ABSTRACT

HOSALLI MUKUND, AADHITHYA. InGaN/GaN Multiple Quantum Well Light-Emitting Diodes grown on Polar, Semi-polar and Non-Polar Orientations. (Under the direction of Dr. Salah Bedair and Dr. Nadia El-Masry).

Cost effective solid-state lighting (SSL) is gaining much attention in recent years. As a result, there has been a great demand for high efficiency light emitting diodes (LEDs). InGaN/GaN multiple quantum well (MQW) based light-emitting diodes (LEDs) emitting in the blue/green region have emerged as promising candidates in realizing the next-generation SSL technology. InGaN/GaN quantum well structures for optoelectronic devices are conventionally grown on the c-plane (polar plane) which has a large polarization field. This large field within the quantum well structures results in a low rate of radiative recombination. This polarization issue is also partly responsible for the “green gap” or the poor external quantum efficiency observed for LEDs emitting in the green region of the visible spectrum and beyond. The alternative to this polarization issue is to grow on semi-polar orientations with a reduced field relative to the c-plane or on non-polar orientations which has zero polarization field. In this dissertation, alternative approaches to grow on semi-polar and non-polar orientations are explored. The first of these approaches explores the possibility of growing on the facets of GaN nanowires that are oriented along desirable orientations from the perspective of polarization. A “proof of concept” LED structure, that has embedded voids, is overgrown on GaN nanowires. Three times improvement in the light-output power is observed for the LED overgrown on GaN nanowires relative to the conventional c-plane LED. The higher light-output power is attributed primarily to reduced piezo-electric fields and improved light extraction as a result of wave-guiding by the embedded voids. The second of these approaches explores the growth of MQW LEDs on semi-polar and non-polar
bulk GaN substrates. A modified growth approach is used for incorporating higher amounts of indium to enable green-emitting MQWs. The challenges with these bulk GaN substrates and the effect of varying polarization fields on the different crystal orientations is discussed. Lastly, an approach to explore the possibility of an N-polar LED is demonstrated. The use of a polarity inverting layer for achieving p-GaN films on N-polar GaN is discussed. This technique is then incorporated to achieve a N-polar LED that has its MQWs grown on N-polar GaN, which is more advantageous for indium incorporation.
InGaN/GaN Multiple Quantum Well Light-Emitting Diodes grown on Polar, Semi-polar and Non-Polar Orientations

by
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A dissertation submitted to the Graduate Faculty of North Carolina State University in partial fulfillment of the requirements for the degree of Doctor of Philosophy

Electrical Engineering

Raleigh, North Carolina

2014

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DEDICATION

Dedicated to a unique human trait – the thirst for knowledge that is motivated by innocent curiosity coupled with a desire to help society.

I sincerely hope this trait is cherished and nurtured further over future generations
BIOGRAPHY

Aadhithya Hosalli Mukund was born at Madras (now known as Chennai), Tamil Nadu, India on the 15th of March, 1985. After a couple of years in the beautiful western ghats of Khopoli and then about six months of play school at Madras, he went on to do his schooling, first at Bombay (now known as Mumbai), then continued to Dammam (in Saudi Arabia) and finally at Bangalore. He then pursued a bachelors degree in electrical and electronics engineering from National Institute of Technology, Karnataka at Surathkal, India for 4 memorable years during 2003 to 2007. After working for a year at Airvana Networks in Bangalore, India, he decided to pursue his graduate studies in the USA. He joined North Carolina State University, Raleigh, NC in August 2008 for a Master of Science degree in Electrical Engineering. After a 2009 summer stint at Kyma Technologies, Raleigh, he was strongly motivated to pursue his graduate studies in the area of wide band-gap semiconductors and joined the research group of Dr. Bedair and Dr. El-Masry in Oct, 2009. He started working towards his Ph.D program in January 2010.
ACKNOWLEDGMENTS

I would like to begin by thanking the following people: Dr. Bedair and Dr. El-Masry, who became parents to me, in a home away from home, and who mentored me to become a more confident and toughened individual, better equipped to take on the real world. I would like to thank them for providing me an opportunity to learn from a diverse team in a very conducive atmosphere. I would like to thank Dr. Bedair for being a constant source and spark for ideas and for demanding that I strive to better myself. To Dr. El-Masry, I am indebted to her patient assistance and mentoring she provided in the lab during difficult times.

To Pavel Frajtag, my senior in the lab, my many thanks for being an enthusiastic and tough teacher and for laying a lot of foundation work that my dissertation was built on. To Dennis and Deon, for putting up with me in the lab, for helping fight through difficult days in the lab, and for being of great assistance for a significant portion of my dissertation. To Geoff, for teaching me fabrication in the cleanroom, and also assisting in a lot of the fabrication work throughout my dissertation. To Josh, Zach, Jeff – the RB II guys – who were ever-ready to lend a helping hand.

I would like to thank Dr. Tania Paskova, for being a great mentor and advising me on how to move my research ahead, and especially for being of great assistance during the bulk GaN project. I would like to thank Dr. Neeraj Nepal, who I interacted with for just a couple of months, but did learn a lot from. To Dr. Colter, I owe a great deal. He was my go-to man for any troubleshooting or queries regarding any equipment in the lab and for also for being a storehouse of information on practically anything, be it semiconductors or history.
I thank Dr. Leda Lunardi and Dr. Mehmet Ozturk for serving on my Ph.D committee and for providing valuable feedback. I would like to thank Kyma Technologies for initiating in me, an interest in Gallium Nitride, during my internship there, and for collaborating with our group on the bulk GaN project. I would like to thank Dr. Henry Everitt and his team from the US Army Research at Redstone Arsenal, AL for their collaboration. I would like to thank Dr. Jian Xu and his group at Penn State for their collaboration. I would also like to Dr. Albena Ivanisevic and her team for collaborating with our lab.

Lastly, there are a number of friends and family who deserve recognition. My PhD tenure would not be so enjoyable without my long conversations on anything under the sun with Suresh, Arunesh, Namita, Abhijeet. To my many room-mates over the course of 5 years, thanks to all your wonderful cooking skills and your great company, which enabled me overcome my frustrations in the lab. I would also like to acknowledge some friends, prior to joining graduate school, whose advice and conversations have influenced me in some way or the other to becoming who I am today – Jinadutt, Niket, Mahesh, Shravan, Srinivas.

Most importantly, to my parents and brother – who have been the strongest pillar of support throughout my life. From my mom, I have learnt patience, hardwork and generosity of heart. From my dad, I have learnt to strive for perfection and the importance of discipline. To my brother, I owe it to him for being my best friend and confidante and for being my most cherishable punching bag.
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CHAPTER 1: INTRODUCTION

1.1. DISSERTATION – MOTIVATION AND ORGANIZATION

The main motivation for this dissertation work is to explore approaches to reduce or eliminate polarization effects within indium gallium nitride (InGaN) quantum wells of nitride light emitting diode (LED) structures. Additionally, we will also investigate the effect of crystal polarity on InGaN multiple quantum well (MQW) LEDs.

The introductory chapter below gives an overview of gallium nitride (GaN) LEDs and the future outlook for the solid state lighting industry. The fundamentals of polarization in the nitride material system as well as its effects on nitride LED structures are discussed. Chapter 2 discusses the metal-organic chemical vapor deposition method, which is the main growth technique used for the dissertation work. It also briefly explains some of the characterization techniques that are employed over the course of the dissertation and discusses device fabrication with respect to nitride LED structures.

The first approach that is explored is for the growth of a novel LED geometry on GaN nanowires (NWs). GaN nanowire surfaces provide an opportunity to grow the active region (light emitting layer) on planes other than the conventional polar c-plane and consequently the approach results in a unique geometry of embedded voids within the LED structure. Chapter 3 first reviews the challenges faced by the scientific community while growing LEDs on GaN nanostructures. It then focuses on the growth mechanism of this specific LED structure and the device fabrication. In addition, thick planar GaN layers are overgrown on
the GaN NWs by a similar growth mechanism and properties of these overgrown GaN layers are characterized and discussed. Chapter 4 first discusses certain concepts of internal quantum efficiency and the extraction efficiency for LEDs in general. The novel LED geometry overgrown earlier is then characterized. The results are analyzed in comparison with a conventional LED. The contribution of each of the salient features of this unique LED towards its performance is discussed. Some finite difference time domain simulation work is discussed in the end to study the light extraction from within this specific LED geometry.

The second of the approaches is to grow LEDs on semi-polar and non-polar bulk GaN substrates with a goal of achieving very green emission. Chapter 5 discusses growth reactor modifications and growth optimizations for growing on the bulk GaN substrates and achieving higher indium incorporation within the quantum wells. The quantum well structures as well as the LEDs are characterized and a comparative study of the various crystal planes is performed as a consequence of the characterization results.

Finally, LED structures grown on N-polarity GaN are explored. The growth of p-type on N-polar GaN is challenging and so a polarity inversion layer is introduced into the LED structure. Chapter 6 gives an overview of the nitrogen polarity and discusses the advantages of growing on surfaces with this polarity. The effect of this inversion layer for both the p-type layer as well as for the LED structures is studied experimentally.
1.2. GALLIUM NITRIDE – AN OVERVIEW

1.2.1. GALLIUM NITRIDE – PROPERTIES

Gallium nitride (GaN), has today, become a very widely used semiconductor in various fields. It is already taking over the billion dollar solid state lighting market and could soon revolutionize the power sector industry as well. This III-V wide bandgap semiconductor has a host of properties like direct band-gap, chemically and mechanically robust, high thermal conductivity, high breakdown voltage etc. which make this an ideal material for many applications. In addition, considerable progress in the growth of ternary nitride alloys (InGaN, AlGaN) and quaternary alloys (AlInGaN) allow for great flexibility in tuning the bandgap and other properties. Figure 1-1 shows the bandgap and lattice constant range for the nitride material system. It can be seen that the variation from 0.7 eV to about 6.2 eV (which covers the visible, ultraviolet (UV) and some of the infrared (IR) regime) for the nitride material system is much larger than other material systems like arsenides and II-VI compounds.
1.2.2. GALLIUM NITRIDE - HISTORY

The earliest work on GaN was begun by Maruska and Tietjen, who first achieved the growth of single crystal GaN growth on sapphire by hydride vapor phase epitaxy (HVPE) method in 1969 [1]. However, the GaN grown had very poor crystal quality owing to the large lattice mismatch between GaN and the sapphire substrate and so for a long time, very limited research was being conducted on GaN by the scientific community. In the 1980s, Yoshida and Amano grew GaN films on sapphire using an AlN buffer layer [2, 3] to improve the crystalline quality. In 1991, Nakamura grew a high quality GaN film on sapphire using a low temperature GaN buffer layer [4] and this drew significant interest from the scientific community and started a revolution in GaN research. P-type GaN had been a significant challenge and needed to be overcome in order to grow device structures. Amano in 1989 [5] and then Nakamura in 1992 [6] achieved Mg-doped p-type GaN films by using post growth low-energy electron beam irradiation (LEEBI) treatment, and thermal annealing under NH₃,
respectively, to overcome the challenge. Nakamura clarified that hydrogen passivation of the dopant atoms was preventing them from becoming electrically active and was the main reason for the challenge. Along with improving the GaN material quality, considerable efforts were being made to achieve high brightness semiconductor LEDs using GaN. Initial experimentations looked at p-n junction type LEDs or double heterostructure type LEDs (InGaN layer sandwiched by n-GaN and p-GaN). Nakamura who was working for Nichia Incorporation, demonstrated high brightness LEDs (blue, yellow and green) with InGaN quantum well (QW) structures [7]. The InGaNGaN multiple quantum wells (MQW) sandwiched by n-type and p-type GaN layers, shown in fig. 1-2, has today become the basic root structure from which all types of commercial visible light LEDs have been derived. The LED structure in fig. 1-2 has sapphire as the substrate. A nucleation layer is used to grow GaN on it. The n-type dopant is silicon and the p-type dopant is magnesium. The active region are InGaN multiple quantum wells surrounded by GaN barriers. Sandwiched between the p-type layer and the active region is a AlGaN layer doped with Mg which acts as a potential barrier to electrons and prevents them from overflowing out of the active region. This basic structure was then used in laser diodes by incorporating waveguide structures. These were estimated to have a lifetime in excess of 10,000 hours under continuous-wave operation at room temperature [8]. This triggered the Blu-Ray technology revolution in data storage. The bigger and more significant revolution that was triggered, was that of solid state lighting by InGaNGaN LEDs. It has taken a while to get started. However, over the last decade or so, it has grown to become a multi-billion dollar market and is expected to continuing growing for many years.
1.3. SOLID STATE LIGHTING (SSL) – OUTLOOK

Energy saving and energy efficiency is becoming very important as we step further into the 21st century. Lighting forms a significant portion of the total energy consumption, e.g. in US alone, it accounts for about one quarter or more of the residential and commercial electrical energy consumption. An effort to reduce the energy consumption in lighting with more efficient sources like inorganic LEDs is seen as the path ahead. Take the case of US alone - in 2012, about 49 million LEDs were installed in the U.S. -- saving about $675 million in annual energy costs. Switching entirely to LED lights over the next two decades could save the U.S. $250 billion in energy costs i.e. an annual saving of ~$12 billion, reduce electricity consumption for lighting by nearly 50 percent and avoid 1,800 million metric tons of carbon emissions [9]. Currently, the biggest challenge faced by the LED
industry is cost and this has become a hurdle towards wider-scale adoption of LEDs for lighting.

Luminous efficacy is a measure of the fraction of light power that is effective for human vision that is produced from one watt of electricity. The sensitivity of the human eye peaks in the green region at about 555 nm, at which wavelength, light has the most lumens in it. Theoretically, the maximum luminous efficacy for monochromatic light at 555 nm is 683 lm/W. For white light with a broadband spectrum in the range of 400-700 nm, the theoretical luminous efficacy limit is considered to be around 280 lm/W or more. The incandescent bulb that accounts for a large portion of the lighting industry, today, has a very low luminous efficacy of ~15 lm/W and a lifetime of less than a year. LEDs on the other hand are already approaching 150 lm/W or more on a commercial scale and can last 5-10 years or more. There is a considerable effort to lower the price of LEDs, boost their efficiency at higher powers and also boost the efficiency when they emit at larger emission wavelengths in the green and beyond. InGaN-based LEDs emit very efficiently in the blue region but their efficiency drops for green and beyond. So to obtain white LEDs, phosphor coatings on the blue LEDs are adopted, whose fluorescence has a broad emission spectrum. Figure 1-3 shows the emission spectrum for a blue-emitting nitride LED structure coated with a phosphor. The most commonly used phosphor is cerium doped yttrium aluminum garnet (YAG:Ce).
Figure 1-4 shows a Department of Energy (DOE) projected plan for the next decade as well as the progress of the last few years for the luminous efficacy of packaged white LEDs available commercially. The emission spectrum of the packaged white LEDs is often classified under two categories called cool-white and warm-white. These are decided by a factor called Correlated Color Temperature (CCT), which is indicative of the light color that is viewed by our eyes from the packaged LED and measured in kelvins (K). Very red would be represented by 1000K and very blue would be represented by 10000K. So the cool-white LED has a white color with a bluish tinge with a CCT of about 4500-7000K, while the warm-white LED has a yellowish color similar to a conventional lamp lighting with a CCT of about 2500-3500K. Phosphor coatings is the more common approach for white LEDs, however, absorption by the coatings can hamper the LED efficiency. So, considerable efforts are being made to obtain a color-mixed LED, i.e. an LED that emits at two or three or more different
wavelengths to obtain white color. The different wavelengths to obtain white are chosen from what is often referred to as a chromaticity chart shown in fig. 1-5. The perimeter points on the chart refer to monochromatic wavelengths while points in the interior of the chart are broad spectrums obtained as sum of other wavelengths. White color can be seen to be obtained in the central region of the chart.

Fig. 1-4: DOE 2012 Program Plan showing the present progress and the future. The dotted lines represent the expected future trend. CM stands for color-mixed LED while PC stands for LEDs with a phosphor coating. Referenced from [10].
1.4. POLARIZATION IN NITRIDES

Gallium nitride exists both in the wurtzite and the cubic crystalline structures. However, when grown conventionally, it tends to preserve the more stable wurtzite structure. The lack of inversion symmetry in the wurtzite crystal system results in a net dipole moment in the c-axis direction as shown in fig. 1-6. The polarization charge density induces an internal electric field and the two are related as:

\[ E = \frac{(D - P)}{\varepsilon} \]

where \( E \) is the induced electric field, \( D \) is the displacement field, \( P \) is the polarization and \( \varepsilon \) is the static dielectric constant. The displacement field is a vector field that accounts for the effects of both bound and free charges within a material. This inherent polarization due to the
crystal structure itself is termed as spontaneous polarization (SP) [11]. This polarization is absent in the zinc-blende form of GaN due to high lattice symmetry. The most conventional plane of growth for GaN is the (0001) plane which corresponds to a Ga-polar surface which is usually achieved by metal-organic chemical vapor deposition. There also exists a N-polar surface, that is commonly achieved by molecular beam epitaxy, for which the polarization dipole direction is completely reversed from the Ga-polar surface.

Fig. 1-6: Schematic illustration of the spontaneous polarization and induced electric field in a (0001) GaN film grown on a substrate. Dipole moment from the Ga atom (grey) to the N-atom (red) in GaN.

GaN is usually grown on a foreign substrate, such as sapphire, SiC, silicon etc and so there is significant lattice mismatch between the GaN epilayers and the substrate. In addition,
there may also be some thermal mismatch during temperature ramping and cooling at the
time of growth. These mismatches induce stress which gives rise to strain and results in
piezoelectric polarization (PZ) [12]. Ternary nitride alloys like In$_x$Ga$_{1-x}$N and Al$_y$Ga$_{1-y}$N
when grown on a GaN film also have both spontaneous and piezoelectric polarizations. The
ternary alloys try to conform to the GaN film resulting in compressive and tensile stresses in
the plane of growth for the In$_x$Ga$_{1-x}$N and Al$_y$Ga$_{1-y}$N films respectively. These stresses in the
ternary alloys contribute to the PZ component which either adds to or subtracts from the SP
component [13] as shown in fig. 1-7 based on the type of stresses present. The piezoelectric
constants for nitrides [12, 14] are large and so the piezoelectric fields even for small strains
can be large in these materials. The typical order of these fields is a few MV/cm.
Fig. 1-7: Piezoelectric and spontaneous polarization components for the different nitrides.

The AlGaN and InGaN ternary alloys are assumed to be grown pseudomorphically to an underneath GaN layer. Referenced from [13].

The polarization charge density $\rho_{pol}$ is related to the gradient of the polarization dipole moment as:

$$\nabla \cdot (\vec{P}_{SP} + \vec{P}_{PZ}) = -\rho_{pol}$$

From the above equation, it can be seen that when we have a heterojunction interface in nitride devices, a polarization sheet charge density will be present arising from a discontinuity in the spontaneous polarization of the 2 materials as well as from a sudden change in the strain state accounting for a discontinuity in the piezoelectric polarization. It
can be seen from fig. 1-8, that the lattice mismatch between GaN and InN is large but the spontaneous polarization difference between the two is small. So InGaN-GaN structures are more greatly influenced by the piezoelectric component [11]. On the other hand, for AlGaN-GaN structures, the spontaneous polarization discontinuity is the more dominant factor contributing to the polarization charges [11].

![Spontaneous polarization coefficients vs lattice constant for the nitrides.](image)

**Fig. 1-8 :** Spontaneous polarization coefficients vs lattice constant for the nitrides.

Referenced from [11].

The induced charges result in an internal electric field that can be of the order of a few MV/cm. This high electric field can have significant effects on nitride devices. As part of this thesis, we look at the effect of this polarization on InGaN-GaN MQW LEDs.
1.5. EFFECT OF POLARIZATION ON NITRIDE LEDS: QUANTUM CONFINED STARK EFFECT

The effect of polarization in nitrides, especially for LED structures, is discussed in this section. The InGaN quantum wells in the active region of the LED structure will experience large internal electric fields predominantly arising from the piezoelectric component. The piezoelectric component is a result of the large compressive strain within the InGaN quantum wells as they conform themselves to the underneath GaN layer. The high fields cause the electronic bands within the InGaN quantum well to bend. The electrons shift to lower energy states while the holes shift to higher energy states causing the transition wavelength from the quantum well to shift to lower energies. This shift in the emission wavelength under the influence of an electric field is referred to as the quantum confined stark effect (QCSE). More importantly, there is spatial separation of the electron and hole wave functions which decreases the overlap of the two wave functions and thus reduces the probability of a recombination event within the quantum well [15]. The rate of spontaneous emission can be described as follows:

$$\Gamma_{rad} = \frac{2q^{2}\omega_{0}^{3}|r_{12}|^{2}}{3\varepsilon_{0}hc^{3}}$$

where $\Gamma_{rad}$ is the rate of spontaneous emission, $\omega_{0}$ is the emission frequency, $r_{12}$ is the dipole matrix element. The dipole matrix element is proportional to the transition probability between states 1 and 2.
The polarization for nitrides is the highest along the c-axis direction. So if the quantum well is grown along other crystal planes that are inclined at an angle to the conventional c-plane, then the influence of the electric field on the band structure in the well can be significantly reduced. Figure 1-9 shows different crystallographic orientations for the GaN wurtzite system. The m-plane and a-plane that are perpendicular to the c-plane will have no polarization along their plane axis and are hence termed as non-polar planes while others that are inclined at angles in between the c-plane and non-polar planes are termed as semi-polar planes. Waltereit et. al. first demonstrated the absence of QCSE for InGaN quantum wells grown on a non-polar plane in comparison to similar wells grown on the polar c-plane [16]. Figure 1-10 illustrates the band structure of both cases and the consequent red shifting and wave function separation for the c-plane quantum wells relative to the m-plane.
The photoluminescence results also confirm the faster rate of spontaneous emission for the m-plane relative to the c-plane. Takeuchi et. al. calculated the piezoelectric fields within a strained In$_{0.1}$Ga$_{0.9}$N quantum well [17], as a function of the growth plane orientation with respect to the polar c-plane as shown in fig. 1-11. This relation is not monotonous and shows, that even among the “semi-polar” planes, we could have a desirable crystal orientation where the piezoelectric field could go to zero. It also shows that there is a lot to be explored with the various crystal planes as there is a wide range of polarization fields possible with these planes. Approaches to employ these different crystal planes within LED structures as well as a study of their effects will be explored in the subsequent chapters.

**Fig. 1-10** : (a) band structure for c-plane InGaN quantum well (b) band structure for m-plane InGaN quantum well (c) Cathodoluminescence intensity from the two quantum wells on the 2 different planes. Inset shows time-resolved photoluminescence measurements at 5K for both quantum wells.
Fig. 1-11: Piezoelectric fields vs crystal orientation with the c-plane for InGaN quantum well. The In% is assumed to be 10% and the thickness of the well is 3 nm. Referenced from [17].

1.6. CONCLUSION

The polar c-plane is the default growth plane for the nitride LED structures but is ridden with very high polarization fields. These fields are responsible for QCSE within the active region of the LED structure that is detrimental to the emission in these LEDs. The semi-polar and non-polar crystal planes provide an alternative to reduce or eliminate the QCSE. Higher light emission from the LED is the need of the hour for the growing solid-
state lighting industry and this provides lot of motivation for the scientific community to pursue efforts to further the understanding of polarization in nitrides.

1.7. REFERENCES


CHAPTER 2 : GROWTH AND CHARACTERIZATION

In this chapter, an overview is provided of the metal organic chemical vapor deposition (MOCVD) growth process, the MOCVD growth system, the fabrication process and various characterization techniques that were used during the course of the dissertation work.

2.1. MOCVD GROWTH

In MOCVD, deposition occurs via chemical reactions at the sample surface and incorporation is dominated by the chemistry and thermodynamics of the growth process. Chemical doping compounds referred to as metal-organics are used as the dopant precursors. For the growth of III-V nitrides, ammonia (NH₃) is used as the precursor species for supplying the V-element, nitrogen. Alkyls of group-III metals (metalorganics) are used as the precursor species for the III-element, which could be Ga, Al or In. The MOCVD process is the go-to process used in industry, these days, for the growth of III-V nitride-based LEDs and lasers. The MOCVD process can be used for growing structures with abrupt composition changes and with a range of growth rates yielding excellent control and film uniformity.

2.1.1. MOCVD REACTOR SYSTEM

The MOCVD reactor system used for the dissertation work was a system, assembled and built in-house. Figure 2-1(a) shows a photo of the MOCVD reactor taken in the lab while fig. 2-1(b) shows a schematic illustration of the growth reactor. The reactor chamber is a double wall high purity quartz chamber with two flanges welded on the top and bottom for
providing mating surfaces for vacuum seals. Copper coils are wound around the quartz chamber and connected to a 7.5 kW Lepel power supply that helps achieve radio frequency (RF) inductive heating of the susceptor. The copper coils are cooled in series with the cooling water for the quartz chamber. The susceptor is made out of graphite and it heats up in response to the eddy currents generated by the alternating current (RF) passing through the coils. The susceptor assembly is comprised of two parts: a mushroom susceptor that accommodates the growth sample and can rotate by the use of a stepper motor, and a triangular ring (temperature reference piece) that is stationary and accommodates a K-type (Chromel-Alumel) thermocouple to measure the temperature. A Eurotherm temperature controller reads the thermocouple output and has a feedback loop to the Lepel power supply to set the appropriate current for heating.

Fig. 2-1 : (a) Photo of the MOCVD reactor in the lab while the growth of GaN at 1000 °C is on-going, (b) Schematic of the MOCVD growth chamber in our lab
Column III and column V reactants flow through two separate gas streams and into a bi-channel inlet tube that is divided into two channels by a thin 1 mm quartz plate to prevent intermixing of the reactants and formation of unwanted particles. The gas delivery system is composed of 2 separate run/vent manifolds that are actually a series of injection valves that divert the gas input into the run line or vent line. The column-III manifold accommodates a number of bubblers that contain the organometallics. N2 carrier gas is “bubbled” through the bubblers (stainless steel containers) and gets saturated with the desired vapor concentration of the organometallic, depending on the pressure and temperature of the bubbler. The exhaust system comprises a 2 stage rotary vane vacuum pump by Leybold, a throttle valve by MKS Instruments to control the pressure and a pressure transducer by MKS Instruments to measure the chamber pressure.

2.1.2. MOCVD GROWTH PROCEDURE FOR GaN

The growth of GaN thin films is performed on double-side polished, 330 µm thick, 2” diameter (0001) sapphire substrates. Prior to loading into the growth chamber, the wafer is scribed into 7 identical square pieces, 14 mm x 14 mm using a diamond scribe, to reduce the consumption of substrates. The wafers/templates are cleaned in hexane, acetone, isopropanol and methanol for 10 minutes each, in a heated ultrasonic bath, and then dried using a N2 gun. The substrate wafer is then loaded into the reactor chamber via the “cube door” of fig. 2-1 and placed on the susceptor. The system growth chamber is then cycled between 0 Torr and 100 Torr in an N2 environment to purge out any air from the chamber. The MOCVD growth procedure then begins and is summarized through the following steps:
Substrate Clean and surface restructuring – the sapphire substrate is heated to a very high temperature (~1050 °C), higher than the GaN growth temperature, 100-350 Torr, for about 20 mins in a H₂ environment to desorb water and hydrocarbons from the substrate surface, and to deplete O₂ from the sapphire (Al₂O₃) surface via reactive atomic hydrogen to obtain an Al-rich surface.

Nitridation – The restructured Al-rich sapphire surface is exposed to NH₃ at ~975 °C for about 5 minutes, to create an AlN surface layer on which the buffer layer is grown.

Buffer Layer Growth – Trimethylgallium (TMGa) is introduced into the chamber at ~500 °C to deposit a thin, GaN buffer layer that is usually between 20-80 nm thick. At this low temperature, the nucleation rate is high, the diffusion rate is low and small islands of cubic GaN are formed. The V/III ratios, the temperature, the thickness of the nucleation layer, all closely influence the GaN buffer layer. This layer is very critical to the surface morphology and dislocation density of the consequently grown GaN film.

Buffer Layer Anneal – The substrate is heated to the actual GaN epilayer growth temperature (~1000 °C) in the presence of NH₃ and H₂ gases and undergoes a short anneal (5 minutes) prior to GaN growth which allows GaN islands to coarsen and coalesce, and initiates transformation of the cubic crystal structure to the hexagonal GaN crystal structure. A much higher overpressure of NH₃ is employed in this step relative to other steps.
GaN Epilayer Growth and other layers – TMGa flows into the chamber at a temperature somewhere in between 960-1030 °C, as appropriate, for the duration of the run. The growth of GaN is typically done in an NH₃ overpressure and the growth rate is controlled by the TMGa flux. It is well-known and commonly reported that the unintentionally doped GaN films (i-GaN) exhibit n-type conduction due to native defects and impurities [1] and so keeping the background donor concentration low, to the order of $10^{15}$ cm⁻³, is critical to the growth. N-type GaN films have Si doping and is achieved using SiH₄ through the use of a dilution line for better doping control. P-type GaN films have Mg doping whose precursor species is biscyclopentadienyl magnesium (CP₂Mg). Achieving p-type is more challenging and requires the thermal annealing of the grown films at around 700 °C under nitrogen atmosphere to break the Mg-H complexes [2].

For InGaN layers, the growth temperature range is much lower (~650-750 °C) and the precursor species used for indium is trimethylindium (TMIn). Triethylgallium (TEGa) is also often used in place of TMGa for InGaN layers to allow for slow growth rates, better quality and lower carbon incorporation. For AlGaN layers, the growth temperature range is much higher than GaN and the precursor species used for Al is trimethylaluminium (TMAI).

2.2. III-NITRIDE LED FABRICATION

The fabrication processing of III-nitride LEDs was performed in a 8’x8’ modular Cleanroom in the lab. The ceiling is covered with four 2’x4’ HEPA filters fitted with high
volume air blowers that provide clean air into the room, which is exhausted from the bottom vents. The cleanroom was tested to be better than Class 100 as measured by handheld particle counters. The room consists of a chemical hood, Chemat Technologies KW-4A spin coater, Karl Suss MJB 3 contact aligner with a 200W/cm² mercury light bulb and Thermionics e-beam evaporator. The etching of the samples was performed outside the cleanroom with a PlasmaTherm RIE etcher. The samples are cleaned in hexane, acetone and methanol for 10 minutes each, respectively, in an ultrasonic bath. Then the wafers are taken into the cleanroom to be processed by the following procedure:

1. Dehydration bake of wafers at 105°C for 5 minutes on hot plate.
2. Futurrex NR9-3000PY negative photoresist (PR) application using the Chemat Technologies spin coater. The resist initially is spun with a slow cycle for 10 secs (2000rpm) to spread the PR on the wafer evenly and a fast cycle at 4000rpm for 40 seconds to remove excess PR. PR thickness typically ranges between 1-5 µm.
3. Soft bake of the resist at 150°C for 60 seconds.
4. Mask alignment in Karl Suss aligner for lithography of the Ni etch mask.
5. Exposure of the negative resist (light power of 17 mW/cm² for 6 seconds).
6. Post exposure bake (hard bake) at 105°C for 90 seconds.
7. Development of the resist in RD-6 developer for 30 seconds.
8. HCl dip for 20 seconds to remove the native oxides from the surface.
9. Deposition of 2000Å thick Ni etch mask layer in the Thermionics e-beam evaporator. Ni deposition is performed at a base pressure of 10⁻⁶ Torr with an average deposition rate of 1.2 Å/s.
10. Warm acetone dip for excess Ni lift-off.

11. Mesa formation via etching down to the n-layer in the PlasmaTherm RIE etcher using BCl₃ plasma chemistry. The etch selectivity of the process, i.e. etch rate ratio of GaN to Ni mask, is larger than 15. The post-etch mesa depth and profiles on each wafer are checked by a Dek-Tak profilometer.

12. Removal of the Ni-etch mask by use of a Ni-etchant solution (mixture of nitric acid, sulphuric acid and acetic acid) which provides an etch rate of 30 Å/min.

13. Repeat of steps 1-8 for p-type metallization lithography.

16. Deposition of contact metals to the p-layer: 500Å Ni/1000 Å Au.

17. Acetone dip for metal lift-off.

18. Annealing of the p-type contacts at 500°C for 4 minutes in air to achieve ohmic contacts to the p-type semiconductor.

19. Repeat of steps 1-8 for n-type metallization lithography.

20. Deposition of contact metal to the n-layer: 250 Å Ti/500 Å Al/1000 Å Au.


The LED devices, that are 400 µm x 400 µm in area, are now ready to be characterized.

### 2.3. Characterization Techniques

The III-nitride films and structures grown with the MOCVD reactor are characterized by a number of techniques. Optical microscopy and scanning electron microscopy (SEM) are used to determine the surface morphology of the films. Typical GaN films, grown by the
above growth procedure, yield transparent, featureless, smooth films. Some of the main characterization techniques used over the course of this dissertation are discussed below.

2.3.1. X-RAY DIFFRACTION

X-ray diffraction (XRD) is a powerful non-contact method used to determine the crystalline phases in bulk materials, thin films and powder samples. XRD is also used to measure the thickness of thin films, and multilayers (i.e. quantum wells), and atomic arrangements in amorphous materials. X-ray diffraction analysis of as grown films was performed on a Rigaku Geigerflex D-Max diffractometer in the Bragg-Brentano configuration with Cu radiation ($\lambda = 1.54058 \text{ Å}$). The constructive interference of x-ray beams, diffracted by the regular periodicity of the atoms in crystalline samples, only occurs at certain angles that satisfy the Bragg’s Law given by:

$$n\lambda = 2d \sin(\theta)$$

where $n$ is the order of diffraction, $\lambda$ is the wavelength of the x-ray beam, $d$ is the interplanar spacing of the reflecting planes and $\theta$ is the Bragg angle. Therefore determination of $\theta$ reveals the interplanar spacing of the crystal phase, and in turn the lattice parameter. $\theta$-2$\theta$ scans were used routinely to determine the composition of ternary In$_x$Ga$_{1-x}$N alloys utilizing Vegard’s Law, according to which the composition $x$ can be estimated by linear interpolation using interplanar spacings ($d_{\text{GaN}}, d_{\text{InN}}$) of pure binary alloys GaN and InN as end points such that:

$$x = \frac{d_{\text{InGaN}} - d_{\text{GaN}}}{d_{\text{InN}} - d_{\text{GaN}}}$$
The above equation does not take into account the strain in the film, thus knowledge of the strain state of the film is required for accurate determination of ternary alloy composition, \( x \).

Any periodicity along the direction of x-ray propagation, such as a MQW structure, through a material can give rise to interference effects in the x-ray diffraction pattern not observed in a scan of the bulk material. A quick analysis can show that the period of the resulting interference (called Pendellosung fringes) on the XRD pattern is related to the periodicity of the superlattice or MQW by:

\[
2\sin(\theta_n) - 2\sin(\theta_0) = \frac{n\lambda}{L_B + L_W}
\]

where \( n \) is the order of the satellite peaks, \( \theta_n \) is their diffraction angle, and \( \theta_0 \) corresponds to the Bragg angle of the zeroth order peak. The sum of the thickness of the barrier, \( L_B \), and the thickness of the well, \( L_W \), is the period of the structure.

### 2.3.2. PHOTOLUMINESCENCE

Photoluminescence (PL) is a process in which a substance absorbs photons and then re-radiates photons as a result of excitation of carriers to a higher energy state and then a return to a lower energy state. When a photon of energy \( h\nu > E_g \) impacts the surface of a direct band gap semiconductor, electron hole pairs (EHP) are generated in the material and this typically is referred to as absorption. When EHP recombine in a direct band gap material, a photon is emitted with an energy representative of the transition. In the case where \( h\nu < E_g \), absorption does not occur since the photon has insufficient energy for creating an EHP. For a strong and narrow band-edge PL signal from a direct bandgap
semiconductor, the formation and stability of excitons is important. In GaN, the exciton binding energy is around 25-28 meV, which means they can be stable even at room-temperature. This allows for GaN to be characterized with clarity by PL at room temperature as well. PL is an important characterization technique for semiconductors that can provide information regarding bandgap, impurity and dopant ionization energies, state of strain, composition of ternary alloys and nature of defects present in a material. PL measurements are performed in the lab using an Omnichrome 35mW He-Cd laser (325 nm), 0.5 m monochromator, a photomultiplier tube and a standard lock-in amplifier. The energy of this laser is suitable to photo-excite GaN and In$_x$Ga$_{1-x}$N alloys. The laser beam is directed onto the sample via a set of mirrors and lenses and the resultant emission from the sample is focused into the monochromator. The output of the amplifier is time co-ordinated with the scanning monochromator and a Lab View program is used to obtain the spectrum.

2.3.3. LED CHARACTERIZATION - ELECTROLUMINESCENCE AND LIGHT-OUTPUT MEASUREMENTS

Electroluminescence (EL) is a phenomenon in which a material emits light in response to the injection of an electric current. In an LED, EL is the result of radiative recombination of electrons and holes that are injected from the n-layer and p-layers, respectively of a p-n junction that is forward-biased. For nitride-LEDs in particular, the EL characterization can reveal information about the strength of the internal polarization field within the active region (InGaN QW). The peak wavelength and the full width half maximum of the EL spectrum can also reveal more information about the optical quality of the quantum wells of the LED. EL measurements were done with a conventional probing
station using tungsten needle probes to contact the metal layers of the LEDs. A Keithley 2430 SourceMeter was used for current injection and could be operated in 2 modes: continuous injection, and pulsed injection. The pulsed mode is preferred when going to higher currents to reduce the adverse effects of thermal heating on the LED. The light emitted was collected from the transparent sapphire end of the LED using a 600 µm diameter optical fiber coupled to an Ocean Optics USB2000 Spectrometer. The optical power output of the fabricated LED devices was measured using a Thorlab DET210 Si p-i-n photodiode, placed 2 cm below the transparent sapphire end of the LED. The diode is connected to the Keithley Sourcemeters to obtain the induced current in it. The responsivity (A/W) of the Si photodiode is known and is used to convert the current induced in the photodiode into power. This is a relative light output power and not an absolute one. Lot of the light escapes through the sidewalls of the sapphire substrate and even among the remaining light, only a small percentage is finally coupled with the photodiode active area. For more accurate measurements, individual LED devices need to be diced, wire-bonded and setup inside an integrating sphere to get absolute power measurements.

2.3.4. HALL MEASUREMENT

A Hall Effect measurement is based on the nature of carrier flow in a material. In the absence of a magnetic field the charge carriers, i.e. electrons and holes, travel through a straight path in a semiconductor. When an external magnetic field, \( B_z \), perpendicular to the current flow is applied, a Lorentz force acts on the charge carriers that pushes majority carriers to one side and minority carriers to the other. An electric field is created because of
the accumulation of charge and results in a Hall voltage, acting perpendicular to both the current flow and the magnetic field, given by:

\[ V_H = \frac{IB}{qnd} \]

where \( V_H \) is the measured Hall voltage, \( I \) is the current, \( B \) is the external magnetic field, \( n \) is the carrier concentration and \( d \) is the thickness of the top layer being characterized. The Hall Effect measurements are performed in the Van der Pauw configuration. These measurements are used for the determination of resistivity as well as the carrier type, concentration and mobility. High purity indium pieces are soldered as metal contacts to 4 corners of square samples of size 5-10mm x 5-10mm. Standard Keithley current and voltage source-meters are utilized to perform the measurements.

2.3.5. THICKNESS BY OPTICAL MEASUREMENTS

It is important to characterize the growth rate of GaN whenever the reactor conditions change to help estimate the thickness of the GaN layers for future runs. Optical transmission measurements are performed on a sample of thick GaN (~2-3 µm) grown on sapphire substrate. A tungsten broadband light source is shone on the GaN film in a direction normal to the sample surface. The light transmitted is collected from the substrate end using an Ocean Optics fiber cable and passed onto a spectrometer to obtain the transmitted spectrum. Due to the higher refractive index of GaN, there are reflections at both the air-GaN interface as well as the air-sapphire interface. The resulting Fabry-Perot interference gives rise to
peaks in the transmitted spectrum. The spacing between the peaks is a function of the GaN epilayer thickness and is related by:

\[ d = \frac{\lambda_m \lambda_{m-1}}{2[\lambda_{m-1} n(\lambda_m) - \lambda_m n(\lambda_{m-1})]} \]

where \( d \) is the GaN film thickness, \( \lambda_m \) and \( \lambda_{m-1} \) are two adjacent peak wavelengths and \( n(\lambda_m) \) is the refractive index of GaN as a function of wavelength. Thicker films (>1.5 µm) and films with a smooth surface will result in a large number of well-distinguishable peaks and thus, enable greater accuracy for the thickness estimation.

### 2.4. REFERENCES


CHAPTER 3 : OVERGROWTH ON GaN NAN WIRES BY EMBEDDED Voids APPROACH – FOR NOVEL LED STRUCTURES AND FOR HIGHER QUALITY GaN FILMS

3.1. INTRODUCTION

In recent years, there has been a trend to grow GaN nanostructures and build the LED device on them. The facets of GaN nanostructures provide a possibility to grow on semi-polar and non-polar planes. As established from the previous chapter, this can help eliminate QCSE within the active region of the LED structures and greatly enhance performance. The GaN nanostructures also provide flexibility to tune different emission wavelengths depending on their shapes, sizes and facets and thus are a possible approach to achieving color-mixed white LEDs [1, 2, 3, 4].

3.2. GaN NANOSTRUCTURES – AN OVERVIEW OF PAST WORK

There have been basically two approaches that have been adopted to build nanostructure-based nitride LEDs.

3.2.1. BOTTOM-UP APPROACH
One popular method in the bottom-up approach is to have metal nanoclusters act as catalysts in the vapor-liquid-solid (VLS) growth process to form triangular facetted GaN nanowires. This is then followed by growth of InGaN/GaN quantum wells and a p-GaN layer in a radial direction to form a core/multishell nanowire structure [1, 5, 6]. These nanowires grown by the VLS process tend to elongate in the <11-20> direction while the quantum wells
grow on the polar and semipolar facets of the wires. The concept of radial growth has also been used for implementing nanoarchitecture LED arrays. In this method, position controlled ZnO nanotube array templates are grown on a SiO$_2$ patterned n-GaN layer on c-plane sapphire substrates. Subsequently, a n-GaN layer is grown by MOVPE on the circumference to give a coaxial ZnO/GaN heterostructure. This is followed by InGaN/GaN multi-quantum wells (MQWs) and a p-GaN layer grown by MOVPE over the circumference of the ZnO nanotube in a radial direction with respect to the nanotube [7, 8]. Another method is to form nanorods from nanometer-sized seeds and then continue to grow the quantum wells and p-GaN in the direction of the nanowire growth i.e. the c-plane [9]. Lastly, there has been an approach to grow a dense array of GaN nano-pyramids by selective area growth. The template used is a SiO$_2$ patterned layer on a GaN layer on c-plane sapphire substrate. The InGaN/GaN quantum well is then grown on the semipolar facets of the nano-pyramid [4, 10].

3.2.2. TOP DOWN APPROACH

In the top-down method, the most popular approach has been to use Ni nanomasks on a planar LED structure followed by inductively coupled plasma reactive-ion etching (ICP-RIE) to give nanorod LED structures [11]. The Ni mask is formed by rapid thermal annealing a thin film of Ni to give the self-assembled structure of Ni nanodots that act as a mask. An alternative masking approach of using Au nanodots has also been employed [12]. Using of e-beam lithography to pattern planar InGaN-GaN quantum wells has been used by Chen et. al. to obtain very precise sizing and positioning of InGaN-GaN nanoposts that are just 10 nm in diameter [13]. In-situ etching of a c-plane GaN surface using a silane treatment process to
form nanostructured semipolar (NSSP) GaN on which the InGaN/GaN MQWs are then grown epitaxially has been yet another approach to create a novel nanostructure [14].

3.2.3. CHALLENGES WITH PRESENT APPROACHES
In order for GaN nanostructure-based LEDs to be adopted on a commercial scale by the industry, many challenges need to be overcome simultaneously. Some of these are:

- The absence of a coalescent planar p-type layer makes device fabrication expensive and device characterization challenging.
- Growing quantum wells on the semi-polar and non-polar facets of the nanowire structures and growing them conformally.
- Masking and patterning steps make the process cumbersome and expensive.

3.3. PREVIOUS WORK: MASKLESS ETCHING AND OVERGROWTH BY EMBEDDED VOIDS APPROACH
In view of the above challenges, Pavel et. al. in the Bedair group demonstrated a technique to obtain GaN nanowires without masking/patterning and then overgrow on them by using an embedded voids approach [15]. The technique is illustrated briefly in fig. 3-1 below. A GaN film, about 2-3 microns thick is grown by metal-organic chemical vapor deposition (MOCVD) technique on a sapphire substrate. The film has a dislocation density in the $10^9$ cm$^{-2}$ range as shown in fig. 3-1(a). This film is then etched without any masks in an inductively coupled plasma reactive ion etcher (ICP-RIE) using a plasma mixture of chlorine and boron trichloride. The etching process was preferentially found to etch away dislocations and result in a dense array of GaN nanowires (NWs) as illustrated in fig. 3-1(b). Similar
observations with a different etching chemistry have been observed before [16]. The etched GaN NW template is then solvent cleaned and loaded back into the MOCVD for overgrowing on it. The template is annealed and overgrown to result in a coalesced planar top surface. The underlying film has embedded voids formed during the overgrowth of the GaN NWs as illustrated in fig. 3-1(c). The voids act as dislocation sinks and the overgrown film has a dislocation density that is reduced by 1-2 orders of magnitude relative to the as-grown GaN film before etching [15]. This overgrowth technique is appropriately referred to as the Embedded Voids Approach (EVA). The EVA technique is employed to grow a novel LED geometry on GaN NWs, which is to be the subject of this chapter as well as the next. The growth mechanism for this LED overgrown on GaN NWs, is discussed in the subsequent sections.

**Fig. 3-1**: Schematic of EVA technique (a) As-grown GaN film with high density of dislocations (b) Maskless etching to produce GaN NWs (c) Overgrowth on the GaN NWs to give a coalesced planar at the top. Voids embedded underneath that act as dislocation sinks.
3.4. Growth Mechanism of NWs LED

The starting film that needs to be etched is chosen to be an n-type GaN film. The bulk n-type GaN templates are grown conventionally by MOCVD at a low pressure of 350 mtorr. A low-temperature (LT) GaN buffer layer of ~60 nm thickness was grown on a sapphire substrate at 475 °C using trimethylgallium (TMGa) source flow of 1.5 sccm. This was followed by annealing and growth of silicon doped GaN to form a total thickness of 2.5 μm at 1000 °C. The electron concentration of the n-type layer is found to be ~2 x 10^{18} cm^{-3} by Hall Effect measurements.

This film is then etched without any masks in an inductively coupled plasma reactive ion etcher (ICP-RIE) using a plasma mixture of chlorine and boron trichloride. The maskless ICP-RIE technique uses a mixture of Cl₂ (27sccm) and BCl₃ (5sccm), etching pressure of 15 mtorr, and ICP/RIE powers 300/100 Watts, respectively. The etching process is optimized such that there is a preferential etching of dislocations with an etching rate of about 213 nm/min. The result is a dense array of GaN nanowires (NWs) that are about 0.8 to 1.5 microns in length and about 30-100 nm in diameter. The random spacing and sizes is a consequence of the random nature of the etching process as well as the random distribution of dislocations which are believed to be the first sites that are attacked during the etching process [17]. The nanowire density is in the range 10^9 –10^{10} cm^{-2} which is of the same order of magnitude of the dislocation density of the starting template. The scanning electron microscope (SEM) images of these GaN NWs are shown in fig. 3-2 (a). It must be mentioned that during etching, it is ensured that the n-type template does not etch down to the sapphire substrate and that there is at least about 0.5 μm of planar n-type GaN film just under the GaN.
NWs. Half of the n-GaN template (14 mm x 14 mm) was covered with a single piece of sapphire (7 mm x 14 mm) during the ICP-RIE etching in order to preserve a reference c-plane planar area.

![SEM images](image.jpg)

**Fig. 3-2**: SEM images of (a) GaN NWs after maskless etching (b) After annealing and slight overgrowth on the GaN NWs. (c) and (d) are schematic representations of (a) and (b).

This GaN NW template is then cleaned in warm solvents (hexane, acetone, isopropanol and methanol) in an ultrasonic bath to get rid of contaminants deposited during the etching or during handling of the sample. It is then loaded into the MOCVD reactor for overgrowing the LED structure on the GaN NWs. Prior to loading, the sapphire piece
masking half the n-type template is removed so that LED structure overgrowth on the conventional c-plane GaN and on the NWs occurs simultaneously. This experiment will thus provide for a comparative study of the two LEDs grown under identical conditions.

The overgrowth recipe begins with 1 minute of high temperature anneal at 1000°C in ammonia (NH3), followed by overgrowth on these nanowires at 1000°C by growth of GaN:Si. SEM images of fig. 3-2(a) and fig. 3-2(b) show the transition from the GaN NWs to a structure after annealing and few minutes of overgrowth. This is schematically illustrated in fig. 3-2(c) and fig. 3-2(d). Adjoining NWs conjoin to grow into a larger structure that is starting to form facets. The GaN NWs broaden in diameter and reduce in number as seen in the SEM image of fig. 3-3. During the annealing and overgrowth process, the GaN NWs look to reduce their large surface energy and transform their surfaces to stable lower energy crystal planes. The tips of the structures orient themselves into semi-polar planes placed in a hexagonal-like geometry while the body has a vertical non-polar facet as can be seen from fig. 3-4. Once the non-polar and semi-polar facets are formed, overgrowth of the active region is carried out. Five In0.2Ga0.8N/GaN quantum well/barriers are grown at 660/690 °C. A Mg-doped Al0.2Ga0.8N layer of ~20 nm (c-plane growth rate) is grown to act as the electron blocking layer and p-type layer of GaN:Mg is grown for ~300 nm (c-plane growth rate). An ammonia flow of 1.25 l/min was kept constant and TMGa flow of 3.25 sccm, (TMAI) flow of 4.8 sccm, trimethylindium (TMIn) flow of 54 sccm, and cyclopentadienyl magnesium (CP2Mg) flow of 31 sccm were used.
Fig. 3-3 : SEM image of GaN NWs after annealing and a bit of GaN overgrowth

Fig. 3-4 : (a) Schematic of GaN NW after forming stable semi-polar and non-polar facets. (b) SEM image of the same.

The cross-section of the MQW overgrowth from transmission electron microscopy (TEM) images of fig. 3-5 show conformal overgrowth of the MQWs on the NW facets. It
also shows that the semi-polar facets grow faster than the nonpolar facets. Growth rates of about 13 and 7 nm/min for the semi-polar (1101) plane and nonpolar (1100) m-plane were estimated, respectively. The higher growth rate causes the semi-polar planes to coalesce first during overgrowth and form a void in between the nanowires. SEM image of fig. 3-6 shows the beginning of void formation. Once the voids are formed, further growth will result in a transition from the low-order semi-polar planes to the very stable c-plane (0001) via higher order semi-polar planes. This is schematically illustrated in fig. 3-7. Figure 3-8 shows the cross-section TEM images of the LED overgrown on GaN NWs with the embedded void network and the overgrown MQWs. The MQWs deposited on the NWs before the initiation of the coalescence process are oriented along the low-order semi-polar plane, (1122) in the [a-zone] view, at the NW tips and along the nonpolar facets on the lower part of the NWs as shown in figs. 3-8(c) and 3-8(d). The MQWs deposited on NWs after the initiation of the coalescence process are oriented along higher-order semi-polar planes as shown in figs. 3-8(b) and 3-8(e). It is during the p-layer growth that complete coalescence and planarization is achieved. Magnesium, which is used for p-type doping, is believed to enhance the lateral growth rate [4, 18] and help in the transition to the c-plane and planarization of the film. When planarization of the overgrown LED is achieved, further growth continues along this plane. In conclusion, a successful LED structure is overgrown on GaN NWs with conformally grown MQWs and completely coalesced and planarized p-type film on type of the NWs. A network of voids is also embedded into the LED structure.
Fig. 3-5: TEM Cross-section image of the conformal growth of InGaN MQWs (x5) on the semi-polar and non-polar facets of the GaN NW [a-zone view]

Fig. 3-6: SEM image of the beginning of void formations between adjacent GaN NWs.
**Fig. 3-7**: Schematic of void formation and transition of semi-polar plane to planar c-plane.

**Fig. 3-8**: XTEM data in [m-zone] views: (a) the LED structure grown on NWs with voids embedded underneath the MQW region (b) the MQWs on adjacent NWs’ semipolar plane facets meeting to form a void, (c) a detailed view of the conformally grown MQWs on the NWs’ non-polar plane facet, (d) a detailed view of the conformally grown MQWs on the NWs’ low-order semipolar plane facet, and (e) the MQWs on the NWs’ are grown conformally on semipolar and nonpolar plane facets.
3.5. MULTIPLE OVERGROWTHS BY EVA – GaN FILMS WITH IMPROVED PROPERTIES

It was established earlier that the GaN layers overgrown on GaN NWs by the EVA method reduces dislocation density in the original film by about two orders of magnitude [15]. So it would be interesting to study the effects of repeating the etching-overgrowth cycle again on an already overgrown film. The 1\textsuperscript{st} generation of overgrown GaN EVA film is put through another process of EVA overgrowth using it as a template material to be etched. The 2\textsuperscript{nd} generation NWs that are formed are overgrown to form a 2\textsuperscript{nd} generation GaN-EVA film. Figure 3-9 shows a schematic representation of the GaN films after one overgrowth and two overgrowths. During each overgrowth, it is ensured that there exists at least about 1-1.5 µm of planar film thickness above the void network. Also, the total thickness of both films is in the range of 3-3.5 µm. The as-grown GaN film that is the starting etching template also has a similar thickness of about 2.8-3 µm. X-ray diffraction (XRD) and photoluminescence (PL) characterization are carried out at the end of each overgrowth step as well for the original as-grown starting GaN film.
The Full width at half maximum (FWHM) of XRD rocking curves are related to the crystal quality of epitaxial films and it is a well-accepted technique for characterization of GaN films [19]. The FWHMs of x-ray rocking curves are related to dislocation density utilizing the equation:

$$N_{\text{screw/edge}} = \frac{\beta_{\text{tilt}}^2}{4.35b_c^2}$$

where $N_{\text{screw/edge}}$ refers to the density of screw dislocations when using $\beta_{\text{tilt}}$ and $b_c$ in the equation and refers to the edge dislocation density when using $\beta_{\text{twist}}$ and $b_v$ in the equation, $\beta_{\text{tilt}}, \beta_{\text{twist}}$ are tilt and twist spreads and $b_c, b_a$ are the Burgers vectors of c- and a-type threading dislocations, respectively [20]. Figure 3-10 shows the FWHMs of rocking curves of “on-axis” and “off-axis” crystallographic planes obtained after each overgrowth and these are compared to a similar thickness of as-grown GaN reference sample. The FWHM obtained from the rocking curve of a specific crystal plane is plotted against the angle of inclination of that plane with the c-plane. Dislocation densities deduced from XRD are higher than what is
previously reported using TEM and AFM techniques [15]. Both TEM and AFM give estimates of dislocation density in the overgrown GaN film on the nanowires, indicating the real defect density of these overgrown GaN films. However, XRD penetrates into the whole structure (~3 μm thick) and includes information from defects close to the interface with sapphire; where very high defect densities are present. Many of these dislocations are terminated by the voids but would still contribute to the XRD line-width broadening. Also, the XRD results confirm that the reduction of dislocations can be repeated at each step of overgrowth. However, the percentage reduction in dislocation density decreases with each successive step.
**Fig. 3-10**: Plot of FWHMs of Rocking Curves on different crystallographic planes. Inclination angle is between c-axis and normal axis of the particular crystallographic plane and curves correspond to: ▲ film as grown; ■ coalesced film on the 1st generation of NWs and ● coalesced film on second generation of nanowires. The dashed lines correspond to the fitting data generated by an appropriately chosen $\beta_{\text{twist}}$.

Figure 3-11 shows the room temperature (300K) photoluminescence (PL) from the GaN film after the first and second EVA overgrowths compared with the as-grown GaN reference sample. Photoluminescence (PL) was carried out using a 325 nm He-Cd laser along with a 0.5 m monochromator, photomultiplier tube and a standard lock-in amplifier. The penetration depth of the laser beam in GaN for the 325 nm laser is about 0.2-0.3 µm. Therefore, the PL signal is not measured from the underlying NWs but only from close to the
surface of the overgrown planar film. This top region of the film is where the dislocation density is significantly reduced. There is an enhancement in PL intensity for the overgrown GaN films indicating an improvement in the optical properties by the reduction of defects and dislocation density and thus, an increase in minority carrier lifetime. The band-gap of a semiconductor is affected by the residual stress in the film. For GaN, compressive stress in the film is known to increase the band-gap. The band-edge peak of the overgrown GaN is red shifted with respect to the peak of the as-grown GaN film. This shift is 10 meV after the first overgrowth and 14 meV after the 2nd overgrowth. GaN grown on sapphire is compressively strained and a reduction of band-gap for the overgrown GaN indicates a relaxation of the compressive strain in the overgrown film. The EVA approach provides a stress relief mechanism for the overgrown film at each step. It is speculated that the surfaces of the voids can accommodate a large amount of strain and hence most of the strain energy will be accommodated by the nanowire bridge between the sapphire substrate and the overgrown planar film, thus providing stress relief to the overgrown film. Most of the relaxation is observed after the first EVA film. The luminescent band-gap of GaN at room temperature, $E_g$, represented by the PL peak, is related to the biaxial stress $\sigma_{xx}$ according to:

$$E_g = 3.4285 + 0.0211\sigma_{xx} \text{ (eV)}$$

The proportionality factor of $21.2\pm3.2 \text{ meV/GPa}$ is derived empirically for GaN by Zhao et al. [21, 22]. Using this, the compressive stress in the as-grown GaN film is estimated to be reduced by $0.49\pm0.07 \text{ GPa}$ after the first overgrowth and then a further $0.19\pm0.10 \text{ GPa}$ after the second overgrowth.
All the samples on which PL was performed were unintentionally-doped samples for which the concentration was in the low to mid $10^{16}$ cm$^{-3}$ ranges. So the carrier concentrations in all the samples are about the same and also low enough that they do not have much effect on the PL intensities. There is a possibility that the band-edge light emission heading towards the substrate from the top surface of these films could be redirected by reflection from the void network and be responsible for the increased PL intensity. However, the top of the overgrown coalesced layer for the EVA overgrown samples is ~1.5 µm away from the voids. The PL emission is concentrated around the band edge where the absorption coefficient in GaN is very high and it is estimated to be around $10^4$-$10^5$ cm$^{-1}$ [23]. So about 80-90% of the light or more would be lost by absorption by the time the PL emission light reaches the voids. So the effect of voids on increasing the PL intensity is expected to be very minimal.
Fig. 3-11: Room Temperature (300 K) PL spectrum of coalesced film after the 1st EVA and 2nd EVA processes and the as-grown GaN film with the band-edge PL peaks indicated.

An additional confirmation of the stress relief effect of the EVA overgrowth is the observed reduction of the crystallographic curvature. Independent measurements of x-ray rocking curves of the 006 reflection were recorded at different horizontal translation positions of the sample. The slight shift in the peak position at different points on the sample was used to estimate the sample curvature.

\[
R = \frac{\Delta x}{\sqrt{(2 \cdot \tan(\Delta \omega/2))}} \approx \frac{\Delta x}{\Delta \omega} \quad [24]
\]

where \( R \) is the radius of curvature, \( \Delta x \) is the horizontal translation between two independent points of measurement and \( \Delta \omega \) is the peak position shift for the rocking curve measurements.
at the two points. The experimental values for the curvature for both as-grown as well as EVA overgrown samples with different thicknesses is plotted in fig. 3-12. The sample overgrown on nanowires with EVA exhibit a smaller curvature by a factor of about 2 with respect to that in regularly grown layers with similar thickness. Figure 3-12 also shows simulated dependence of the curvature on the film thickness following the model by Etzkorn and Clarke [25] for a bilayer system, assuming spherical bending and isotropic in-plane biaxial stress. A comparison with the experimental results indicates that while the data for regularly grown crack-free layers without voids [26] is in a very good agreement with the theoretical predictions, the data for the layers grown by EVA noticeably deviates. The latter is indicative that an additional strain component needs to be accounted for and that the bilayer model is not directly applicable in these layers. The smaller crystallographic curvature results in less wafer bow, which is an additional benefit for the subsequent device growth and processing.
Fig. 3-12: Curvature as a function of GaN layer thickness. The experimental values are shown by symbols for layers grown by standard approach without voids (full symbols) and for layers grown by embedded void approach (open symbols). The simulated curve, following the model by Etzkorn and Clarke [25] is shown by solid line.

3.6. CONCLUSION

A novel LED structure is overgrown using the EVA overgrowth technique to overgrow GaN on GaN NWs. The MQW active region is grown conformally on the semi-polar and the non-polar facets of the GaN NWs. The GaN NWs are obtained by maskless etching and so there is a lot of motivation for industry to scale-up the process to their needs without much additional cost or complexity. The final overgrown p-layer is coalesced and planar and this provides for the use of conventional fabrication. Apart from the NWs-LED, EVA overgrown layers are characterized for crystal quality, optical properties and strain. The
effect of repeating the etching and overgrowth technique on an already overgrown layer is also studied.

### 3.7. REFERENCES


CHAPTER 4 : LED OVERGROWN ON GaN NANOWIRES –
INVESTIGATING THE POTENTIAL FOR IMPROVED PERFORMANCE
OVER CONVENTIONAL C-PLANE LEDS

4.1. INTRODUCTION

Similar to the Moore’s law of IC packaging, Haitz’s law [1] was formulated many
years ago for light-emitting diodes. It stated that the lumen flux per package would increase
and the cost per lumen would decrease at very fast rates for the last two decades. The present
progress in LEDs has already surpassed the improvements predicted by that law. Improving
the nitride LED performance has been one of the main goals for the lighting industry as well
as the scientific community researching in the area of nitrides or optoelectronic devices.
Greater efficiency will lead to greater energy savings and thus increase the adoption of
nitride LEDs in the commercial lighting sector which will further bring down their market
prices and make them a more serious competitor to other existing alternatives in the lighting
industry.

In the previous chapter, a novel LED structure on GaN NWs was grown by the
embedded voids approach and fabricated. It had a unique geometry and many novel features
like conformal MQWs on GaN NWs and a planarized top p-layer. In this chapter, the NWs-
LED is fabricated, characterized and its performance is compared to conventional LEDs. The
results are investigated and the potential of this “proof of concept” LED structure is explored.
Prior to the analysis of the NWs-LED, an introduction to the efficiency of the LED, the
factors contributing to it and basic overview of the work done in literature are discussed.
4.2. LED EFFICIENCY

The external quantum efficiency (EQE) of a LED is defined as the ratio of the number of photons emitted from the LED into free space per second to the number of electrons injected into the LED per second and is given by the equation:

$$\eta_{\text{ext}} = \frac{P}{Iq} = \frac{Pq}{Ih\nu}$$

where $\eta_{\text{ext}}$ is the external quantum efficiency, $P$ is the measured light-output power in Watts, $I$ is the current injected into the LED and $\nu$ is the frequency of the emitted light. There are 3 basic components to the EQE which are given by the equation:

$$\eta_{\text{ext}} = \eta_{\text{inj}} \cdot \eta_{\text{int}} \cdot \eta_{\text{ext}}$$

where $\eta_{\text{inj}}$ is the injection efficiency which is the proportion of electrons injected into the active region of those that are passing through the device,

$\eta_{\text{int}}$ is the internal quantum efficiency which is the proportion of carriers injected into the active region that radiatively recombine to produce photons,

$\eta_{\text{ext}}$ is the extraction efficiency which is the proportion of photons generated in the active region that escape from the device.

It must be mentioned that $\eta_{\text{inj}}$ is often considered to be a component of $\eta_{\text{int}}$. 
4.2.1. INTERNAL QUANTUM EFFICIENCY (IQE)

This quantity determines the efficiency of light generation within the active region of the LED or how effectively, the electron-hole pairs that are injected into the active region of the LED can recombine radiatively. Any electron which exists in the conduction band will eventually stabilize to a lower energy position in the valence band. When this occurs, it must move into an empty valence band state. Therefore, when the electron stabilizes back down into the valence band, it also effectively removes a hole. This process is called recombination. There are three recombination mechanisms possible for an electron-hole pair in the semiconductor, namely Shockley-Read-Hall recombination, radiative recombination and Auger recombination. These are illustrated in fig. 4-1.

![Fig. 4-1: Main mechanisms for recombination or annihilation of an electron-hole pair within a semiconductor](image)

a) Radiative Recombination
For direct band-gap semiconductors like GaN, radiative recombination is usually the dominant mechanism of recombination. In radiative recombination, an electron from the conduction band directly combines with a hole in the valence band and releases a photon; and the spontaneously emitted photon has energy equal to the band gap. In indirect band-gap semiconductors, there is a large momentum change as well that is associated with this band-to-band transition and this requires the emission of a phonon or heat. This makes radiative recombination unlikely for indirect band-gap semiconductors. The rate of radiative recombination, \( R \) is given as:

\[
R = Bnp
\]

where \( B \) is the bi-molecular recombination co-efficient, \( n \) is the electron concentration and \( p \) is the hole concentration. In LEDs, this is the mechanism responsible for light emission and we would like this to be the most dominant mechanism in the LED active region to increase the internal quantum efficiency.

b) **Shockley-Read-Hall Recombination (SRH recombination)**

This is the recombination through defect levels. This process is trap-assisted, utilizing a crystal lattice defect or an impurity atom, which introduces a localized energy level \( E_t \) within the semiconductor band-gap. The excess energy during recombination and the necessary energy for generation of the electrons or holes (formed by trapping a hole or electron) are transferred to and from the crystal lattice (phonon). The rate at which a carrier moves into the trap energy level in the forbidden gap depends on the separation of the introduced energy level from either of the band edges. Therefore, if an energy level is
introduced close to either band edge, recombination is less likely as the electron is likely to
be re-emitted to the conduction band edge rather than recombine with a hole which moves
into the same energy state from the valence band. For this reason, energy levels near mid-gap
are very effective for SRH recombination. SRH recombination can be a dominant mechanism
of recombination for highly defective semiconductor crystals. For the nitride system that has
a high density of defects and dislocations of the order of $10^9$-$10^{10}$ cm$^{-3}$, this recombination is
a loss mechanism that needs to be minimized.

c) Auger Recombination

This is a mechanism that involves three carriers to participate. An electron and a hole
recombine, but rather than emitting the energy as heat or as a photon, the energy is given to a
third carrier, an electron in the conduction band. This electron then thermalizes back down to
the conduction band edge. Since this process is a three-particle interaction, it is normally only
significant in non-equilibrium conditions when the carrier density is very high. It is most
important at high carrier concentrations caused by heavy doping or high level injection. The
rate of Auger recombination, $R_{\text{auger}}$ is given by the equation:

$$R_{\text{auger}} = c_n (n^2 p - n_i^2 n) + c_p (np^2 - n_i^2 p)$$

where $c_n$ and $c_p$ are the Auger recombination coefficients for the electrons and holes
respectively, $n$ and $p$ are the electron and hole carrier concentrations respectively, while $n_i$ is
the intrinsic carrier concentration. This mechanism is widely regarded as the main cause for
the efficiency droop that is observed in nitride LEDs at higher current densities [2, 3, 4].
4.2.1.1. EFFORTS TO IMPROVE IQE IN NITRIDE LEDS

One of the main methods to improve the IQE in nitride LEDs has been by minimizing the impact of the polarization field and thus reducing or eliminating the quantum confined Stark Effect (QCSE), which decreases the radiative recombination efficiency within the quantum wells (QWs). Polarization effects can be eliminated by growing devices on alternative orientations of bulk GaN crystals such as \( \{10\tilde{1}0\} \) m-planes, \( \{1\tilde{1}20\} \) a-planes, or reduced by growing on semipolar planes. This method often involves the use of expensive bulk GaN substrates (non-polar or semi-polar) that are also limited in availability. LEDs based on sidewall m-plane epitaxy of etched GaN/sapphire templates have been earlier reported by the Bedair group as an alternative to these expensive stand-alone non-polar/semi-polar bulk GaN substrates [5, 6]. LEDs by growing on facets of GaN nanowires or nanopyramids has been another alternative but is faced with a lot of challenges especially to scale-up the technique for industrial adoption [7, 8]. There have been efforts at growing higher quality epitaxial layers to improve the performance for the LED structures by epitaxial lateral overgrowth [9, 10], pendeo epitaxy [11], or using SiN treatment [12] etc. Electron spillage or overflow is often reported to be the cause for reduced radiative efficiency in the LEDs as electrons are often transported across the entire active region without participating in the light emission. To prevent this, AlGaN electron blocking layers in between the p-layer and the MQW region, with a slightly higher band-gap, are almost always used these days for the LED structure to act as a potential barrier to the electrons and confine them within the active region.
4.2.2. EXTRACTION EFFICIENCY

This quantity determines the efficiency with which the light that is generated within the active region of the LED can be extracted into free space from within the device structure. A large amount of light usually gets trapped within the LED device structure as a consequence of the large refractive index of the semiconductor. When light travelling inside a higher refractive index region is incident on the interface with a lower refractive index region, then the light can get totally internally reflected when the angle of incidence reaches a critical value. This critical value is determined by Snell’s Law. This law describes the relationship between the angle of incidence \( \theta_i \) and the angle of refraction \( \theta_r \) when light passes the boundary between two regions with refractive indices \( n_2 \) and \( n_1 \):

\[
\frac{\sin \theta_i}{\sin \theta_r} = \frac{n_2}{n_1}
\]  

[13]

At \( \theta_r = 90^\circ \), total internal reflection (TIR) will begin. So the critical angle of incidence for the TIR phenomenon will be:

\[
\theta_c = \sin^{-1}\left( \frac{n_{\text{external}}}{n_{\text{semiconductor}}} \right)
\]  

[13]

Above, it is assumed that the two regions are the semiconductor and the external surrounding which could be air or sapphire substrate. For GaN, the refractive index at around 500 nm (visible range) is about 2.4 [14] which is higher than either air (n=1) or sapphire (n=1.7) and so the light generated within an LED will undergo total internal reflection while escaping the device. The critical angle \( (\theta_c) \) for the GaN-air or the GaN-substrate interface, determines an “escape cone” for the light to be extracted, from within the LED. Figure 4-2
diagrammatically illustrates both the total internal reflection phenomenon as well as the escape cone for an LED structure. Strictly speaking, there would be six escape cones, associated with the six faces of the cuboidal LED structure. However, there would typically be a metal coating for contact, either on the top or bottom facet, which would prevent light to escape from that facet. For the side facets, the light would have to travel a significant distance, especially with large-area devices. During this travel, there would be significant losses in the form of absorption by metal contacts, absorption in the active region etc and so the side emission will be considerably reduced.

![Diagram](image)

**Fig. 4-2**: (a) Refraction for a ray moving into a lower refractive index material and the total internal reflection phenomenon (b) Escape cone for light generated within an LED

For the light within the escape cone, there is also some reflection even at angles less than the critical angle which arises from Fresnel reflections at the interface. The fraction of light that is reflected when moving from one medium to another are determined by the Fresnel equations,
\[ R_s = \left| \frac{n_1 \cos \theta_i - n_2 \cos \theta_t}{n_1 \cos \theta_i + n_2 \cos \theta_t} \right|^2 \quad \text{and} \quad R_p = \left| \frac{n_1 \cos \theta_i - n_2 \cos \theta_t}{n_1 \cos \theta_i + n_2 \cos \theta_t} \right|^2 \]

where \( R_s \) and \( R_p \) are the reflectances for the s-polarized (transverse electric) and p-polarized (transverse magnetic) light respectively, \( \theta_i \) and \( \theta_t \) are the angle of incidence and angle of transmittance respectively, and \( n_1 \) and \( n_2 \) are the refractive indices of the two medium. Figure 4-3 shows the Fresnel reflectance for the GaN-air and GaN-sapphire interfaces that are calculated using the above equation as a function of the incident angle. For each incident angle, the corresponding angle of transmittance is calculated using the Snell’s law. The reflectance peaks to 100% reflection at \( \theta_c \) value corresponding to that interface and stays at that level beyond the critical angle. For the GaN-air interface, the larger difference in refractive indices means there is a greater range of incident angles (24-90°) at which total internal reflection would occur. Also, the Fresnel reflectance for the GaN-air interface at incident angles lower than \( \theta_c \) can hover around 10-30% which is not negligible.
Neglecting the Fresnel reflection, the fraction of the total generated photon flux that lies within the escape cone is the flux that will be extracted. Assuming an isotropic spherical emission from a point source, the extraction efficiency can be approximated to the fraction of the surface area subtended by the escape cone to the total spherical surface area around the point source,

$$C_{\text{ext}} = \frac{1 - \cos \theta_c}{2} \quad [15]$$

In fig. 4-3, the angle at which the reflectance value goes to 1 will be the critical angle for TIR at that interface. For the GaN-air interface that has a $\theta_c \approx 24^\circ$ that is indicated in fig. 4-3(a), $C_{\text{ext}}$ would be about 4%, while for the GaN-sapphire interface that has a $\theta_c \approx 48^\circ$ that is...
indicated in fig. 4-3(b), the $C_{ext}$ would be about 16%. The low numbers for the extraction efficiency show why light extraction is a very serious issue in LEDs. As a result, there has been a considerable effort to come up with approaches to tackle this issue that shall be discussed in the next section.

4.2.1.2. EFFORTS TO IMPROVE LIGHT EXTRACTION IN NITRIDE LEDS

There have been a number of approaches aimed at increasing the extracted light from the LED chip. Some of the major ones are listed below:

- **Surface Roughening/Texturing**: The external surfaces of the LED where total internal reflection takes place are roughened to reduce the possibility of reflection. The light instead tends to scatter outwards while the light that reflects back into the LED is diffused and so reduces its chance of being permanently trapped in the LED chip. Many groups have explored this approach [16, 17, 18]. Wet chemical texturing of the N-polar GaN surface i.e. the bottom surface of the LED chip is one of the most popular methods [19]. However, it is difficult to achieve good repeatable roughness or predict the extraction improvement using this approach with good accuracy.

- **LED Geometry Modification**: Significant changes to LED geometry were explored to extract the laterally travelling light that predominantly gets trapped and absorbed within the LED. Some approaches to extract this lateral light like growing the LED on ZnO nanorod arrays [20] or growing sidewall LEDs [5, 6] have been demonstrated. However, these methods can introduce significant challenges for device design and fabrication.
Photonic Crystals: The use of periodic nanostructures to diffract the laterally guided modes of light within the LED (that are trapped) into the leaky modes (that leak into air or are extracted) is another approach that is often used [21, 22]. These are referred to as photonic crystals (PCs) and this approach requires well controlled dimensions (often sub-micron) that utilizes elaborate and expensive lithography and the grating must be in close proximity to the MQWs for efficient coupling. This imposes several restrictions in device design.

External Modifications: The use of PDMS coatings with concave micro-structured array geometries on the LED surface have helped improve the extraction efficiency [23]. Deposition of dielectric pillar stacks with a graded refractive index (GRIN) on the N-polar surface of GaN to reduce the total internal reflection has been another approach [24].

4.3. COMPARATIVE STUDY OF NW LED VS C-PLANE CONVENTIONAL LED

In Chapter 3, the growth of the novel LED structure overgrown on GaN NWs was discussed. This novel LED structure had unique features like conformal overgrowth of MQWs on the semi-polar and non-polar facets of GaN NWs, coalesced and planarized top surface of the LED, a network of embedded voids within the LED. In this section, the device characterization of the NWs-LED is discussed. The NWs-LED structure was grown side-by-side with a conventional c-plane LED structure using identical recipes and conditions. The
conventional LED shall be used as a reference LED to perform a comparative study with the NW LED. Figure 4-4 shows a schematic illustration of both these device structures.

![Fig. 4-4: LED structure Schematic for (a) c-plane conventional LED (b) NW LED](image)

### 4.3.1. DEVICE FABRICATION

Prior to device fabrication, both of the LED structures were annealed in N₂ at 740°C for 15 min in order to activate the holes in the p-type layer. The planarized top surface of the LED structure overgrown on GaN NWs enabled the use of conventional LED fabrication techniques. The LEDs were fabricated into mesas 400 μm x 400 μm. Figure 4-5 shows a schematic of the fabricated LED overgrown on the GaN NWs.
The etching for mesa formation is done in a Plasma Therm RIE machine using only BCl₃ for the plasma chemistry. The void-NW network indicated in fig. 4-5 can tend to etch down fast because of the large empty volume from the voids. The etch rate was ~260 Å/min, which was slow enough to allow more control as the etching progressed into the void-NW network of the MQW and n-type layer. The etching was monitored by removing the sample and performing photoluminescence (PL) measurements on the etched areas after every ten minutes of etching. The different layers could be identified by their different PL spectrums. P-type GaN gives a broad-band blue emission around the 430-440 nm range, while the MQWs would give a very strong emission at blue or cyan wavelengths. The n-type GaN, however, would give an emission dominated by the band-edge peak for GaN at 365 nm (and very weak yellow luminescence). Since the NW heights were very random across the sample, care was taken to monitor multiple points of the sample. If the PL signal resembled the
MQW or the p-type, then the sample was taken back to etch for a further 10 minutes. When majority of the sample gave PL emission resembling the band-edge peak for GaN (n-type) and no other emission, the etching process was stopped and was concluded to have penetrated enough into the n-type layer.

Both p-type and n-type metallic contacts were deposited via electron beam evaporation followed by annealing at 500 °C under N2 for four minutes. Ni/Au metallic layers as a p-type contact were 500 Å and 1000 Å thick, respectively. Ti/Al/Au metallic layers as a n-type contact were 250 Å, 500 Å, and 1000 Å thick, respectively. The top p-type contact has a ring shape and light was collected from the back surface of the sapphire substrate. The device characterization and analysis of the results is discussed in the next section.

4.3.2. DEVICE CHARACTERIZATION

Electroluminescence (EL) characterization of both the NW LED as well as the c-plane LED was carried out by using tungsten needle probes for contacting the metal. A Keithley 2430 SourceMeter was used for current injection and was operated in a continuous wave (CW) mode. The light emitted was collected from the sapphire substrate end of the sample. The light was collected normal to the substrate using a 600 μm diameter optical fiber coupled to an Ocean Optics USB2000 spectrometer.
Figure 4-6 shows the EL spectrum for both the NW LED and the c-plane LED at different injection currents. Different orientations of the NW MQWs contribute to the EL spectrum of the NWs LED shown in fig. 4-6(a). Based on TEM results, the (1101) and (1122) are the dominant semi-polar plane orientations for the NW MQWs while the (1100) [m-plane] and (1120) [a-plane] are the non-polar plane orientations for the NW MQWs. The c-plane LED shows a 17 nm shift in the 40-100 nm applied current range as well as lower EL intensity, probably due to QCSE in the polar orientation, while a smaller shift of about 1 nm and higher EL intensity is observed for the NWs-LED, as its MQWs are oriented along semi-polar and non-polar orientations which have reduced QCSE and no QCSE respectively.
The relative light-output power was measured by using a Si photo-detector placed about 2 cm below the device. Figure 4-7 shows the light-output power for both the LEDs with increasing injection currents. A 3 times increase is clearly observed from the NW LED compared to the c-plane LED. This huge improvement in light-output from the NW LED could come from multiple factors that are discussed in the next section.

![Graph showing light output intensity vs injection current for NWs LED and c-plane LED.](image)

**Fig. 4-7**: Light output intensity of the c-plane LED and the NW LED vs injection currents.

Both these investigated LED structures were grown again, but this time without the p-layer and the electron-blocking layer. The MQW region was instead capped with a thin layer of GaN, about 30-40 nm. These MQW structures were sent to Pennsylvania State University as part of a collaborative study for temperature-dependent PL characterization. The results are shown in fig. 4-8(a) and fig. 4-8(b). The room temperature PL intensity of the NW-
MQWs integrated over its emission band was found to be 10 times that of the c-MQWs. This improvement in light emission properties is even greater than that observed from the EL emission. This is probably due to greater participation from the non-polar planes during PL relative to their participation in the EL emission. As seen in fig. 4-8(c), the p-GaN layer, sometimes, does not connect to the non-polar MQWs and thus there is negligible hole injection into the non-polar MQWs, thereby reducing their participation for the EL emission process.

Fig. 4-8: Temperature dependent PL spectra of (a) NW MQWs and (b) c-plane MQWs. (c) NW LED Schematic for the case when the p-layer does not connect to non-polar MQWs.

4.3.3. FACTORS CONTRIBUTING TO HIGHER LIGHT OUTPUT

Listed below is a discussion of the various factors that could contribute to the higher light output observed for the NW LEDs.
**Reduction of Dislocation Density**: Dislocations and defects can increase the rate of non-radiative recombination and impact the internal quantum efficiency of the LED. The GaN NWs template, on which the NW LED is grown, is obtained by maskless etching. The formation of these NWs in GaN is attributed to the etching away of dislocations [25, 26] and so the NW template on which the LED is grown should have a reduced dislocation density. The reduction in dislocation density has been shown to be in the range of 2-3 orders of magnitude for the GaN overgrown on the GaN NWs [25, 26]. This reduced dislocation density could have some effect on the higher light output though the contribution is expected to be minor as the efficiency of In$_x$Ga$_{1-x}$N-based LEDs is less sensitive to defects and dislocations. Compositional inhomogenities in the InGaN layer induce localization of carriers to form quantized excitons, whose density exceeds that of the defects, resulting in a low probability of carriers interacting with a defect [27]. However, various groups have shown that a lower density of dislocations in the GaN template can result in improvement in the LED emission [28, 29, 30].

**Reduction of QCSE**: The MQWs for the NW LED are grown on the semi-polar and non-polar facets of the GaN NWs. The dominant orientations of these facets are indicated in fig. 4-9. The reduced piezoelectric field on the semi-polar MQWs will reduce the spatial separation between the electrons and hole wave-functions within the quantum well and thus result in a higher rate of radiative recombination. The non-polar MQWs have zero
piezoelectric field but their contribution to EL emission from the NWs-LED is expected to be very less as discussed earlier.

**Fig. 4-9**: Schematic of conformally overgrown MQWs on the semi-polar and non-polar facets of the GaN NWs. The indicated orientations are the dominant ones observed from TEM studies.

It is known that the band bending within the quantum well due to QCSE will red-shift the transition wavelengths. Figure 4-10 shows the shift in the peak wavelengths of both the investigated LEDs with increasing current density. With increasing current density, the injected carriers begin to screen the piezoelectric field induced by the polarization charges at the interfaces of the well. Lesser of a field is now experienced within the well and so the bands within the quantum well will begin to flatten and the emission wavelengths will blue shift as seen in fig. 4-10. The NW LED exhibits a smaller shift of 8 nm relative to the 17 nm shift for the c-plane LED. This reduced peak wavelength shift is attributed to the reduced
piezoelectric field for the semi-polar quantum wells in the NW LED relative to the large piezoelectric fields in the polar quantum wells of the conventional c-plane LED. Also, the peak wavelength for the NW LED starts to saturate at a much lower current density than for the c-plane LED. This is indicative of a reduced carrier density required to screen the smaller piezoelectric fields for the NW LED and further reiterates the reduced QCSE for the NW LED. At higher current densities beyond 50 A/cm$^2$, there may be a very minor shift arising from band-filling effects and it is extremely gradual [31, 32].

From the temperature-dependent PL measurements, shown earlier in fig. 4-8, the IQE for the NW MQWs was estimated to be about twice that of the c-plane MQWs [33] and this improvement is primarily attributed to the reduced QCSE.

![Electroluminescence peak wavelengths for both NW LED and the c-plane LED vs current density.](image)

**Fig. 4-10**: Electroluminescence peak wavelengths for both NW LED and the c-plane LED vs current density.
**Increased MQW Area** : MQWs on the semi-polar planes will have an effective area larger than that of the c-plane by a factor $2^* \frac{1}{2\cos(\theta)} = \frac{1}{\cos(\theta)}$ where $\theta$ is the inclination angle between c-axis and normal axis of the particular crystallographic semi-polar plane as shown in fig. 4-11.

![Schematic for the relative increase in MQW area of NWs-LED relative to conventional planar c-plane LED.](image)

**Fig. 4-11** : Schematic for the relative increase in MQW area of NWs-LED relative to conventional planar c-plane LED.

The dominant semi-polar orientations for the MQWs are (1101) and (1122), which make angles of 62° and 58° respectively with the growth plane or c-plane. This would provide a relative increase of about 2 times for the total surface area of MQWs for the NW LED compared to the c-plane LED for identically sized devices. There would also be an extra area contribution from the non-polar MQWs. This increased active area of light emission could be a reason for the higher light output.
Wave-guiding by embedded voids: The NWs-LED has an embedded void network within it. The voids’ dimensions can vary from 0.2-0.5 μm in diameter and 0.5-2 μm in height. These voids are filled with N₂ and H₂ gases during the growth and thus have a refractive index similar to air of ~1. As a result of this, the higher index GaN region in between two adjacent voids forms an embedded waveguide for the light generated within the LED. It is already known that for a conventional LED, majority of the light is outside the light escape cone and gets trapped within the LED structure by total internal reflection. This is illustrated in fig. 4-12(a). In fig. 4-12(b), the embedded voids of the NW LED help redirect or guide some of the photons into the light escape cone through reflection and diffraction. Also, as the voids are in close proximity of the light source (MQWs), there is greater interaction of the light with the voids. This wave-guiding effect of the embedded voids can be a significant factor to the higher light output observed with NW LEDs.

While measuring the light output power with the current Si photodetector setup, the light leaving the side walls of both the investigated LEDs (c-plane and NW) is not captured. However, it is expected that the emission from the side walls of an LED structure is only a small proportion of the total light emission especially for large area LEDs as the laterally travelling light gets absorbed by the active region, by metal contacts etc [34, 35, 36, 37]. The absorption coefficient for GaN in the visible range, which is less than the band gap of GaN, has been reported to be about 100 cm⁻¹ [14]. Though this value is small, the absorption loss could become significant over 100-200 μm of propagation, eg. for α ~ 100 cm⁻¹, more than 60% of the light could be lost by propagating about 100 μm laterally within the LED chip.
The redirection of photons by the embedded voids is thus, believed, to recover some of the laterally travelling light that would be lost.

**Fig. 4-12**: Schematic illustration of light extraction mechanisms for the conventional c-plane LED as well as the NW LED.

### 4.3.4. RELATIVE CONTRIBUTIONS OF THE VARIOUS FACTORS AT DIFFERENT CURRENT DENSITIES

In the previous section, four factors were attributed to the higher light output for the NW LED compared to c-plane LED. Of these, the reduced QCSE and the reduced dislocation density contribute towards the IQE and will be dependent on the current (carrier) density in the LED as defined by the ABC model below. On the other hand, the wave-guiding by the embedded voids and the higher MQW surface area are dependent on the geometry of the LED and they would not be affected by the current density. The external quantum efficiency of an LED that is a product of the IQE and the extraction efficiency can be rewritten using the ABC model for carrier recombination as,
\[ \eta_{\text{EQE}} = C_{\text{ext}} \eta_{\text{IQE}} = C_{\text{ext}} \frac{Bn^2}{An + Bn^2 + Cn^3} \]

where \( \eta_{\text{EQE}} \) is the external quantum efficiency, \( C_{\text{ext}} \) is the extraction efficiency, \( n \) is the carrier density in the active region of the LEDs, \( A \) is the non-radiative SRH recombination coefficient, \( B \) is the bimolecular radiative recombination coefficient and \( C \) is the Auger recombination coefficient. The reduced QCSE will increase the radiative recombination term, \( Bn^2 \), while the reduced dislocation density will decrease the non-radiative recombination rate through defect levels which is represented by the \( An \) term of the above equation.

To better understand the interplay of the 4 factors contributing to higher light output in the NW LED, the ratio of the NW LED light output to that of the c-plane LED is calculated and referred to as \( R \). This ratio, \( R \) is then plotted for increasing current densities in Fig. 4-13. From the earlier light output measurements, the NW LED was estimated to be about three times brighter than the c-plane LED. However, from fig. 4-13, it can be seen that at the lower current densities, the \( R \) is much higher. The higher \( R \) is attributed to the reduced QCSE phenomenon for the NW LED relative to the c-plane LED. With increasing current density, the carriers will screen the piezoelectric field within the quantum wells of both LEDs and the reduced QCSE factor might be less of an added advantage for the NW LED and thus, \( R \) starts to drop till it reaches about 3. It can be seen that \( R \) approaches 3 around 50-55 A/cm\(^2\) and then stays constant. From fig. 4-7 earlier, it was observed that the EL peak wavelength for the c-plane LED starts to saturate around 40-50 A/cm2 which would coincide with the carriers completely screening the internal electric field and negating the QCSE. The effect of reduced dislocation density for the NW LED, though minor for InGaN-based LEDs, is
expected to be relevant only at the lower current densities [28]. This might also contribute a bit to the higher ratio $R$ observed at lower current densities in fig. 4-13.

![Graph: Ratio of light-output intensity of NW LED to c-plane LED](image)

**Fig. 4-13**: Ratio of the NW LED light output to the c-plane LED light output plotted vs current density.

For higher current densities, the $R$ stays almost constant at 3. The wave-guiding of light by the embedded voids and the higher MQW surface area would still be active in the NW LED as they arise from the geometry of the LED structure and do not depend on the current density. So, the 3 times increase in the higher current density regime is mostly attributed to better light extraction and greater surface area for light generation. The better light extraction by the presence of voids is explored further in the next section.
With identical currents injected into both the investigated LEDs and assuming identical carrier injection into the MQW region for both, the increased area of MQWs for the NW LED is expected to result in a lower carrier density within the MQWs. The radiative recombination rate increases with the current density and so the increased MQW area is speculated to add less of an advantage for the NW LED relative to the c-plane LED.

At the very high current densities, Auger recombination is expected to be relevant in both the investigated LED structures. So the injected current densities are restricted to less than 100 A/cm\(^2\) where the effect of Auger is expected to be small enough to not impact the investigation significantly.

### 4.4. MODELING OF VOID-LIGHT EXTRACTION BY FDTD SIMULATIONS

From the previous section, it is understood that the wave-guiding by embedded voids might have a very significant contribution to the higher light output of the NW LED. So, in this section, it is attempted to model and simulate the light extraction by these voids and understand it better.

#### 4.4.1. INTRODUCTION TO THE SIMULATION MODEL

The finite difference time domain (FDTD) algorithm is useful for design and investigation in a wide variety of applications involving the propagation of electromagnetic radiation or heat transfer through complicated media. For FDTD implementation, the time-dependent Maxwell’s equations in partial differential form are discretized in space and time over a computational domain region to form a finite-difference set of equations. The
computational domain is simply the physical region over which the simulation will be performed. The E and H fields are determined at every point in space within that computational domain. The material parameters and their variations over the computational domain must also be specified. The output of the simulation is usually the E or H field at a point or a series of points within the computational domain. The simulation evolves the E and H fields forward in time. In this manner, a time evolving solution for the fields is obtained. To obtain a steady state field profile at a specified frequency, a discrete fourier transform of the time domain solution over the computational domain is performed. Multiple field profiles at multiple frequency points over a broadband source could be weight-averaged to obtain an approximate steady state profile for a broadband source.

Lumerical FDTD is the software package that is utilized below to model and simulate the intended LED structure. The simulation in this software is based on the FDTD algorithm. The basic simulation model is explained below. Figure 4-14 illustrates a basic simulation model, designed using the software, which would be used to replicate the LED structure. The model is a 2D-plane representation of the basic LED structure and surroundings. The various components of the model are described below:

- The regions marked as GaN of fig. 4-14 represents a region with refractive index of 2.4 which is that of GaN [14]. These regions are in black.
- The blue rectangle of fig. 4-14 represents a region with refractive index of the substrate for the LED. The index is set to 1.7 when representing the case of sapphire substrate. Sometimes, the substrate is separated from the LED by a laser lift-off
process and in this case we would have the LED surrounded by air on all the surfaces.

To represent this scenario, the index could be set to 1.0.

![Diagram of LED structure](image)

**Fig. 4-14**: Model to represent the LED structure and its surroundings for the FDTD simulation.

- The orange rectangular boundary line of fig. 4-14 demarcates the region within which the simulation is performed. Separate boundary conditions are set for the different
surfaces of the rectangular boundary line. The bottom, left and right surfaces of the rectangular boundary behave like a perfect electromagnetic (light) absorber that does not reflect any light back into the simulation region. This would mean that any light that reaches these 3 surfaces has been sucked out of the simulation region and will not reflect back in. These are commonly referred to as perfectly matched layers (PML) for electromagnetic simulations. On the other hand, the top surface behaves like a 100% reflector. It is intended to simulate the effect of a top metal contact that reflects the light back into the LED.

- The electromagnetic source is chosen to be an electric dipole point source which is the preferred model for emulating the MQW emission in these LEDs based on other FDTD simulation efforts performed for InGaN-based LEDs [38, 39]. The point dipole source propagates in the 2D-plane of the simulation region and has its electric field in the direction perpendicular to the 2D-plane. The source spectrum of the dipole is shown in fig. 4-15. The emission spectrum is reasonably broad to represent that of an LED.

![spectrum vs wavelength](image)

**Fig. 4-15**: Spectrum of the electric dipole point source used in the FDTD simulations.
The regions in the model are not designed with any absorption properties. So the electromagnetic waves (light) do not lose any power during propagation within the simulation structure and exit the region only when they are incident on the PML boundaries. This would mean any absorption within the active region or by the metal contacts has not been accounted for in the model. The region of GaN within the simulation boundary measures 2.6 µm in the vertical direction that is representative of the total thickness of the GaN LED structure (n-layer + MQWs + p-layer).

4.4.2. NW LED MODEL

To model the NW LED features, additions are made to the above basic model. These are shown in fig. 4-16. The voids are modeled as elliptical regions with a refractive index of 1 and have dimensions of 0.4 µm and 1.2 µm along the lateral and vertical directions of the LED. The spacing between adjacent voids is 0.8 µm. The elliptic voids are periodic and thus, 6 voids are included within the 8 µm lateral dimension of the simulation model.
4.4.3. EFFECT OF POSITION OF THE LIGHT SOURCE FOR THE NW LED

The distance and position of the point light source from the voids is expected to have an effect on how much redirection of the light could be caused by the voids. As a result, two different positions of the light source are investigated, both of which would represent points that lie within the MQWs grown along the facets of the GaN NWs. Figure 4-17(a) represents a point on the top of the tip of the GaN NWs that is in the middle of the embedded waveguide while fig. 4-18(a) represents a point very close to the void that would lie at the edges of the embedded waveguide. The substrate refractive index is set to 1.7 to represent sapphire in this case. The angle for total internal reflection in this case would thus be about 45° for the GaN-sapphire interface.
The dipole source has an electric field component in the direction perpendicular to the 2-D simulation plane, referred to as the z-axis. The steady state profile for $E_z$ is obtained for the two cases of positions of the dipole source previously mentioned. In the first case shown in fig. 4-17(b), it can be seen that the electric field intensity is quite high within the waveguide just below the dipole source arising from metal reflections at the top surface and Fresnel reflections at the bottom surface. It is also interesting to observe that the profile of the intensity takes the curved shape of the adjacent void suggesting a guided mechanism for the light propagating through. In the second case shown in fig. 4-18(b), the light source is very close to the void and hence experiences strong diffraction, so much so that the light is seen to be extracted from the sapphire substrate at an inclined angle rather than from the normal direction. The diffraction effects are stronger when the distance between the source and the diffracting object (embedded void) are of the order of a wavelength. Wavelength inside another medium would change to $\lambda/n$, so a wavelength of around 470 nm for the light photon, would be equivalent to around $470/2.4 \sim 196$ nm when inside the GaN material. In the first case then, the point source would be about 2-3 wavelengths distance away from the voids, leading to less pronounced diffraction.

The conventional c-plane LED case is also simulated by removing the embedded void structures from the case of fig. 4-17(a). The corresponding $E_z$ profile obtained is shown in fig. 4-19. In the absence of any diffracting obstacles, it is observed that no directional nature is observed in the light that is extracted into the substrate.
Fig. 4-17: (a) Model representing source dipole position in the center of the embedded waveguide (b) Steady state $E_z$ profile for the model in (a).
Fig. 4-18: (a) Model representing the source dipole position very close to an embedded void (b) Steady state $E_z$ profile for the model in (a).
4.4.4. LIGHT EXTRACTION BY SIMULATION

In this section, we compare the light extraction abilities of the NW LED and the c-plane LED structures by simulation. In the previous section, it was observed that the position of the light source for the NW LED can have a significant effect on the light path. To average out the effect of position in the NW LED, multiple dipole point sources are used. A series of 9 dipole point sources of equal strengths are used in either LED structures and are assembled in the center of the LED model. Figure 4-20 shows the dipole positions for either LED structures. For the NW LED, the dipole assembly is placed between the 2 center voids and resembles the semi-polar MQWs conformally overgrown on the GaN NWs as shown in fig. 4-20(b) while for the c-plane LED, the dipole assembly is placed in a straight line shown in fig. 4-20(a) with roughly the same inter-source spacing as in the NW LED.
The steady-state solution is obtained for a specific frequency or for a monochromatic source. It is numerically very intensive to obtain such a solution for a broadband source like that of the LED. In addition, with a monochromatic source, the steady solution can be strongly influenced by strong temporal coherence between the adjacent dipole sources. So, the following time-domain simulation methodology is followed to obtain the light extraction ability of each of the investigated LEDs:

Each of the point dipoles are designed to emit a single gaussian pulse each, of a short duration. The gaussian pulse has a broadband representation in the frequency domain. The pulse-width of adjacent dipoles is chosen to be different values to induce randomness. The
total simulation time is designed to be much longer than the pulse duration as shown in fig. 4-21. This is done so to allow the pulses to propagate over the simulation region for a sufficiently long time. The intensity of the pulses slowly dies down during the simulation time, when any electromagnetic (EM) field is incident on the left, right and bottom boundaries of the simulation region because they act as perfect absorbers (acting like PML layers as discussed earlier). The top boundary, on the other hand, acts as a 100% reflector as discussed before. Any EM field that avoids undergoing total internal reflection and enters the sapphire substrate, is assumed to be extracted as the measured light-output power of the LED. The model for this simulation is shown in fig.4-22. The yellow line recorders on the left, right and bottom boundaries of the sapphire substrate are $E_z$ field intensity recorders to capture the intensity that enters the sapphire substrate. These recorders record the $E_z$ intensity as a function of the simulation time and also record it for each point along the length of the recorder. These recorders are named as C-1, C-2 and C-3 for the bottom, left and right recorders of the c-plane LED structure in fig. 4-22(a) and are named NW-1, NW-2 and NW-3 for the bottom, left and right recorders of the NW LED structure in fig. 4-22(b). Each of these recorders yield a 2-D profile plot that has the position along the length of the recorder as the x-axis, has the progressing simulation time along the y-axis and the color on the 2-D plot represents the strength of the intensity. Blue represents zero intensity and the more red the color, the higher the intensity recorded.
Fig. 4-22: Model for FDTD simulation of (a) c-plane LED and (b) NW LED. The yellow lines in the substrate are field recorders that record the $E_z$ field intensity with time over their length.

The resulting 2-D profiles for the 3 recorders in both of the LED models of fig. 4-22 are shown in fig. 4-23. For each of the profiles, at the start of the simulation time, zero field intensity is recorded (blue color) because it takes some time for the dipole pulse to propagate through the LED structure, the sapphire substrate and finally reach the recorders. Some of the EM field would undergo reflections from the top surface (metal contact) or reflections from the voids (for the NW LED case) and thus they would reach the recorders a certain time delay after the initial recording. Thus, there would be time gaps between the field recordings corresponding to reflections and these are observed in the profiles of fig. 4-23. For figs. 4-23(a)-(c) of the c-plane LED, it is observed that there are just one or two delayed bands of recorded fields which is most likely occurring from the reflection at the top metal contact. For the figs. 4-23(d)-(f) of the NW LED, there are continuous recurrences of field recordings for a much longer time and with much smaller time delays compared to that for the c-plane
LED. These are indicative of multiple reflections with adjacent voids, path diversions due to diffraction as well as the reflection from the top contact resulting in varying time delays.
Fig. 4-23: $E_z$ field intensity profiles. X-axis is the length of the recorder, y-axis is the simulation time. Dark blue color represents zero $E_z$ intensity and more red color represents high intensity on the color scale. (a), (b) and (c) are profiles for the c-plane LED for the C-1, C-2 and C-3 recorders respectively. (d), (e) and (f) represent profiles for the NW-1, NW-2 and NW-3 recorders for the NW LED.
The 9 dipoles used for either LED models had identical design parameters except for their location position. So the initial input EM field to both LEDs was the same. This would mean if the total intensity recorded in fig. 4-23 for either LEDs, over the entire simulation time, could be calculated then we would have a comparison of their extraction efficiencies. The total intensity calculation is obtained by the following methodology:

Each 2-D profile plot of fig. 4-23 is composed of many tiny pixels. Each pixel, defined by a particular position on the recorder and a particular instant of time, has an associated color depending on the $E_z$ intensity value. If the $E_z$ intensity values over the entire 2-D profile area are all added up, it would correspond to the total field intensity recorded by a particular recorder over the entire simulation time. The total EM field that entered the sapphire substrate and was incident on a specific recorder has thus been obtained. By summing up the extracted EM fields from all the 3 recorders (left, right and bottom) of a particular LED model, the total extracted field is estimated.

By summing up the total field-power extracted over the entire simulation time in both of the investigated LED structures, a 2.88 times higher extraction ability was demonstrated for the NW LED. This is close to the 3 times higher light output observed for the NW LED relative to the c-plane LED. It is believed that the relative advantage of NW LED over the c-plane conventional LED arises from a combination of both, better light extraction and reduced QCSE. It is speculated that this model might be over-estimating the extraction ability to a certain extent as there are a number of factors that are not accounted for in the simulation model. Some of these unaccounted factors are:
Absorption in the top metal contact layer has not been accounted for. This could significantly impact the light output obtained for either investigated cases. With the NW LED relying on many multiple reflections for a single photon, each incidence with the top metal contact would result in some losses.

The void dimensions and interspacing are random and vary significantly over the sample and it would not be possible to include the randomness of these dimensions into the model and make an estimate. However, it might be worthwhile to study the effect of these dimensions on the light extraction ability for the NW LED.

Absorption in the MQW InGaN region or the GaN region has also not been accounted for.

LED is strictly speaking, an incoherent light source. However, for the simulation, there could be some coherence since all the dipole sources emit at the same time. The resulting interference can result in redirection of the propagating vector of the electromagnetic light wave and show up as erroneous extraction or lack of extraction.

This is a 2D planar simulation and only one orientation of the electromagnetic field of the light wave ($E_z$) has been considered.

4.5. CONCLUSION

The LED overgrown on GaN NWs is fabricated and characterized. It was observed to have a light output power that was 3 times higher than that of a conventional c-plane LED which was grown and fabricated alongside the NW LED. The higher light output power was attributed to four factors, namely, reduced dislocation density, reduced QCSE phenomenon, 

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increased MQW surface area and better light extraction through waveguiding by the embedded voids network. The better light extraction by waveguiding was in particular, believed to be responsible for a large part of the higher light output, especially at the higher current densities. FDTD simulations were performed to further the understanding of the waveguiding phenomenon and also simulate the better extraction ability of the NW LEDs relative to the c-plane LEDs.

4.6. REFERENCES


CHAPTER 5 : INGaN-GaN MQW STRUCTURES AND LEDS GROWN ON SEMI-POLAR AND NON-POLAR BULK GaN SUBSTRATES WITH HIGH INDIUM PERCENTAGES

5.1. INTRODUCTION

Increasing the lumen per watt as well as the lumen per dollar for nitride-based LEDs will enable wide scale adoption of these LEDs and greatly reduce energy consumption. One area where these LEDs incur losses is the use of phosphor coatings, which are used to achieve white color or broad emission spectrums. The nitride LEDs emit efficiently in the blue region but the efficiencies drop significantly for the green spectral region and beyond. The yellow and red spectral regions are currently addressed using AlGaInP LEDs. The absence of an efficient LED solution for the green spectral region is commonly referred to as the “green gap” issue, which is illustrated in fig. 5-1. Additionally, the human eye is most sensitive to green light and thus, the green spectral region is very critical to display systems and lighting. The luminosity function, that represents the human eye responsivity to light is also indicated in fig. 5-1 and can be seen to peak at 555 nm. Thus, it is of great interest to the scientific community to explore approaches for improving the green emission from nitride LEDs.
This green gap issue is closely related to the large piezoelectric fields and the poor quality of InGaN films with high indium percentages. A large internal electric field is present in the quantum wells of almost all commercial LEDs available today, as the conventional growth plane for the LEDs is the polar c-plane. One approach to tackle the green gap issue is to grow on semi-polar and non-polar GaN films. In this chapter, InGaN-GaN MQW LED structures grown on semi-polar and non-polar bulk GaN substrates are characterized. The potential of different crystal orientations is studied. The use of a novel growth approach to enable greater indium incorporation (for greener emission) is also discussed.
5.2. WHY SEMI-POLAR/NON-POLAR BULK GaN FOR GREENER LEDS?

For InGaN-GaN MQW LEDs, there are primarily two approaches to obtain green emission:

- Increase the indium percentage – The In\textsubscript{x}Ga\textsubscript{1-x}N band gap decreases with increase in x and so a higher indium percentage within the quantum well will mean the emission from the well will be at a larger wavelength. Increasing the indium percentage can increase the compressive strain in the well. The resulting large piezoelectric field will reduce the emission intensity from the wells owing to QCSE.

- Wider quantum wells – For thinner quantum wells, the quantum confinement energy will be greater and will blue-shift the transition energy within the quantum well. A wider quantum well can thus reduce the quantum confinement energy and increase the wavelength of emission from the quantum well. In the presence of a band-bending within the quantum well, the electron and hole wave-function overlap will be much reduced for a wide quantum well. This will again reduce the emission intensity from the well.

The conventional growth plane for the InGaN-GaN MQW LEDs is the polar c-plane. As discussed in earlier chapters, the large piezoelectric fields will cause band-bending within the quantum wells grown on the c-plane which spatially separates the electron and hole wave-functions and reduces the probability of radiative recombination. This is illustrated in fig. 5-2(a). This QCSE phenomenon is worsened in either of the above approaches used for greener emission. By increasing the indium percentage, there is a greater lattice mismatch which
induces greater compressive strain within the InGaN quantum wells. This will result in a greater piezoelectric field and thus more severe band-bending within the quantum well. For wider quantum wells, there is greater separation of the electron and hole wavefunctions, which further reduces the wave-function overlap and thus, their rate of radiative recombination. Thus, with the conventional polar growth planes, achieving efficient green emission becomes very challenging and hence it becomes important to explore the semi-polar and non-polar crystal orientation for growing the greener emitting MQWs.

**Fig. 5-2**: Electronic band structure for the InGaN quantum well grown on a (a) polar c-plane and (b) a non-polar crystal plane.

The non-polar planes, especially the a-plane and m-plane, do not have a piezoelectric field along the axis of these planes. There is thus, complete elimination of the band bending
within the MQWs on these planes as shown in fig. 5-2(b) which enables very good overlap of the electron and hole wave-functions. These planes, thus, provide an ideal solution for green LEDs. Alternatively, the semi-polar orientations that have a reduced piezoelectric field are also an attractive candidate for the green LEDs and require investigation. The piezoelectric field in these semi-polar planes is a function of both the orientation of the crystal plane with the c-plane as well as the percentage of indium. Theoretical studies for the variation of the field with the inclination angle of the plane with the c-plane have been conducted [2]. It has been concluded that certain orientations of the semi-polar planes can also have a zero piezoelectric field along their growth axis, similar to the non-polar planes and hence further experimental investigation of the semi-polar planes is desired. However, finding suitable substrates to grow the non-polar and semi-polar GaN films has been challenging. By making c-oriented hydride vapor-phase epitaxy (HVPE) GaN grow thick enough (~5 mm), it is possible to then slice in different orientations, thereby obtaining non-polar and semi-polar bulk GaN substrates. This is illustrated in fig. 5-3. Such samples were provided by Kyma Technologies and have been used for the growth of MQW structures and LEDs discussed in this chapter.
Fig. 5-3: Obtaining non-polar and semi-polar bulk GaN substrates by slicing c-plane bulk GaN boules

5.3. HIGH INDIUM INCORPORATION

5.3.1. INDIUM INCORPORATION – OVERVIEW AND CHALLENGES

As discussed earlier, it is desired to achieve green emission from the LEDs grown on the non-polar and semi-polar bulk GaN substrates. This would require incorporating high indium percentages within the InGaN quantum wells. The fundamental difficulty in incorporating indium during the epitaxial growth of In$_x$Ga$_{1-x}$N layers arises from the high equilibrium vapor pressure of N$_2$ required during growth to prevent In-N bond from dissociating [3]. In addition, a weak In-N bond restricts the growth to low temperatures where it is more difficult to satisfy the vapor pressure requirements. A growth model for InGaN was developed by Bedair in the 90s [4] and is illustrated in fig. 5-4. With a simple mass balance, the flux for the various processes can be written as,

\[ F_{in} = F_s + F_d + F_m \]
where $F_{in}$, $F_s$, $F_d$ and $F_m$ represent the fluxes for total incident indium, indium incorporation in the solid, indium desorption from the surface and indium metal droplet formation, respectively, all in atoms/cm$^2$·s. The residence lifetime of an In adatom at the surface is:

$$\tau = \tau_0 e^{E_d/kt}$$

where $E_d$ is the activation energy for desorption, $k$ is the Boltzmann’s constant and $T$ is the temperature. Therefore, the desorption rate, $F_d$, which is inversely proportional to the residence time of the In atom on the growth surface can be written as,

$$F_d \propto e^{-E_d/kt}$$

It is well recognized that the $F_d$ for In is much higher than that of Ga [5] since the In-N bond is weaker and this is particularly observed from higher indium incorporation at lower temperatures. This would suggest a very small residence lifetime for the indium adatom at the growth surface. Thus, low temperatures, sufficient In flux and high nitrogen pressures favor In atom adsorption at the surface.
In addition to the above growth issues, there is the issue of a fairly high lattice mismatch when growing InGaN on GaN, especially for higher indium percentage alloys. This mismatch implies that the critical layer thickness (CLT) for the generation of misfit dislocations can be quite small. When the InGaN layer starts to grow on GaN, it is initially strained to the GaN layer and then beyond a certain thickness, referred to as the CLT, relaxation begins to set in and misfit dislocations, in particular V-defects [6], are introduced into the InGaN layer. Also, the higher the indium percentage, smaller will be the critical thickness. The Bedair group quantitatively established the CLT for InGaN/GaN heterostructures [7] and obtained a value of ~50 nm for 20% InGaN films. Some recent work has shown that the CLT could be even smaller [8]. This could impose strict tolerances on the
number of quantum wells or their widths, for the LEDs operating in the green spectral region which would have a higher indium percentage.

Lastly, the large difference in interatomic spacing between GaN and InN gives rise to a solid phase miscibility gap. This gap results in phase separation for high indium containing InGaN layers [9]. This will make it challenging to achieve homogenous InGaN layers and will degrade the optical quality for the greener LEDs.

5.3.2. NEW GROWTH APPROACH FOR HIGHER INDIUM INCORPORATION

Prior to growing on the semi-polar and non-polar bulk GaN substrates, it is decided to first optimize the growth conditions by growing on sapphire substrates to achieve high indium incorporation in the InGaN quantum wells and efficient green emission. As discussed in the previous section, lower growth temperature for the InGaN layer would reduce the In desorption rate and enable higher indium incorporation. An n-type GaN:Si layer, about 1 μm thick was grown on the sapphire substrate followed by 4 periods of InGaN/GaN quantum well-barriers. The quantum wells were grown for an intended thickness of 2 nm. This structure was completed with a final thin cap of GaN, about 20 nm thick. This cap was thin enough to enable the laser beam during photoluminescence (PL) characterization, to penetrate and reach the MQW region easily.
Fig. 5-5: Room temperature PL for c-plane InGaN-GaN MQW structures grown on GaN films on sapphire. (a) PL at different MQW temperatures and (b) PL variation on 2 different points on the sample.
Figure 5-5(a) shows the room temperature (RT) PL spectrum for 4 different MQW structures grown at different temperatures for the InGaN quantum well region. It can be seen that though the wavelength gets longer with lower temperatures, the emission spectrum gets broader, weaker and is no longer single-peaked. This indicates the possible onset of phase separation in the InGaN layers or relaxation of the InGaN quantum well layers due to the increasing percentage of indium. The introduction of defects during relaxation of the InGaN film will lead to more deterioration in the optical quality of the InGaN quantum wells and suggests that continued reduction in temperature may not be desired to obtain green emission. Figure 5-5(b) shows the room temperature PL spectrum at the center and much away from the center for the MQW temperature grown at 660° C. There is a shift of about 12 nm between the PLs of the 2 points. The growth rate variation across the 14 mm x 14 mm sample is about 10-20% and so the quantum well thickness variations across the wafer is expected to be small. This would mean that the blue shifting due to well thickness dependent quantum confinement should not be large enough to account for the 12 nm shift observed in fig. 5-5(b). Also, it is expected that the temperature is relatively uniform throughout the sample during growth.
To explain the shift across the wafer, the growth reactor setup is shown in fig. 5-6. There are 2 gas flow channels separated until about few centimeters above the susceptor. The metalorganics, namely trimethyl indium (TMIn) and triethyl gallium (TEGa), and the N\textsubscript{2} carrier gas, flow through one channel while NH\textsubscript{3} (cracked NH\textsubscript{3} – source of nitrogen atom to bond with In, Ga) flows through the other channel. The flows in either channel are balanced. It is believed that sufficient NH\textsubscript{3} flux may not be reaching under the III-column channel and sufficient TMIn flux may not be reaching under the V column channel. The rotation speed of the susceptor is 60 rpm. So the In atoms from the III-channel that impinge the surface take about half a second to come under the influence of the NH\textsubscript{3} flux. As discussed earlier, the indium atom has a low residence lifetime and a large desorption rate. This will result in the indium atoms desorbing much before they come under the influence of NH\textsubscript{3} and get stabilized. The center of the growth sample would receive a more balanced gas flux from
both channels and hence the indium atom could get stabilized more quickly by the ammonia flux. This would enable more In incorporation at the center of the sample and would explain the shift observed in fig. 5-5(b).

The above study indicated that a change in growth mechanism might be required. So the growth reactor was modified as shown in fig. 5-7. For the conventional growth, the injection valve would not be activated, but during the growth of the entire MQW active region, the injection valve would be activated while simultaneously switching off the gas inlet valve for the V-column flux. The gas fluxes of both channels are now together forced through the III-column channel alone to have a “1-column” growth mode. The conventional and the new growth mode are illustrated in fig. 5-8. In the “1-column” growth mode, the entire growth surface area experiences both the TMIn flux as well as the NH₃ flux simultaneously. As was shown in fig. 5-4, there is a competition between the desorption and incorporation pathways for the flux of indium atoms. The indium atoms that are now constantly under the influence of the NH₃ flux throughout the sample have a greater chance to be stabilized and get incorporated into the growing film.
Fig. 5-7: Growth reactor modification to introduce the option of a “1-column” growth mode

Fig. 5-8: Two mechanisms for growth in the reactor, which are (a) conventionally used 2-column flow and (b) new 1-column flow
The MQW structure grown previously (fig. 5-5) is now grown under the new “1-column” growth mode with the InGaN quantum well growth temperature set to 650° C. It must be mentioned that the n-GaN layer underneath the MQW region is grown conventionally with the 2-column growth mode. Figure 5-9 shows the PL comparison between MQW structures grown using “1-column” and “2-column” growth modes. Green emission with a single peak wavelength of 540 nm is obtained for the “1-column” growth mode compared to the blue emission (456 nm) of the “2-column” growth mode. This longer wavelength may be a result of both: (a) greater indium incorporation, and (b) thicker wells because of a higher growth rate with the modified growth approach. Thus, a mechanism to obtain green emission has been established and will be used during the subsequent growths on semi-polar and non-polar bulk GaN substrates.
5.4. GREEN EMISSION FROM SEMI-POLAR AND NON-POLAR BULK GaN SUBSTRATES

The bulk GaN substrates, provided by Kyma Technologies, were of both semi-polar and non-polar orientations. The semi-polar orientations provided were the crystal planes - (10\(\bar{1}\)1), (20\(\bar{2}\)1), (20\(\bar{2}\)1) while the non-polar orientations provided were the crystal planes - (1\(\bar{1}\)20), (\(\bar{1}\)00), referred to as the a-plane and m-plane respectively. The polarization-induced
internal electric field within the InGaN quantum well varies for the different orientations and the study below looks to explore and investigate this aspect. Theoretical studies have been conducted in literature to study the variation of the polarization as a function of the crystal plane orientation with the c-plane and one such study [10] is shown in fig. 5-10. The semi-polar orientations investigated in this study are indicated on the figure and it can be seen that these orientations have a much reduced polarization relative to the polar c-plane.

![Graph showing total polarization for an InGaN layer grown on GaN vs angle of the semi-polar orientation with the c-plane. The curve is shown for different indium percentages. Adopted from [10].](image)

**Fig. 5-10**: Total polarization for an InGaN layer grown on GaN vs angle of the semi-polar orientation with the c-plane. The curve is shown for different indium percentages. Adopted from [10].
5.4.1. GROWTH ON SEMI-POLAR AND NON-POLAR BULK GaN SUBSTRATES

The substrates were obtained by slicing a thick boule of c-plane bulk GaN along its thickness by using a diamond wire saw in a particular direction, to expose a desired crystal orientation for the cut piece. They were then diced, smoothened and polished to make them epi-ready. These substrates were about 5 mm x 10 mm in size. Since GaN has a higher thermal conductivity than sapphire, the bulk GaN sample surface can get much hotter in the growth reactor than a conventional sapphire substrate sample for the same set temperature. So the growth temperatures of the recipe used for growing GaN on c-plane sapphire substrate, was lowered by about 30° C. Two separate structures were grown on each of the semi-polar and non-polar oriented bulk GaN substrates that were provided. One was a MQW structure capped by a thin GaN film that was intended for PL characterization and the second one was a complete MQW-LED structure that was intended for EL and complete device characterization. The bulk GaN substrates were initially solvent cleaned in an ultrasonic bath. They were then loaded into the reactor. An initial in situ etch, that acts as a chemical clean, was performed for 2 minutes at 980 ºC in an atmosphere of H₂ and NH₃. Deposition on these substrates was then carried out in the conventional 2-column flow mode with a system pressure of 350 mTorr and using a trimethylgallium (TMGa) source producing a V-III ratio of 7700. First a 750 nm layer of intrinsic GaN was deposited, followed by a 2.5 μm n-type layer of GaN:Si deposited at 975ºC. Next, the reactor was switched to a 1-column flow mode for growing the MQWs using flow of 0.75 μmol/min of TEGa and 7.64 μmol/min of TMIn. A higher ammonia flow of 2.5 L/min was used to increase the V-III ratio for the MQW
growth. Four In$_{x}$Ga$_{1-x}$N/GaN QWs were grown at 620/650°C for the well/barrier respectively. After the growth of the MQW region, the reactor was switched back to the 2-column growth mode. For the MQW structures intended for PL characterization, a thin GaN cap of about 40 nm was grown following the MQW active region. For the LED structures, the MQW active region was followed by a 20 nm thick AlGaN layer that acts as an electron blocking layer and then a 300 nm thick p-GaN layer, GaN:Mg, grown at 950 °C.

5.4.2. CHARACTERIZATION OF MQW STRUCTURES ON THE SEMI-POLAR AND NON-POLAR BULK GaN SUBSTRATES

The bulk GaN samples had variations in their crystal off-cut, thicknesses of the sample, the surfaces had scratches and damages caused during the sawing and polishing of the sample and all these factors would affect the quality of the consequent growth on the sample. So the subsequent growth of the MQW structures on the bulk GaN samples were inspected by optical microscopy for uniform growth and smooth surface and by PL for optical quality and three particular orientations, namely the a-plane, the m-plane and (2021) plane were chosen to perform transmission electron microscopy (TEM) and energy dispersive x-ray spectroscopy (EDS). The TEM characterization was performed at the Evans Analytical Group and EDS characterizations were performed by the Army Research Center at Redstone Arsenal in Alabama. The TEM images of the cross sections for the 3 samples are shown in fig. 5-11 and are used to obtain the quantum well thicknesses for each of the samples. Since the same growth recipes are used for each of the samples, the well thicknesses are indicative of the growth rates in each of the samples. It is observed that the well and
barrier thicknesses gradually increased for subsequent well-barriers. The reason for the different thicknesses is not exactly known, however, it is speculated that the gradual increase in growth rate occurs because of the 1-column growth mode used for the active region. There is no downward gas flow in one of the columns during this growth mode and the gas inlet to it is shut. Thus, it is speculated that there could be upward diffusion of some of the TEGa into this column without reaching the sample growth surface. With time, the rate of diffusion would decrease and thus more TEGa would make it to the growth surface resulting in an increased growth rate. The TMIn might also diffuse, but owing to a high In/Ga ratio, it is expected that the In incorporation would be uniform for all of the wells and would not be sensitive to the quantity of incident In flux on the growth surface [5]. Experimental studies of indium incorporation on different crystal orientations have been performed in literature. The (20\overline{2}1) orientation has been observed to have the highest indium incorporation among commonly studied orientations [11, 12] while the c-plane, m-plane and the (20\overline{2}1) orientations have been observed to have very similar incorporation of indium [13]. EDS on the TEM samples was conducted to obtain the indium composition of each of the QWs. Highest indium incorporation was estimated in the (20\overline{2}1) orientated wells of the three and this is in conformity with the literature [11, 12]. Table 5-1 summarizes the well thicknesses, growth rates and In percentages for the 3 samples.
Fig. 5-11: TEM images of InGaN-GaN MQWs grown on bulk GaN substrates of orientations (a) (2021) plane (b) a-plane and (c) m-plane.

Table 5-1: Summary of QW thicknesses, relative growth rates and In compositions for the MQW structures on a-plane, m-plane and (2021)

<table>
<thead>
<tr>
<th>MQW – a-plane</th>
<th>Thickness (nm)</th>
<th>Relative Growth Rate</th>
<th>In % composition range by EDS</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>QW – 1</td>
<td>QW – 2</td>
<td>QW – 3</td>
</tr>
<tr>
<td>MQW – m-plane</td>
<td>2.7</td>
<td>2.9</td>
<td>3.5</td>
</tr>
<tr>
<td>MQW – (2021)</td>
<td>2.3</td>
<td>2.5</td>
<td>2.7</td>
</tr>
</tbody>
</table>

Room temperature PL characterization was performed for the MQW structures grown on the different semi-polar and non-polar oriented bulk GaN substrates and the results are shown in fig. 5-12(a). The PL from the reference c-plane MQWs (1-column growth mode) grown on sapphire substrate shown on the same figure has the longest wavelength of 540 nm. Even though the indium incorporation on the c-MQW was not quantified by EDS, the QCSE-
induced red-shifting of the PL peak is believed to be the largest for the polar c-plane and thus, responsible for the long emission wavelength observed from it. The emission from the (20\overline{2}1) plane is red shifted with respect to the m-plane by ~17 nm and this is attributed to a combination of two factors, which are: higher indium incorporation (Table 5-1) and the presence of an internal electric field due to some polarization for (20\overline{2}1) MQWs relative to the zero polarization for the non-polar m-plane, as was observed in fig. 5-10. The emissions from the other semi-polar orientations, i.e. (20\overline{2}1) and (10\overline{1}1) are also are also red shifted relative to the m-plane. The indium incorporation for these latter two semi-polar orientations was not quantified by EDS. However, assuming their In incorporation to be similar to that of the m-plane, it could be said that the red-shifting of their PL peak relative to the m-plane is a consequence of the QCSE phenomenon present in these wells. It must be mentioned that the substrates provided by Kyma had varying surface morphologies, varying degrees of miscut for the crystal plane owing to polishing on the edges etc. Uniformity across the sample which was required to be able to compare trends across different substrates, was thus, very challenging.

It must be mentioned that because of the varying well widths for each structure, it is difficult to estimate if the PL is the dominant emission of a particular well or is an overlapping contribution of all the wells. Investigative studies were performed using time-integrated photoluminescence spectroscopy (TIPL) on the a-plane MQW structure by the Army Research Center at Redstone Arsenal as part of a collaborative effort. Figure 5-12(b) shows the temperature sequenced TIPL results obtained from the a-plane MQWs. It can be
seen that the a-plane sample has a much shorter wavelength than the other planes shown earlier and this is attributed to: (a) the lower growth rate (thin wells) that would result in a large quantum confinement energy that would blue-shift the PL peak wavelength, (b) lesser band-bending owing to zero polarization field for this non-polar plane, and (c) lesser indium incorporation on this plane relative to others as indicated from Table 5-1. It was found that at low temperatures, the PL emission from each of the QWs could be spectrally resolved while at higher temperatures, the lowest energy QWs (widest) started to dominate as shown in fig. 5-12(b). It is believed that a combination of thermal activation and resonant tunneling of carriers coupled the QWs and resulted in the above behavior [14]. This behavior is typical of non-polar asymmetric MQWs and thus, should be expected in the m-plane as well. The PL emission for the m-plane MQW shown in fig. 5-12(a) is reasonably narrow and this could be attributed to the dominance of the widest QW at room temperature.
Fig. 5-12: (a) Room temperature PL of MQW structures on semi-polar and non-polar bulk GaN substrates and c-plane MQW on sapphire (b) PL from a-plane MQW – Temperature sequenced TIPL from a-plane InGaN MQWs from 12 K to 300 K. The grey bands refer to regions of emissions for each of the QWs with 1 referring to the thinnest and 4 is the thickest well.
5.4.3. CHARACTERIZATION OF MQW LED STRUCTURES ON SEMI-POLAR AND NON-POLAR BULK GaN SUBSTRATES

Conventional LED fabrication techniques were carried out on the MQW LED structures. Owing to a number of difficulties like small sample sizes, rough growth surface, absence of a UV-transparent sapphire substrate, and the limited quantity of these expensive substrates to optimize with; successful fabrication of a complete device on these samples was very difficult to achieve. A successful fabrication was finally completed on the (2021) LED sample to yield devices of size 400 μm x 400 μm. As a reference, a c-plane MQW LED grown on a GaN film on sapphire substrate was also fabricated. For the reference sample, the active region was grown with the same growth recipe and mechanism used to obtain the 540 nm green emission earlier (fig. 5-9). Electroluminescence (EL) was carried out on both the LEDs using pulsed current injection (duty cycle of 25%) and was captured from the bottom surface of both LEDs. The EL spectrums and the peak wavelength shifts for the (2021) LED are shown in fig. 5-13 and for the c-plane LED are shown in fig. 5-14. No appreciable EL emission could be captured from the (2021) LED below 11.7 A/cm^2. This was indicative of a not-so-efficient (2021) bulk GaN LED which could be because of an unoptimized LED or poor extraction efficiency of the bulk GaN LED relative to the c-plane LED on sapphire. The peak wavelength, in either of the investigated LEDs case, blue-shifted with increasing current injection. The c-plane LED showed a peak wavelength shift of about 29 nm compared to the 22 nm shift observed for the (2021) LED. The shifts are larger than expected and there could be two possible reasons that attribute themselves to the observed blue shifts which are:
The screening of the internal electric field at higher current densities and thus the energy bands within the quantum well could begin to flatten and result in a higher energy emission.

As observed from earlier, the “1-column” growth mechanism resulted in variable widths for the quantum wells and so their emission energies will vary depending on the contribution from the quantum confinement energy (or the quantum size effect). For asymmetric MQW LED structures, the percentage contribution of each of the quantum wells to the total EL spectrum could change with increasing current density as has been observed in literature [15, 16, 17]. A number of factors like differences in the transport of electrons and holes, relative efficiencies of the various wells etc. will decide which wells dominate at what current density. Further investigation would be required to establish the interplay of the various factors for the case of the above investigated LEDs. Since the widest QW is closest to the p-layer, it could be speculated that at lower currents, enough holes do not reach the narrower QWs due to poor hole transport, but with increasing currents, greater number of holes make it to the narrower QWs resulting in a blue-shift.
Fig. 5-13: (a) Electroluminescence spectra with increasing current densities for (20\,2\,1) bulk GaN LED and (b) EL peak wavelength shift with increasing current density for (20\,2\,1) bulk GaN LED.
Fig. 5-14: Electroluminescence spectra for reference c-plane LED on sapphire substrate at (a) low current densities (b) slightly higher current densities and (c) EL peak wavelength shift with increasing current density for the c-plane LED on sapphire.

The other notable observation was that the EL emission from the c-plane reference LED was much brighter than the (20\bar{2}1) LED. One of the primary reasons for this was that the bulk GaN LED has a GaN/air interface at the bottom surface. This interface has a very small escape cone (angle for total internal reflection = 23^\circ) owing to the high mismatch in
refractive indices, i.e. \( n_{\text{GaN}} = 2.4 \) and \( n_{\text{air}} = 1 \). For the reference c-plane LED, the sapphire substrate with an intermediate refractive index of 1.78 reduces the mismatch and now the GaN/sapphire interface has a larger escape cone (angle for total internal reflection = 48°). This will result in better light extraction for the c-plane LED on sapphire relative to the (0001) bulk GaN LED. The fabry-perot interference fringes observed in the c-plane LED are indicative of smooth interfaces and also of a thin GaN layer within which reflections occur. The thick GaN layer in the bulk GaN LED can also absorb a large portion of the generated light within the LED. Even though the light emission energy is below the band-gap of GaN, there can be significant absorption within the GaN layer for the bulk GaN LED, primarily arising from free carrier absorption, because the light has to travel 300\( \mu \text{m} \) of GaN to get to the bottom interface in comparison to the 4-5\( \mu \text{m} \) of GaN that is travelled in the reference c-plane LED on sapphire. The sapphire substrate has negligible light absorption in the visible region.

The other issue for the bulk GaN LEDs was that they are far from optimized because of the limited availability of these expensive substrates. Figure 5-15 shows the I-V curves for both the LEDs. The high series resistance for the (0001) bulk GaN LED could be attributed to a resistive p-layer due to unoptimized p-GaN growth conditions and unoptimized hole activation annealing conditions. The higher thermal conductivity of bulk GaN relative to sapphire would require re-establishing of temperature conditions for the above.
Fig. 5-15: I-V curves for (2021) bulk GaN LED and the c-plane reference LED on sapphire substrate

M-plane device structures were also tried out but conventional fabrication techniques failed. So, large, circular Ni/Au contacts (0.5 mm radius) were deposited on the top p-layer of the m-plane bulk GaN LED by shadow-masking. The LED sample was etched down to the n-type using the p-metal contacts as an etch mask. Indium contacts were used to contact the n-type layer and electroluminescence characterization was conducted by injecting current and the results are shown in fig. 5-16. For calculating the current density, the area under the circular contacts was used. The m-plane is expected to show minimal or no peak wavelength shift as the piezoelectric polarization induced electric field is zero within the quantum wells. There is some shift observed though and this is attributed to changing percentage
contribution of each of the quantum wells (varying widths) to the EL spectrum with changes in current density.

**Fig. 5-16**: Electroluminescence of the m-plane LED with increasing current density.

### 5.5. CONCLUSION

MQW structures and MQW-LED structures were grown on the semi-polar and non-polar bulk GaN substrates. A modified growth approach to increase the indium incorporation was used with reasonable success. The growth rates and indium incorporation for different orientations of bulk GaN substrates were characterized. The m-plane PL peak wavelength was blue shifted relative to the (2021) PL peak wavelength and this was attributed to the absence of QCSE as well as lower indium incorporation on m-plane. EL characterization for
the (2021) bulk GaN and a reference c-plane LED on sapphire substrate was conducted and blue shifting of the EL peak wavelength with increasing current densities was observed in either case. Asymmetric MQW widths for the MQW LED structures made it difficult to ascertain whether the shift could be solely attributed to QCSE. Much reduced EL emission intensity was observed for the (2021) bulk GaN LED relative to the c-plane LED on sapphire substrate. This was attributed to poor light extraction from the bulk GaN LED owing to high refractive index mismatch at the bottom interface and large light absorption within the bulk GaN substrate.

5.6. REFERENCES


CHAPTER 6 : INVERSION FROM N- TO Ga-POLAR GaN AND ITS APPLICATION TO MQW LEDS

6.1. INTRODUCTION

III-Nitrides with their excellent optical properties have become the material of choice for solid-state lighting and other opto-electronic devices. InGaN-based light emitting diodes (LEDs) operate exceedingly well in the blue region of the visible spectrum but longer wavelength LEDs in the green spectral region and beyond have severely degraded efficiencies. This is often referred to as the “green gap” and was discussed earlier at the start of chapter 5. Hence, there has been considerable interest towards approaches for growing high indium percentage multiple quantum well (MQW) LEDs. N-polar GaN has emerged as one such approach that could be investigated for greener LEDs [1]. The higher stability of InN on N-polar GaN surface enables the incorporation of higher indium in N-polar GaN compared to Ga-polar GaN at identical growth temperatures [2, 3]. Also, the polarization field in N-polar MQWs is reversed compared to Ga-polar; this assists in reducing the injection barriers for electrons and holes and achieving lower turn-on voltage for the LEDs [4, 1, 5]. Figure 6-1 illustrates an energy-band simulation for a single quantum well (SQW) LED on both Ga- and N-polar surfaces. The N-polar surface has flattened bands and no energy barriers for both electrons and holes compared to the Ga-polar surface. For p-GaN, in particular, where achieving high hole concentration is difficult, the hole injection barrier could severely hamper the LED efficiency. The polarization field for N-polar GaN is
opposed to the applied external field during forward bias and assists the quantum well regions to suffer less from the stark effect across them.

![Simulated energy-band diagrams of Ga- and N-polar SQW LEDs. Adopted from Reference 4.](image)

**Fig. 6-1**: Simulated energy-band diagrams of Ga- and N-polar SQW LEDs. Adopted from Reference 4.

Research studies in the area of N-polar GaN, however, have so far been limited because of a rough hexagonal surface morphology of the N-polar GaN [6]. In addition, these rough surfaces have a high tendency for impurity incorporation [7, 8], especially oxygen that acts as a shallow donor, thus resulting in background electron concentration in the range of mid-$10^{17}$ cm$^{-3}$ or higher for unintentionally doped N-polar GaN. Thus achieving good p-type, required for N-polar MQW LEDs, can be challenging. One approach to achieve a smoother
N-polar GaN film and reduced background electron concentration has been to grow on c-plane sapphire substrates with an off-cut angle. This has helped achieve good p-type films and a successful N-polar MQW based LED structure [5, 9]. However, sapphire substrates with an off-cut are limited in availability and expensive and so, a more conventional approach would be preferred.

The deposition of GaN layer, heavily doped with Mg or the exposure of N-polar GaN to high Mg flux, using plasma-assisted molecular beam epitaxy [10] as well as by ammonia-based molecular beam epitaxy [11], has been observed to invert the nitrogen polarity and result in Ga-face GaN. Formation of an Mg$_x$N$_y$ compound is believed to be responsible for inverting the polarity. There have also been some efforts towards non-Mg induced inversion from N-polar to Ga-polar [12, 13]. The Mg-related work though has focused on molecular beam epitaxy (MBE) growth and no reports have been found of Mg-induced inversion of N-polar to Ga-polar by metalorganic chemical vapor deposition (MOCVD) technique.

The focus of this chapter will be an MOCVD approach of inversion from N-polar surfaces to Ga-polar ones using a thin GaN layer with heavy Mg doping. The effect of this inversion layer on a test structure intended to achieve a p-type GaN with conventionally doped Mg is then studied. Next, the growth and device characterization of MQW LEDs on N-polar GaN on conventional c-sapphire substrates by the use of this inversion layer that is grown after the active MQW region and prior to the p-type GaN growth will then be carried out. This LED structure will thus take advantages of the higher indium incorporation for the MQW active region on the N-polar surface and of an improved p-type film on the inverted
Ga-polar surface. Schematic for the Mg-doped test structure is shown in Fig. 6-2(a) while the N-polar MQW LED with inversion layer is shown in Fig. 6-2(b).

![Schematic Diagram](image)

**Fig. 6-2**: Schematic of the (a) Test Structure for Hall measurements which is a GaN:Mg film on N-polar GaN template with an inversion layer (b) N-polar InGaN/GaN MQW LED using an inversion layer for the p-type film on top

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6.2. P-TYPE FILMS ON N-POLAR GaN WITH AN INVERSION LAYER

6.2.1. EXPERIMENTAL CONDITIONS

The planar N-polar (000-1) GaN template shown in Fig. 6-2(a) was grown by a two-step growth process using MOCVD under 350 mTorr pressure on (0001) standard sapphire substrates which did not have any miscut. This 2-step process is not the same as that for conventional GaN where the first step of growing the nucleation layer is conducted at a very low temperature of 450-500 °C and is thin (20-80 nm). In this process for growing an N-polar GaN template, the first layer was ~600 nm thick GaN grown at 850 °C using trimethylgallium (TMGa) flux of 6.94 µmol/min. The second layer of GaN was grown at 1100 °C with a thickness of ~800 nm. In the absence of a low temperature nucleation layer, these templates were observed to be N-polar and they did etch in hot H₃PO₄ acid to form a pyramid structure commonly observed elsewhere with N-polar GaN wet etching [14]. These N-polar GaN templates had an electron concentration of about 6-8 x 10¹⁷ cm⁻³ that will be difficult to convert to p-type film in an LED structure. Inversion from N-polar to Ga-polar was achieved during plasma-assisted MBE by using a temperature, about 200 °C less than the growth temperature, and using a high Mg flux [10]. It is believed that Mg incorporation increases significantly at lower temperatures and it is this magnesium that assists in polarity inversion. To reciprocate a similar approach for MOCVD, a thin “inversion layer” was then deposited on the N-polar GaN films at 850 °C using a high flux of 77 nmol/min of bis(cyclopentadienyl)magnesium (CP₂Mg) and low TMGa flux of 3.2 µmol/min. This was followed by 400 nm thick p-type GaN layer grown at 1090 °C with conventional Mg doping.
of 54.5 nmol/min of CP$_2$Mg and TMGa flux of 6.94 µmol/min. The ammonia flow rate throughout the growth was 1.25 slpm. The samples were then annealed in N$_2$ at 740 °C for 10 min to activate the p-type layer.

6.2.2. RESULTS AND DISCUSSION

Figure 6-3 shows the scanning electron microscopy (SEM) images of the surface morphology of the test structures with different inversion layer thicknesses. The growth rate of the inversion layer was estimated by SEM of sample cross-sections to be 8 nm/min. The thickness of the inversion layer was varied by changing the growth time, keeping all other parameters identical. Since the inversion layer is grown at a lower temperature than the actual p-type layer, Mg atoms (radicals) are more efficiently incorporated onto the growth surface. The formation of Mg$_x$N$_y$ has been reported in literature to initiate surface reconstruction; and thus, cause inversion of the surface polarity in GaN [10, 11, 15] which we believe is the same mechanism in the current study. A Ga-polar surface is associated with smoother surfaces and the absence of hexagons. Thus, the trend of decreasing hexagon density and surface smoothening for the GaN:Mg layer as the inversion layer thickness is increased from 16 nm to 80 nm could be attributed to an increasing percentage of polarity inversion on the surface as shown in figure 6-3. We have not yet achieved 100% Ga-polar surface for the 80 nm thick inversion layer shown in figure 6-3, since it was observed to slightly etch in heated H$_3$PO$_4$ indicating that some regions still had nitrogen polarity. There exists some degradation of the N-polar surface for very thin inversion layers, however, after a
certain inversion layer critical thickness; we speculate that Mg-induced surface restructuring and polarity inversion start to become dominant.

![SEM images of the growth surface of GaN:Mg layers grown on N-polar GaN with inversion layer thicknesses of (a) 0 nm (b) 16 nm (c) 48 nm (d) 80 nm.](image)

**Fig 6-3**: SEM images of the growth surface of GaN:Mg layers grown on N-polar GaN with inversion layer thicknesses of (a) 0 nm (b) 16 nm (c) 48 nm (d) 80 nm.

The results from Hall measurements of the Mg-doped test structures are detailed in Fig. 6-4. The depletion region between the top p-film and the underlying n-type template, N-polar, as well as the resistive inversion layer, due to heavy Mg doping, ensure that the Hall
current is restricted to the Mg doped GaN layer. Without the inversion layer or even with a thin inversion layer, the Mg doped GaN film still measured to have n-type nature. This is attributed to a dominant nitrogen polarity that has a high background electron concentration and not been compensated for by the activated Mg acceptors. Significant inversion to a Ga-polar surface is achieved on increasing the inversion layer thickness to 48 nm or more and a p-type surface is achieved. The range for the critical thickness for significant polarity inversion from Fig. 6-3 is consistent with the thickness range for carrier type inversion from the Hall measurements shown in Fig. 6-4.

Room temperature photoluminescence (PL) of these test structure samples is shown in Fig. 6-5. The blue luminescence band observed in all of the samples is associated with the Mg doping and is consistent with the literature [16]. Samples with thin or no inversion layer have a clear shoulder of a yellow luminescence band, however, this shoulder is absent for the thicker inversion layer samples. Yellow luminescence observed in GaN is believed to be the result of a transition from a shallow donor to a deep level Ga vacancy and has often been associated with the presence of oxygen [17]. Substitutional oxygen is known to act as a shallow donor [18] and the oxygen incorporation on the N-polar surface has been reported to be more than an order of magnitude greater than the Ga-polar surface [7, 8]. This can explain the disappearance of the yellow luminescence for the thicker inversion layer samples which have a greater percentage of an inverted Ga-polar surface and thus lower oxygen concentrations.
Fig. 6-4: Carrier concentration and type of the GaN:Mg films grown on N-polar GaN with different inversion layer thicknesses. Concentration, type and mobility of the carriers were characterized by Hall Effect Measurements.
Fig. 6-5: Room temperature photoluminescence (PL) of the GaN:Mg films grown on N-polar GaN with different inversion layer thicknesses.

Thus, both Hall measurements and photoluminescence have confirmed that an inversion of the film from N-polarity to Ga-polarity has taken place.
6.3. N-POLAR MQW LEDS WITH AN INVERSION LAYER

6.3.1. EXPERIMENTAL CONDITIONS

As an application for the above p-type film on N-polar GaN, LED structures shown in Fig. 6-2(b) were grown. N-polar GaN was grown using the same two-step process mentioned earlier and was additionally doped with silicon for an electron concentration of 1-2 x 10^{18} cm^{-3}. Four periods of InGaN/GaN MQWs were then deposited on the N-polar GaN surface at 660/690 °C for 1 min and 5 min using triethylgallium (TEGa) and trimethylindium (TMIn) fluxes of 0.5 µmol/min and 3.82 µmol/min for the quantum well and barrier layers, respectively. Immediately after the MQWs, an inversion layer followed by a Mg-doped film for the p-type were grown and then annealed with conditions identical to the Hall test structures. Another LED structure with identical growth conditions but without the inversion layer was grown for comparative studies.
Photoluminescence characterization was conducted on identical recipe MQW samples grown on both the N-polar and conventional Ga-polar surfaces. The results are shown in fig. 6-6. The peak wavelength for the MQW on the N-polar GaN surface was found to be 477 nm compared to 448 nm for the Ga-polar MQWs and this is attributed primarily to the higher indium incorporation on the N-polar surface. To estimate the indium percentage from the PL peak wavelengths, a model previously developed by Emara et. al. in the Bedair group was used [19]. The Ga-polar sample was grown with a previously characterized recipe for 2 nm well width. The InGaN growth rate for both the Ga-polar as well as the N-polar surface was assumed to be same and so the well width for the N-polar samples was also assumed to be the same 2 nm. Using this well width of 2 nm and the PL peak wavelengths from fig. 6-6 in the Emara Model, indium percentages of 16% and 21% were obtained for the Ga-polar
MQWs and the N-polar MQWs respectively. It is speculated that the N-polar surface might have a slightly higher growth rate that also contributed to longer PL peak wavelength and so the estimated In percentage for the N-polar MQWs might be an upper bound.

The LED samples, grown earlier, were then etched into 400 x 400 μm mesas using a Plasma Therm reactive ion etcher and standard lithography procedures. Metal contacts were deposited via electron beam evaporation. The p-type mesa contacts consist of Ni/Au metallic layers with thicknesses of 500 Å and 1500 Å, respectively. The n-type ring contacts consist of Ti/Au metallic layers with thicknesses of 250 Å and 1000 Å, respectively. The LED emission was collected from the back surface of the sapphire substrate.

6.3.2. RESULTS AND DISCUSSION

Electroluminescence (EL) spectra for increasing drive currents for a 48 nm “inversion layer” N-polar MQW LED is shown in Fig. 6-7. Single peak emission at 500 nm, in the blue-green region with uniformly increasing EL intensity with increasing currents is observed. Figure 6-8 shows the peak wavelength to blue-shift with increasing current density which is consistent with other N-polar LEDs [1]. A total shift of about 12-14 nm is observed in the current density range of 1-11 A/cm². The shift is attributed to screening of the polarization field by injected charges at the higher current densities. The built-in depletion field acts in the same direction as the piezoelectric polarization field in the N-polar quantum wells. Its maximum value is estimated to be about 300 kV/cm. This was estimated using the formula for maximum electric field in a p-n junction,

\[ E_m = \frac{qN_d x_n_0}{\varepsilon_{GaN} \varepsilon_0} \]
where the doping $N_d$ for n-side is taken to be $1 \times 10^{18}$ cm$^{-3}$, $\varepsilon_{\text{GaN}}$, the dielectric constant for GaN is taken to be 9.7 and $x_{n0}$, the junction depletion on the n-side is calculated from,

$$x_{n0} = \frac{W}{1 + (\frac{N_d}{N_a})} = \frac{1}{1 + (\frac{N_d}{N_a})} \sqrt{\frac{2 \varepsilon_{\text{GaN}} \varepsilon_0 V_0 (\frac{1}{N_d} + \frac{1}{N_a})}{q}}$$

where the doping $N_a$ for the p-side is taken to be $1 \times 10^{17}$ cm$^{-3}$ and the $V_0$ for these doping conditions was found to be 3.22 V. The $x_{n0}$ was found to be 17.7 nm which was used for the electric field calculation. The $E_m$ was obtained as 330 kV/cm.

This built-in field is much smaller in comparison to the polarization field which would be above 2 MV/cm for wells with about 21% indium (from earlier estimation), and hence does not contribute much to band-bending within the quantum well. For comparison, EL inspection was also carried out on a similar fabricated N-polar LED structure but without the inversion layer. EL emission was not observed for the LED structure without the inversion layer; because of non-existent or negligible hole injection into the quantum wells from the intended p-layer.
Fig. 6-7: Electroluminescence (EL) spectra at different injection currents for the fabricated N-polar LED with the inversion layer.

Fig. 6-8: The EL peak wavelength shift with increasing injected current densities.
The current-voltage (I-V) characteristic for the N-polar LEDs, both with and without the inversion layer, was also carried out and is shown in Fig. 6-9. The LED with the inversion layer exhibits very typical diode characteristics with a turn-on voltage of 4.26 V. The inversion layer is expected to be resistive but is very thin and does not seem to have had an adverse effect on the LED emission except for some added series resistance to the I-V characteristics. However, the LED without the inversion layer exhibited ohmic-contact like behavior. This is attributed to the fact that the intended p-GaN layer still exhibited n-type characteristics as found from the earlier Hall measurements. The rectifying behavior at low voltages is associated to a p-metal contact on an n-type semiconductor resulting in a metal-semiconductor contact that is slightly rectifying.
Fig. 6-9: I-V characteristics for the fabricated N-polar LED, with and without the inversion layer.

6.4. CONCLUSION

In conclusion, an approach has been developed for inverting the N-polar surface to Ga-polar surface based on MOCVD growth using an inversion layer. The effectiveness of polarity inversion increases beyond a critical thickness for the inversion layer and assists in achieving a p-type film. Without the inversion layer, the background electron concentration was high and had a dominating effect. This approach was then incorporated into a N-polar LED structure grown on conventional c-plane sapphire substrates that gave a single peak EL emission in the blue-green wavelength region with a blue shift with increasing current densities. This approach allows an LED structure to take advantages of the high InN
incorporation on N-polar relative to Ga-polar structures, while achieving a p-type GaN through the insertion of an inversion layer.

6.5. REFERENCES


CHAPTER 7 : CONCLUSION

7.1. DISSENTATION SUMMARY

There are a number of challenges still to be addressed, in order for nitride-based light emitting diodes to be widely adopted for lighting purposes, both commercial and residential. The InGaN/GaN MQW LEDs that are conventionally grown on the polar c-plane have a large polarization field present within the InGaN quantum wells. These fields reduce the rate of radiative recombination and are thus, deleterious to the performance of the LED. The crystal-plane orientation of the growth plane and its polarity can have a significant effect on the polarization field value and direction. This dissertation serves to present research focused on exploring these other growth planes with the aim of reducing the polarization fields and improving the LED performance.

The first of these approaches was aimed at growing InGaN-GaN MQWs along the facets of GaN nanowires (NWs). The driving motivation was that the facets of these GaN NWs were shown to be oriented along both semi-polar and non-polar crystal planes which have a reduced piezoelectric field or none at all, respectively. A novel LED structure was overgrown on the GaN NWs that had conformally overgrown MQWs, an embedded network of voids that formed when adjacent NWs tried to coalesce, and finally an overgrown p-layer that completely coalesced and planarized to result in a continuous and smooth top surface that enabled the use of conventional fabrication to make devices for characterization. The NW LED was grown and fabricated alongside a conventional c-plane LED for comparative studies. Electroluminescence revealed a much reduced peak wavelength shift with increasing
injection currents for the NW LED relative to the c-plane that was attributed to the reduced piezoelectric field for the MQWs of the NW LED. The relative light-output power from the NW LED was found to be about 3 times higher than the conventional c-plane LED at identical injected currents and this was attributed to a combination of factors; primarily, reduced quantum confined stark effect (QCSE) owing to the reduced polarization fields and better light extraction by void wave-guiding and to a smaller extent by larger MQW surface area and reduced dislocation density. The wave-guiding by the embedded voids was further investigated by finite difference time domain (FDTD) simulations to demonstrate diffraction effects by the voids as well as an improved extraction ability compared to conventional planar LEDs. The NW LED has features that are advantageous to both, the IQE as well as the extraction efficiency of the LED, and the growth and processing methodology has potential to be scaled up for commercial purposes, and it is this combination that provides uniqueness to this LED structure among other proposed LED structures in literature.

QCSE is more severe for the LEDs that operate in the green spectral region or beyond. With this in mind, InGaN-GaN MQW LED structures were grown on different semi-polar and non-polar bulk GaN substrates. A novel growth approach was employed to enable higher indium incorporation and green emission was realized. The MQW structures were characterized by PL and the device structures were characterized by EL for different crystal planes.

Lastly, the N-polar GaN surface was explored. It has higher indium incorporation than the Ga-polar surface and a polarization field that is reversed in direction relative to the conventional Ga-polar c-plane. However, high electron background concentration has made
it difficult to achieve p-type on N-polar GaN. To overcome this issue, a thin inversion layer with high Mg flux was used to invert the N-polar surface to Ga-polar GaN. To the best of the author’s knowledge, this is the first reporting of Mg-induced inversion of N- to Ga-polar GaN using MOCVD. This technique was employed to achieve p-GaN films on N-polar surfaces. The properties of these p-GaN layers were characterized for films with varying inversion layer thicknesses. An optimized inversion layer thickness of 48 nm was incorporated into a N-polar MQW LED structure that gave a single peak EL emission. The peak blue-shifted with increasing current density and this was attributed to the internal polarization field. This approach allowed the LED structure to take advantages of the high InN incorporation on N-polar relative to Ga-polar structures, while achieving a p-type GaN through the insertion of an inversion layer.

7.2. FUTURE WORK

The NW LED structure is very unique and further exploration of this device is needed to identify its true potential. During the investigation of the NW LED device, current densities were restricted to less than 100 A/cm². It would be very interesting to perform the comparative studies of the NW LED versus the conventional LED at much higher current densities. This would require packaged LEDs mounted on heat sinks. So laser-lift off to separate the substrate from the device, for both the investigated LEDs, would be required to be done. Individual LED devices would need to be diced, wire-bonded and then mounted on heat sinks to perform high current density measurements. Such high current densities would
also enable the study of efficiency droop for both investigated LEDs. Use of an integrating sphere to obtain absolute light output powers for both LEDs would also be an interesting path to investigate and pursue.

The varying MQW widths for the growth on bulk GaN substrates made it difficult to estimate the contribution of each of the wells to the emission and thus, made it difficult to quantify peak wavelength shifts. The varying growth rate with the 1-column approach brought about the well width ambiguity. It is speculated that this growth rate could stabilize with time and thus, it might be possible to obtain symmetric wells with the same growth approach. This would better enable a thorough study of polarization field effects for the various semi-polar and non-polar orientations.

Lastly, for the N-polar LEDs with an inversion layer, further investigation of the effects of other growth parameters on the inversion layer properties may be attempted. Also, characterizing the percentage of inversion from N- to Ga-polar with increasing thickness of the inversion layer might help establish whether 100% inversion is achievable by this technique.