows the µ-Raman spectra from two different regions of the GaN film grown by HiPIMS and figure 18(b) shows the spatial distribution of two differently strained domains corresponding to the two µ-Raman-shift maps of 569 cm⁻¹ and 570.6 cm⁻¹ wavenumbers.

4.8 Scanning Electron Microscopy / Cathodoluminescence

When an electron beam interacts with a material, different radiations are produced, e.g., X-rays, Auger electrons, Secondary electrons, Cathodoluminescence (CL), etc., by detecting these radiations by their relevant detectors, a lot of information about the irradiated sample can be obtained, e.g., microstructure of the sample, surface morphology, composition, and optical properties of the materials [83]. In a scanning electron microscope (SEM), secondary electrons are used to produce the images. In this work, SEM was used quite extensively to study the cross-sectional and top-view of GaN nanorods and an example is shown in figure 4.19.
Figure 4.19: SEM micrographs showing cross-sectional (on left) and top-overview (on right) from GaN nanorods grown on a HF dipped Si(111) substrate at 15 mTorr pressure (from Paper IV).

Figure 4.20: a) Room temperature CL spectrum showing the band edge (BE) luminescence and b) Room temperature CL image from GaN films containing different domains, grown by HiPMS.
In CL energetic electrons produce electromagnetic radiation in the infrared to ultraviolet range. Using CL, information about band gap of semiconductor materials is obtained. It also helps in identifying different areas in the samples with different optical properties, by CL imaging [84]. In this work a LEO field emission scanning electron microscope (FEG-SEM) is equipped with an Oxford Research Instrument CL spectrometer. Monochromatic wavelength spectra were collected with UV light gratings. The experimental details can be found in reference [85]. Typical room temperature CL spectrum and a CL mapped image from the GaN films grown by HiPIMS with different domains are shown in figure 4.20.
Summary of the Results

5.1 GaN Epilayers

In the beginning of the project two growth techniques DC-MSE and HIPIMS were implemented to grow GaN epilayers. Paper I deals with the growth of GaN epilayers by reactive DC-MSE. In this paper we reported the growth of high quality GaN (0001) epilayers directly onto Al₂O₃ (0001) substrates by using a liquid Ga sputtering target in an Ar/N₂ atmosphere at a moderate temperature of 700 °C. The as-grown GaN epitaxial films exhibit low threading dislocation density on the order of ≤ 10¹⁰ cm⁻² determined by transmission electron microscopy and the modified Williamson-Hall plot technique. X-ray rocking curve of the best sample 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 material is considered having excellent structural and optical properties as it is grown on without any buffer layer of AlN or low-temperature GaN nucleation layer, which is usually the case by other methods. This result shows that MSE is a suitable method for large scale production of electronic grade GaN epilayers onto very large substrates thanks to the scalability of magnetron sputtering.

In Paper II GaN (0001) epitaxial layers were grown by a reactive MSE process using HiPIMS, directly onto Al₂O₃ substrates. Micrometer thick films, however,
consist predominantly of compressively-strained domains that surround disc-shaped almost fully relaxed domains. The more strained domains are explained by highly energetic ion bombardment as a consequence of high power pulses used during deposition, causing a high point defect density, while the less strained domains form due to relaxation through a point defect diffusion process during the growth. The two domain types have good structural and optical properties which are reflected in the XRD, μ-Raman, μ-PL, and CL data. The more strained domains have an XRD ω-FWHM value of 1024 arcsec and a low temperature band edge luminescence peak at 3.48 eV, and the less strained domains have a corresponding ω-FWHM of 825 arcsec and luminescence at 3.47 eV as well as an expected Raman peak shift at 569.9 cm$^{-1}$ which corresponds to the measured strain level. Also, room temperature luminescence from the relaxed domains is demonstrated by μ-PL and CL imaging. This study shows that high power impulse magnetron sputter epitaxy has a potential to grow high quality relaxed epitaxial GaN films directly on sapphire provided that the mechanisms for the creation and diffusion of the point defects can be understood and controlled.

We have studied in Paper III, the real time stress evolution during DC-MSE growth of GaN (0001) epilayers at different growth temperatures, directly onto Al$_2$O$_3$(0001) substrates, by using an in-situ curvature measurement method. We establish a correlation between the growth mode and growth stress evolution in MSE epitaxial films and we demonstrate that in the case of MSE a layer-by-layer growth can be achieved at lower temperatures compared to MOCVD, specifically 700 °C and 800 °C. This is a direct consequence of the higher adatom mobility in MSE. We further show that for the MSE epitaxial films grown in a layer-by-layer mode, a compressive stress evolution occurs during the growth. These GaN films also exhibit better structural properties with lower mosaicity, lower threading dislocation densities and smoother surface morphologies, compared to GaN epilayers grown directly onto sapphire by MOCVD. In contrast, when the films are grown at yet lower temperatures, i.e., 600 °C, a lower adatom mobility leads to a 3D growth mode, which results in tensile stress, high dislocation densities,
and inhomogeneous strain distribution over the film thickness similar to the case of CVD-growth.

5.2 GaN Nanorods

**Paper IV** and **V** are about the growth of GaN nanorods by the DC-MSE technique under different growth conditions i.e., with different total working pressures in pure N₂ or N₂/Ar mix environments.

In **Paper IV** we reported the growth of single-crystal GaN nanorods directly onto Si(111) substrates by reactive DC-MSE in pure N₂ atmosphere at different total working pressures ranging from 5 to 20 mTorr. Aspect ratio (length/diameter) of nanorods seem to increase linearly with increasing working pressure and aspect ratio values of 8 and 35 are found for 5 and 20 mTorr pressures, respectively. X-ray diffraction results show that all the rods are highly (0001)-oriented. The nanorods exhibit an N-polarity, as determined by convergent beam electron diffraction methods. The as-grown GaN nanorods exhibit very good crystal quality from bottom to top without stacking faults, as determined by transmission electron microscopy. The crystal quality is found to increase with increasing working pressure. Sharp and well-resolved 4 K photoluminescence peaks at ~3.474 eV with a FWHM ranging from 1.7 meV to 35 meV are attributed to the intrinsic GaN band edge emission and corroborate the superior structural properties of the material. Texture measurements reveal that the rods have a random in-plane orientation when grown on Si(111) with its native oxide, while they have a definite in-plane epitaxial relationship of GaN[1120] // Si[110] when grown on substrates without surface oxide.

In **Paper V** we report the growth of GaN nanorods on Si(111) substrates at a low working pressure of 5 mTorr. By diluting the reactive N₂ working gas in DC-MSE with Ar, it is possible to achieve favorable growth conditions for high quality GaN nanorods onto Si(111) at a low total pressure of 5 mTorr. This total working pressure is 4 times less than previously reported for growth in pure N₂.
environment, which will allow for better purity of the as-grown nanorods thanks to a lower probability of contamination from residual gases. A process window in terms of Ar partial pressures is found ranging from $P_{Ar} = 0.5$ mTorr to 2.5 mTorr, where GaN nanorods are formed. The highest aspect ratio was achieved for $P_{Ar} = 0.5$ mTorr while the best optical properties were achieved at $P_{Ar} = 2.5$ mTorr. For lower $N_2$ pressure, a continuous film was achieved. The changes in Nanorod morphology upon Ar-dilution of the $N_2$ working gas are explained by increased nucleation density in combination with a transition from N-rich growth conditions, promoting narrower rods, to Ga-rich growth conditions which favors GaN layer formation. At $P_{N_2} = 2.5$ mTorr, the Ga-target is close to a non-poisoned state which in this case gives the most perfect crystal quality. This is reflected in an exceptionally narrow BE emissions at 3.479 eV with a FWHM of only 1.7 meV. Such structural and optical properties are comparable to rods as reported in Paper IV, grown at 3 to 4 times higher total working pressures of pure $N_2$. 

Contributions to the Field

♦ I have pioneered and developed the magnetron sputter epitaxy for use of liquid source materials. Sputtering from a liquid target is really a unique and exciting feature of this project. Before this study nobody has ever describe in detail the sputtering from a Ga liquid target. Finding the right shape and material for crucible containing the liquid Ga is also an important contribution. I have also shown that the importance of having pure growth conditions in order to achieve a stable growth process without formation of bubbles in liquid target and without formation of thick nitrided layer on the target surface.

♦ I have pioneered the growth of electronic-grade GaN epilayers directly on the sapphire substrates with very good structural and optical properties using DC-MSE. (Paper I)

♦ I have studied the real time stress evolution during growth of GaN by DC-MSE at different growth temperatures and tried to explain it on the basis of different growth modes. (Paper III)

♦ I have shown for the first time the possibility of growth of a semiconductor material using a newly emerging sputtering method called HiPIMS. (Paper II)

♦ I have developed another dimension and strength of DC-MSE by successfully demonstrating the growth of semiconductor quality GaN nanorods on technologically important substrate Si. (Paper IV and V)
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